PTFE Gas Separation Membranes "POREFLON NANO"

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Porous polytetrafluoroethylene (PTFE) membranes were first developed by Sumitomo Electric Industries, Ltd. as "POREFLON." Thanks to its high chemical and heat resistance, POREFLON has been used for microfiltration in various industrial applications. With advanced technological innovations, Sumitomo Electric has newly developed a nano-porous PTFE membrane "POREFLON NANO" and confirmed its high degassing and gas separation performance.

Keywords: PTFE, gas separation, degassing, module

1. Introduction

Sumitomo Electric Industries, Ltd. developed a porous polytetrafluoroethylene (PTFE) membrane(1) ahead of the rest of the world, and has since been manufacturing and selling it under the trade name of "POREFLON." POREFLON can be used as microfiltration membranes with a pore diameter of 0.05 µm (50 nm) to 10 µm. These membranes with high chemical resistance are mainly used for industrial wastewater treatment and for removing foreign substances from chemical agents in the manufacturing processes of semiconductors and other electronic devices.(2) For semiconductors, in particular, the wafer cleaning agent is required to be purer than ever to improve the degree of integration.

Sumitomo Electric succeeded in the development of an original PTFE membrane, "POREFLON NANO" with a pore size of less than 50 nm, to continuously meet the future needs for the removal of fine foreign substances.(3) This paper describes the improved performance of the latest POREFLON NANO that has a pore size of 10 nm or less, its gas separation performance, and degassing performance as hollow fiber modules.

2. Application Fields

Advancing separation (purification) technology is essential to develop the environment, energy, materials, electronics, life science, and various other fields. In separation technology, there are distillation, coagulation, adsorption, and membrane separation. Membrane separation, in particular, is high-efficiency (capacity) and energy-saving separation technology among these technologies.

POREFLON NANO is a porous PTFE suitable for separation membrane. A membrane (PN10) with a pore diameter 10 nm can be used for degassing and gas-dissolving in liquid treatments. A membrane (PN0.3) with a pore diameter of 0.3 nm can be used for gas separation, where the components of a mixed gas are separated according to their molecular sizes in mixed gas treatments. Owing to the excellent heat resistance, chemical resistance, solvent resistance, and biocompatibility of PTFE, together with its antifouling property derived from non-adhesiveness, water resistance, and oil resistance, POREFLON NANO finds a variety of industrial applications.

For semiconductor exposure apparatuses, for example, there is a need to improve the patterning accuracy. To meet this demand, a solvent-resistant, compact, and high-efficiency degassing module is necessary to remove the gases dissolved in the photoresist and developing fluid immediately before these agents are fed to the dropping nozzle.

In the energy industry, there is demand for membranes having high acid resistance to organic acid and hydrogen sulfide for carbon dioxide/methane gas separation from biomass/methane fermentation gas. For hydrogen gas/carbon dioxide separation from steam-reformed natural gas, there is a need for separation membranes having high heat resistance.

Sumitomo Electric believes that POREFLON NANO provides technological innovations to separation processes conducted under severe operating conditions.

3. POREFLON NANO Degassing Module (PN10)

3-1 Structure/dimensions of hollow fiber

Table 1 compares POREFLON NANO (PN10) and conventional POREFLON in porous characteristics. The lower limit of the pore diameter*1 made by conventional porous material manufacturing technology (stretching) is

Table 1. Porous characteristics and dimensions of POREFLON NANO hollow fiber (Comparison with conventional POREFLON)

	POREFLON NANO	POREFLON (conventional technology)	
	PN10	TB-21	OTB-21
Material	PTFE	PTFE	PTFE
Pore diameter [nm]	9.4	1,200	66
Porosity	63%	62%	19%
IPA bubble point [kPa] *3	2,200< (off-scale high)	80	350
Outer diameter [mm]	0.50	2.0	2.0
Inner diameter [mm]	0.25	1.0	1.0
Wall thickness [mm]	0.13	0.5	0.5

approximately 50 nm. Since the pore diameter and porosity control are in a trade-off relationship, the porosity*2 of conventional smallest-pore membrane is as low as 20% or less. In contrast, POREFLON NANO achieves an ultrafine pore diameter of 10 nm or less and a high porosity of 60% or more. In addition, the Company has acquired a technology that can manufacture thinner hollow fibers with an outer diameter of 0.5 mm and inner diameter of 0.25 mm. Thus, the gas diffusion ratio of the membrane wall increases by three times and the membrane area of the module increases by four times compared with the conventional values, enabling the manufacturing of more compact and higher efficiency degassing modules.

3-2 Degassing performance

Figure 1 shows a schematic diagram of the degassing mechanism. When a liquid on the inside of the POREFLON NANO hollow fiber membrane (internal perfusion method) and the outside of the hollow fiber is depressurized, the gas dissolved in the liquid is diffused and removed through the porous wall by the partial pressure difference.

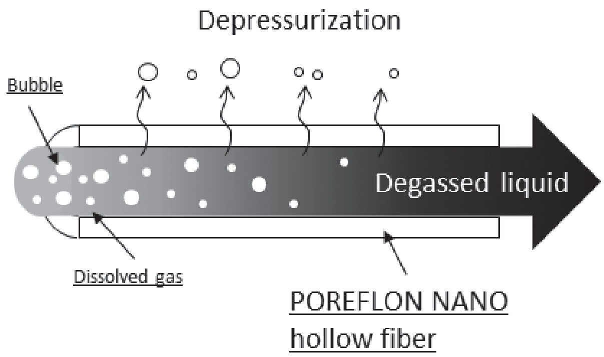

Fig. 1. Degassing action of POREFLON NANO hollow fiber

Figure 2 shows the external dimensions and internal structure of a compact POREFLON NANO degassing module. To enhance installation space efficiency, this module is designed as compact as possible. In particular, it is cuboid. The dimensions are H 23 mm × D 23 mm × L 70 mm. In addition, all protruding ports (ISO594-2 compliant luer locks) are on one side.

Table 2 shows three modules with different membrane areas evaluated for degassing performance. The pure water flow rates of those modules at a head difference of 300 mm H_2O are 160 ml/min with a membrane area 200 cm^2 type and 70 ml/min with a small membrane area type (80 cm^2). Because of their practically acceptable low pressure-loss characteristics, these compact modules are expected to save the liquid feeding power of the degassing system and reduce the cost of the system by eliminating the need for the liquid feeding device.

Figure 3 shows the degassing performances of these modules at a vacuum pressure of -85 kPa when oxygen-saturated water is used as the test liquid. The degassing rate, in terms of the membrane area ratio, of POREFLON

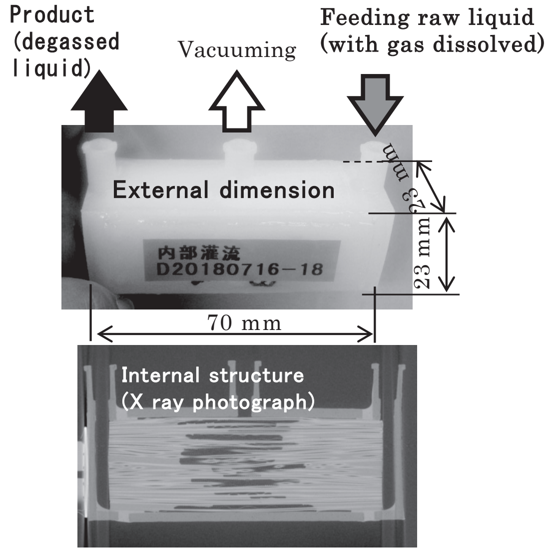

Fig. 2. External appearance and internal structure of POREFLON NANO degassing module

Table 2. POREFLON NANO modules used for degassing evaluation

	POREFLON NANO module		
	No.1	No.2	No.3
Type	internal perfusion	internal perfusion	internal perfusion
Hollow fiber	PN10	PN10	PN10
	210 fibers	420 fibers	530 fibers
Membrane area [cm^2]	80	160	200
Water flow rate at 300mmH_2O [ml/min]	70	130	160

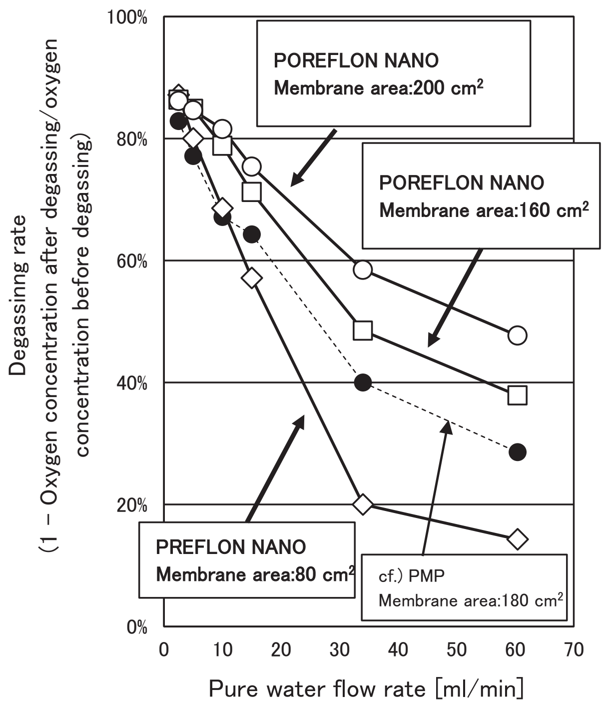

Fig. 3. Degassing performance of POREFLON NANO modules

NANO (PN10) is 1.5 times higher than that of a polymethyl pentene (PMP) membrane, showing the highest degassing ratio among polyolefin membranes.

4. POREFLON NANO with Gas Separation Function (PN0.3)

4-1 Cross-sectional structure

Figure 4 shows a scanning electron microscope (SEM) photo of a cross section of a POREFLON NANO (PN0.3) which was freeze-fractured with liquefied nitrogen. The gas separation layer of the PN0.3 is thinned to approximately 5 µm to enhance gas permeability, and it is unified the POREFLON supporting layer to form a multilayer structure.

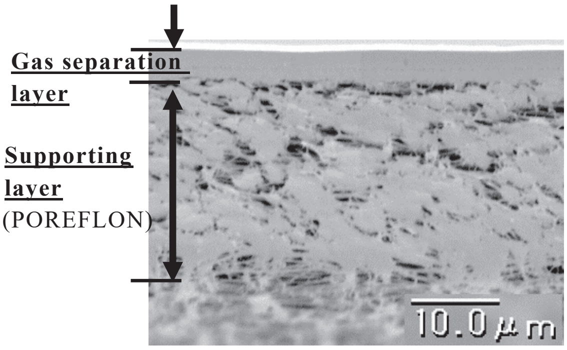

Fig. 4. Cross-sectional SEM photo of POREFLON NANO (PN0.3)

4-2 Gas permeability and gas selectivity

For the performance evaluation of a gas separation membrane, the permeability of the target gas (permeated gas flow rate) can be used as the processing capability index, and the gas selectivity, which is the separation accuracy index, can be determined from the permeability ratio between gas X and gas Y.[4] Single gases of helium (He), hydrogen (H_2), carbon dioxide (CO_2), nitrogen (N_2), and methane (CH_4) were used as the test gases. For the measurement, the differential pressure method (JIS K7126-1GC) was used under the conditions of 23°C, 0% RH, 100 kPa on the upstream side, and 0 kPa on the downstream side.

As shown in Fig. 5, the permeability of these single gases increased exponentially as their molecular diameter decreased.[4]

The gas separation accuracy (gas selectivity) is shown in Table 3. The ratio of helium gas to methane gas, the ratio of hydrogen gas to carbon dioxide, and the ratio of carbon dioxide to methane gas were as high as 29, 7.9, and 2.1, respectively. Since the ratio of oxygen gas to nitrogen gas was also as high as 2.5, POREFLON NANO (PN0.3) is expected to be also useful for oxygen enrichment. Furthermore, the permeability coefficient, one of the characteristics of a material, is 82×10^{-10} [cc (STP) • cm/cm^2 • s • cmHg] for hydrogen gas. This coefficient is 1.5 to 5 times higher than that of membranes made of different materials, such as cellulose acetate, polysulfone, and polyimide.[4] On the other hand, the permeability coefficient for carbon dioxide is as low as 11×10^{-10} [cc (STP) • cm/cm^2 • s • cmHg], which is equivalent to those of different materials. This result verified that POREFLON NANO (PN0.3) can be used for hydrogen production to improve the processing capacity and separation accuracy.

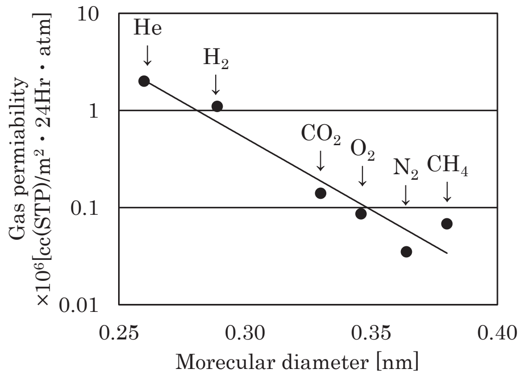

Fig. 5. Gas permeability of POREFLON NANO (PN0.3)

Table 3. Permeability ratio of POREFLON NANO (PN0.3) (gas selectivity)

		Permeability ratio (y/x)					
y	He	1.0	1.8	14	23	57	29
	H_2		1.0	7.9	13	31	16
	CO_2			1.0	1.6	4.0	2.1
	O_2				1.0	2.5	1.3
	N_2					1.0	0.51
	CH_4						1.0
		He	H_2	CO_2	O_2	N_2	CH_4
		x					

4-3 Experimental results for industrial use model

Table 4 shows the separation performance of model gases in hydrogen production from steam-reformed natural

Table 4. Model Experiment results. Composition of industrial use model gases and experimental results for model gas separation

Expected application	Hydrogen production	Methane production	Life science
Function	Natural gas reforming, H_2/CO_2 separation	Biogas, CO_2/CH_4 separation	Atmospheric composition control, O_2 enrichment
Expected gas composition	H_2:O_2 =80%:0%	CO_2:CH_4 =40%:60%	O_2:CO_2:N_2 =21%:0.1%:78%
Model gas (measured)	H_2:CO_2 =75%:25%	CO_2:CH_4 =40.1%:59.1%	O_2:CO_2:N_2 =21%:0.1%:79%
After the first separation (measured)	H_2 84.4%	CO_2 93.1%	O_2 46.4%
After the second separation (calculated)	H_2 90.7%	CO_2 99.6%	O_2 72.0%
After the third separation (calculated)	H_2 94.6%	CO_2 99.98%	O_2 81.0%

gas, methane production from biomass/methane fermentation gas (biogas), and the oxygen enrichment of the atmosphere. Under the same evaluation conditions as those in section 4-2, the compositions of each model gas and the gas after the first separation were measured by gas chromatography, while the compositions of the gases that were passed through the second and third separation processes were calculated from the gas permeability ratios obtained by the first separation results.

For the natural gas steam-reformed gas model, the hydrogen concentration increases from the initial 80% to 94% or more by a three-stage separation process. For the biogas model, the experiment shows a possibility of removing 99% or more of the carbon dioxide by a two-stage separation process. For the atmospheric model, the oxygen concentration increases from initial 21% to 46% after one-stage separation process. Inhalation of 30% concentration of oxygen is effective to relieve psychological and physical stress, making the entire residential area a healing space. When used in an automotive air conditioner,(5) the enriched oxygen can reduce fatigue and prevent drowsiness (awakening) of the driver when driving.

5. Conclusion

Sumitomo Electric has acquired separation membrane and separation module technologies through the development of its proprietary PTFE membrane, POREFLON NANO. This membrane removes 50 nm or smaller size foreign substances, which was not possible with any conventional membranes, and thus demonstrates high degassing and gas separation performance. The advancement of separation technology is indispensable for the development of science and technology. The Company will continue to develop and advance its original PTFE porous technology to bring innovation to separation technology in a variety of application fields.

Technical Terms

∗1 Pore diameter: The peak pore diameter measured by a pure-water-injection-type pore size distribution measuring device.

∗2 Porosity: The ratio of pore (void) volume to hollow fiber membrane volume.

∗3 IPA bubble point: The minimum air pressure required to overcome capillary force when air pressure is applied to the inside of a hollow fiber soaked in isopropanol (IPA). The IPA bubble point increases as pore diameter decreases.

References

(1) Japanese Examined Patent Application Publication No.42-13560

(2) Sumitomo Electric Industries, Ltd. Website https://global-sei.com/products/ptfe/, http://www.sei-sfp.co.jp/english/products/poreflon-membrane.html

(3) H. Katayama, F. Hayashi, N. Shimbara, A. Uno, Y. Suzuki and Y. Okuda, "Next-Generation Nanoporous PTFE Membrane," SEI TECHNICAL REVIEW No. 83, pp. 50-54 (October 2016)

(4) Ricard W. Baker, Membrane Technology and Applications 2nd Edition, ed. John Wiley & Sons, Ltd. pp. 88, pp. 309, pp. 538 (2004)

(5) T. Oketa, H. Nishida, K. Yasui, N. Isoda, Y. Moriya, Evaluation of the Amenity based on the Air of 30% Oxygen Concentration (Part 11 Evaluation of the Stress Reduction), The Society of Heating, Air-Conditioning Sanitary Engineers of Japan, C-46, pp. 949-952 (August 2005)

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