Desalination and Water Treatment
www.deswater.com

17 (2010) 99–105
May

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doi: 10.5004/dwt.2010.1704

Preparation of nanoporous inorganic membrane on supports with graded structure

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Received 28 July 2009; accepted 3 November 2009

ABSTRACT

It is expected to develop an inorganic separation membrane for use in wastewater treatment at high temperatures. For this purpose, we have developed pore-size-graded inorganic microfiltration membranes and applied them to the supports of nanosized porous inorganic membranes. The preparation procedure is the subsequent following three steps. First, graded support discs were prepared from crushed AMAKUSA china stone by filtration-sedimentation method, followed by firing at 1,473 K. Then the support surface was modified by the electrophoretic deposition method using the alumina particles, followed by sintering at 1,523 K. Finally, titania colloidal sols were coated on the deposited support disc, and subsequently sintered at 723 K. As a result, nanosized porous titania top-layer having average pore size of about 3.5 nm was successfully prepared.

Keywords: Nanoporous inorganic membrane; Graded support; Filtration-sedimentation; Electrophoretic deposition; Sol–gel method

1. Introduction

Nanofiltration (NF) membranes have a large number of potential applications in industries such as paper, sugar, food and textile in which the operating temperature can be high and may even reach 363 K [1]. Polymeric NF membranes are reported to show a drastic decrease in separation performance over 333 K due to glass transition [2]. It is necessary prepare the inorganic substances as a raw material to prepare membranes that can be used at the high temperatures. On the other hand, the waste of a lot of stones is generated by mining the stone used for the raw material of pottery and chinaware in the AMAKUSA region [3]. The particle size distribution of AMAKUSA china stone is wide. Therefore, effective use of this abandoned stone is expected. In general, the particle sedimentation follows Stoke's law in the solvent. That is, large particle sediment early, and the sedimentation of a small particles is late. Therefore, structure of the deposit can be made graded by using gravity and the centrifugal force. Tubular structures of a continuous

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Presented at the Fifth Conference of the Aseanian Membrane Society Aseania 2009 "Recent Progress in Membrane Science and Technology", 12–14 July 2009, Kobe, Japan.

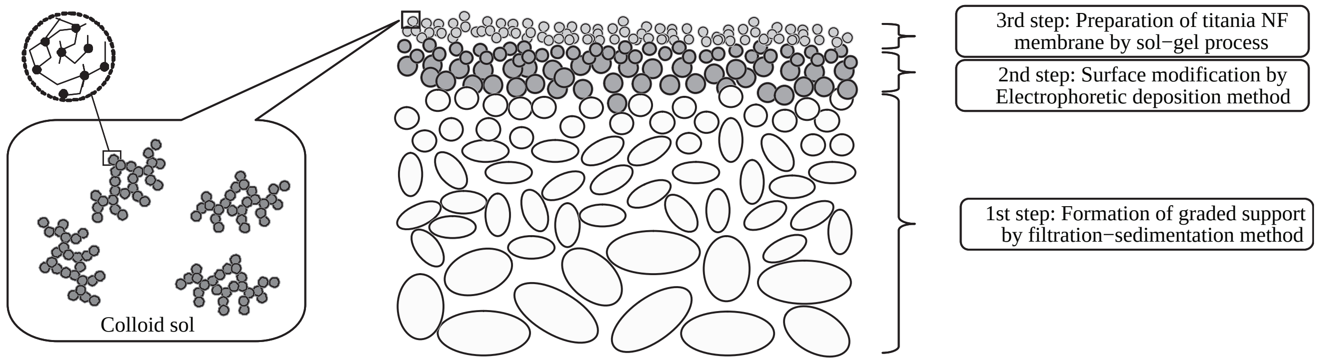

Fig. 1. Schematic image of nanoporous inorganic membrane on graded support.

particle size gradient were reported and a hollow cylindrical mold filled with a suspension of dispersed powder with a size distribution is centrifuged around its center axis [4].

In this study, we investigated the preparation of inorganic graded support discs that made use of the abandoned stone as raw materials first. The particle size distribution of the raw materials was widely dispersed. A green disc that has the graded structure in pore size ranging from less than 0.1 to 100 μm can was prepared by filtration-sedimentation method in the powder dispersed suspension, subsequently sintered.

Then, the microstructure on the surface of support disc was uniformly controlled by the electrophoretic deposition (EPD) method. The EPD process is one of several ceramic powder assembling technologies using a simultaneous colloidal process and electrochemical driving force. This process is very simple; the dispersed and charged particles in a solvent migrate to an electrode substrate under a certain electrical field using a DC power source [5]. So, the preparation of laminate structure such as 3Y-TZP (yttria tetragonal zirconia polycrystal)/alumina and LM (lanthanum manganate)/YSZ (yttria stabilized zirconia)/NiO-YSZ were reported [6,7]. In this study, three different sizes of alumina particles were orderly deposited by EPD on the support discs for the surface modification of support discs.

Finally, to prepare nanoporous inorganic membranes having controlled pore sizes, nanoporous titania (TiO_2) membranes were fabricated by sol–gel processing [8,9].

Thus, it is assumed to be our purpose to achieve preparing the NF membrane that has the support in the graded structure based on waste material by combining three methods of filtration-sedimentation, EPD, and sol–gel coating as shown in Fig. 1.

2. Instruction

2.1. Formation of graded supports by filtration-sedimentation method

Table 1 shows the chemical composition of AMAKUSA china stone [10]. Crushed AMAKUSA china stone, the particle size of which was widely distributed in the range of less than 0.1 to 100 μm, was used as raw materials of support discs. Crushed AMAKUSA china stone was dispersed in water. Poly-vinyl-alcohol (PVA, ACROS ORGANICS, m.w.95,000) was used as pore forming materials. Positive charged acrylonitrile styrene copolymer (AS, Soken Chemical & Engineering Co., Ltd., SX-5000) was used as a dispersant. Three types of suspension were prepared. The composition was controlled as the following weight ratio, and PVA saturated aqueous solution were added. The composition of AMAKUSA china stone: H_2O = 0.45: 3, AMAKUSA china stone: H_2O: PVA*aq.* = 0.45: 2: 1 and AMAKUSA china stone: H_2O: PVA*aq.*: AS = 0.45: 2: 1: 0.0075. Green support discs were prepared by sedimentation in the suspension, subsequently filtration. These suspensions were poured in Büchner funnel that paved the filter paper (5 A). The time spent on filtration is approximately 2–3 h. The dried green support was heated at a rate of 1.6 K/min and fired at 1,473–1,488 K for 2 h.

Table 1
Molar ratio of AMAKUSA china stone

SiO_2	Al_2O_3	Fel_2O_3	MgO	K_2O	Na_2O	IgLoss
78.90	14.09	0.27	0.16	2.90	0.09	3.58

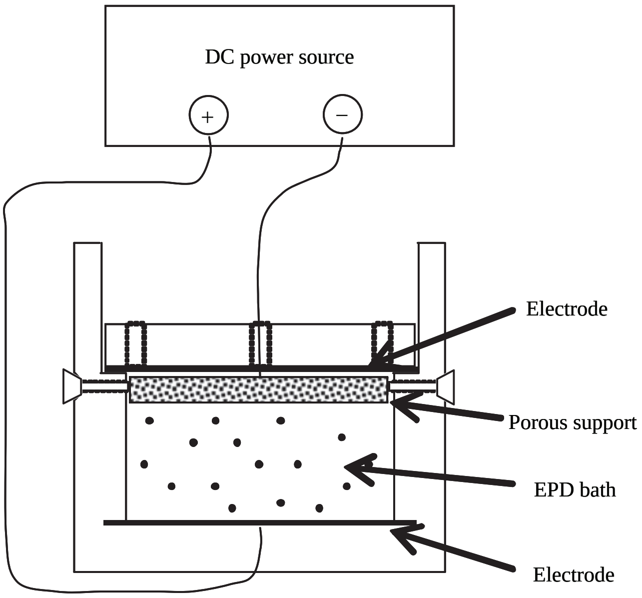

Fig. 2. EPD cell configuration.

2.2. *Surface modification by EPD method*

Three types of alumina particles with the average diameters of 0.7, 0.4 and 0.08 μm, were orderly deposited by EPD method on the above support disc and/or commercial support discs (ø30 mm, *t*1.7 mm, pore size 0.7 μm, porosity 37%) for the surface modification of support discs. These alumina particles were supplied by Showa Denko Co. Ltd (diameter: 0.7 μm; AL45-H, 0.4 μm; AL47-1 and 0.08 μm; AL160-SG3). 95 vol% MeOH–5 vol%HClaq. (pH 2.2) was used as an EPD bath [11]. A powder concentration of AL45-H, AL47-1, and AL160 SG3 are 0.5, 0.6, 0.1 g/L, respectively. EPD bath was ultrasonically dispersed before EPD. EPD was operated so that the particle migrates upward as shown in Fig. 2. Porous support is between both Pt mesh electrodes and the electrode distance is ca. 5 mm. AL45-H powder was EPD the first on porous support. Next, EPD bath was substituted and AL47-1 powder was deposited. Similarly, AL160 SG3 powder was deposited at the end. Each EPD was operated at 100 V for 20 min. The deposited support disc was heated at a rate of 3 K/min and sintered at 1,523 K for 1 h in air.

2.3. *Preparation of titania NF membrane by sol–gel process*

Titania colloidal sols were prepared by hydrolysis and condensation of titanium tetra-isoproxide in isopropanol solutions with HCl catalysts. NF membranes were prepared by coating titania sols on support disc modified by EPD, followed by firing at 723 K [8].

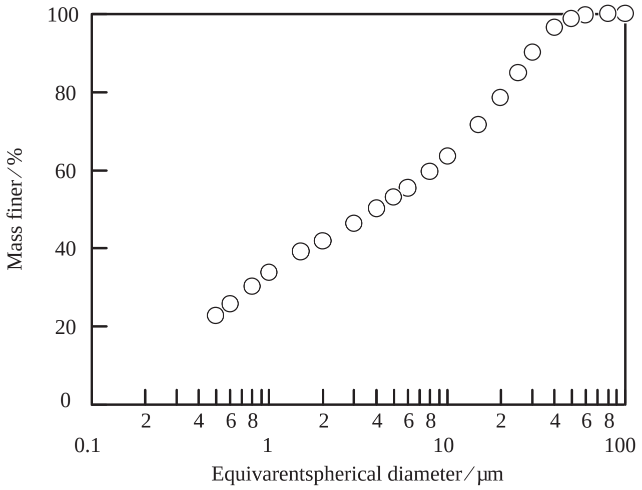

Fig. 3. Particle size distribution of crashed AMAKUSA china stone.

The surface and cross section morphology of the membrane was observed using a scanning electron microscopy (SEM) and a confocal laser scanning microscope (KEYENCE VK9500, Japan). Pore size distributions of porous membranes were evaluated using Porometer 3G (Bel Japan Inc.) and Nano-PermPrometer (Seika Sangyo Co., Japan). Sedimentation property of the particle was evaluated using Turbiscan Lab Thermo (Formulaction, France).

3. Results and discussion

3.1. *Formation of graded supports by filtration-sedimentation method*

The particle size distribution of the crushed AMAKUSA china stone was shown in Fig. 3. The particle size is widely dispersed from less than 0.1 to 100 μm with the average particle size of 4 μm. Suspension properties were measured as shown in Fig. 4. The vertical axis shows the height of bath. The height of 40 mm was the surface of bath. A horizontal axis shows intensity of transmission. The transmission intensity in each height was measured at constant intervals. The time between measurements of Figs. 4a and b are 10 min, and c is 6 h, respectively. The profile shifted to the right and under with the time passage. The shift to the right means cohesion of the dispersed powder. The shift to the under means the sedimentation of the particles. In case of using H_2O suspension, an irregular sedimentation and cohesion were observed as shown in Fig. 4a. Then, PVA was added. As a result, it was necessary to adjust the time between measurements from 10 min to 6 h to detect a clear subsidence. It means that the addition of PVA has increased the dispersion of the

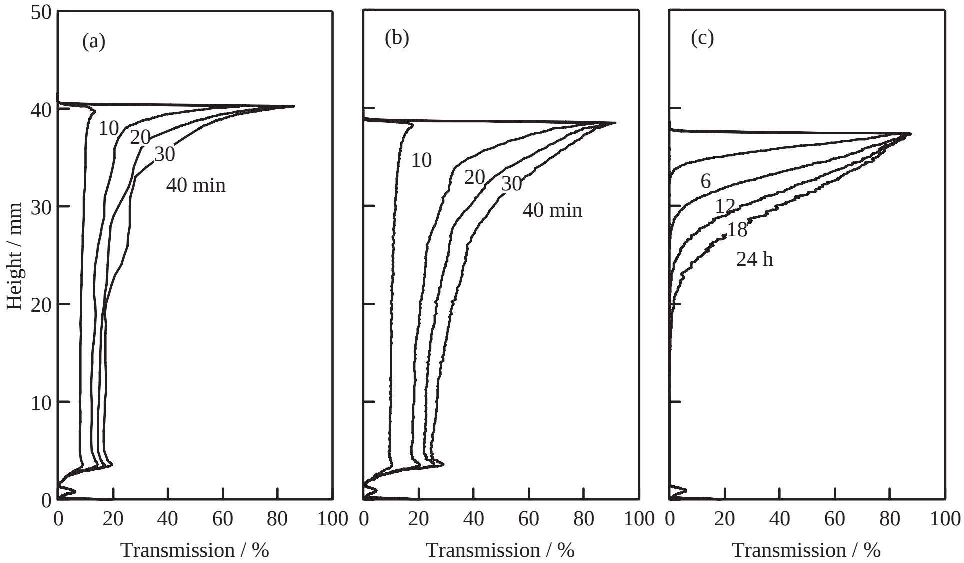

Fig. 4. Sedimentation property of the crashed AMAKUSA china stone. Composition of (a) AMAKUSA china stone: H_2O = 0.45: 3 (weight ratio), interval; 10 min, (b) AMAKUSA china stone: H_2O: PVAaq. = 0.45: 2: 1, interval; 10 min, and (c) AMAKUSA china stone: H_2O: PVAaq.: AS = 0.45: 2: 1: 0.0075, interval; 6 h.

particles. When suspension that added PVA was used, neither irregular cohesion nor the sedimentation was observed as shown in Fig. 4b. However, the sedimentation and the cohesion of (a) and (b) are remarkable within 1 h. In addition, the effect of the addition of positive charged AS copolymer was examined. As a result, dispersion property has improved. It is thought that this is because of AS's adsorption to the particle, and having charged positively. The particle that charged positive was repulsed each other, and the sedimentation and cohesion were decreased as shown in Fig. 4c. The interval time of Fig. 4c is 6 h. Therefore, the sedimentation became remarkably slow, and the bulk density of deposition became lowered. In other words, porosity of deposition became increased. Here, even if the particle sedimentation slows, a large particle is promised to subside early. Therefore, obtained deposition becomes graded structure. From these results, model of sedimentation is considered as shown in Fig. 5. After sintering at 1,473 K, the sintered support disc had graded structure. The disc size is ca. ø30 mm and *t*2 mm. The cross section view of close to the top and bottom are shown in Fig. 6. Fig. 6a is a whole image in the cross section. Fig. 6b is close to the top view, Fig. 6c in middle part and Fig. 6d is close to the bottom view. The pore size of close to the top is small and that of close to the bottom is large. Thus, the graded support was able to be made in the process of one time. The membrane performances were different at the sintering temperature as shown in Table 2. In case of sintered at 1,473 K (Test piece No. 2), the maximum pore size of dense surface is ca. 1.340 μm by bubble point method and the pure water flux was ca. 39.9 $m^3/m^2/$ d at 0.05 MPa. In case of sintered at 1,488 K (Test piece No. 1), the maximum pore size of dense surface is ca. 0.520 μm and the pure water flux was ca. 5.43 m^3/m^2 d at 0.05 MPa.

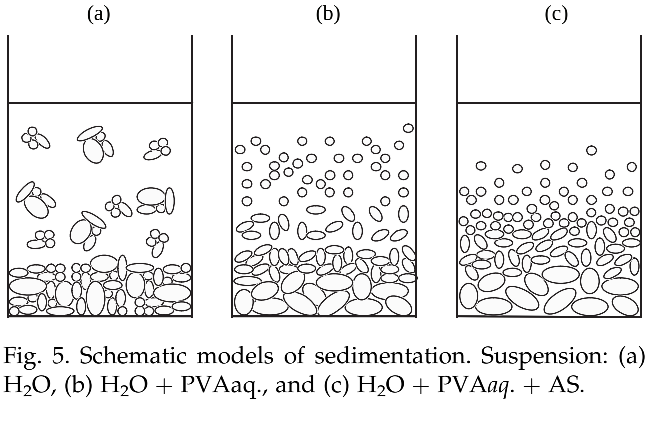

Fig. 5. Schematic models of sedimentation. Suspension: (a) H_2O, (b) H_2O + PVAaq., and (c) H_2O + PVA*aq*. + AS.

3.2. Surface modification by EPD method

Three types of alumina particles with the average diameters of 0.7, 0.4 and 0.08 μm, were orderly deposited by EPD method on the above support disc and/or commercial support discs having pore size of less than 0.7 μm. Each EPD bath concentration was 0.6, 0.5 and 0.1 g/L, respectively. These particle size distributions in each EPD bath are shown in Fig. 7. The distribution of each particle is narrow. The orderly deposition

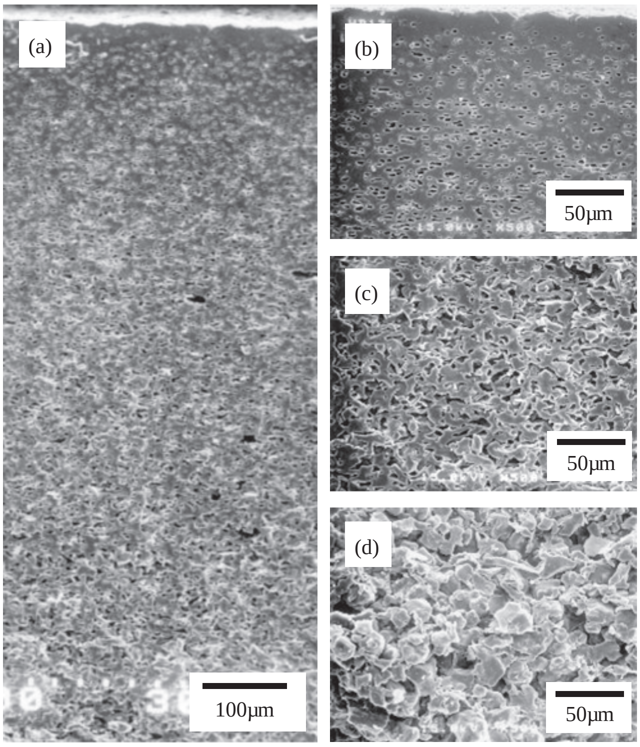

Fig. 6. SEM images of the cross sections of the whole (a), close to the top (b), middle (c), and bottom (d) of graded support made by sedimentation method.

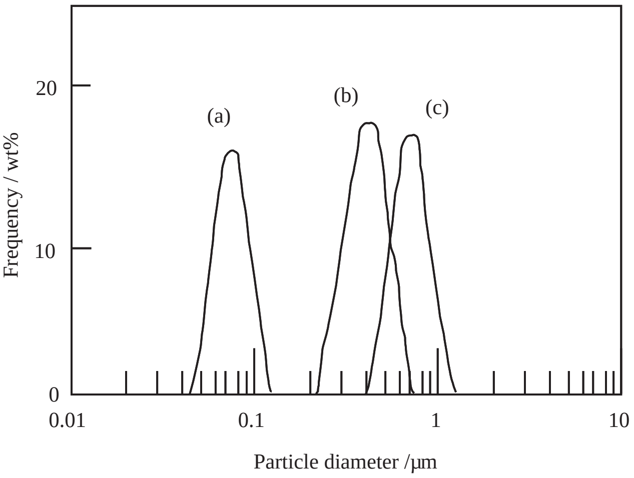

Fig. 7. Particle size distribution of (a) AL160-SG3, (b) AL47-1, and (c) AL45-H in EPD bath.

image is shown in Fig. 8. An increase in weight by the EPD of three kinds of particles is 1 mg/cm^2 or less. Therefore, it is difficult to show the data of the weight change of each EPD because these amounts were very small. Ref. [10] describes reported detail investigation of orderly EPD of aluminum particles in 95 vol%MeOH–5 vol%HCl*aq*. (pH 2.2) EPD bath. The deposited support disc was sintered at various temperatures. The hardness of deposition layer is estimated by pencil hardness test as shown in Table 3. The sintering temperature was recommended over 1,473 K because the hardness drastically increased around 1,473–1,523 K. Fig. 9 shows photograph of the sample. The surface was flat and the roughness of the surface is approximately 2 μm. Table 4 shows the membrane performance of EPD support disc which were prepared only by EPD of large particles, EPD of large particle subsequently middle size particles and EPD of large particles, middle particles and small particles orderly. As a result, the minimum pore size of the surface has become small stepwise with 0.20, 0.17 and 0.10 μm respectively.

3.3. Preparation of titania NF membrane by sol–gel process

Titania colloidal sols were coated on the deposited support disc, and subsequently sintered at 723 K. The permeance of the nitrogen of various support discs were 4.8–15.8 × 10^{-6} mol/m^2 s Pa at room temperature as summarized in Table 5.

Fig. 10 shows dimensionless permeability of nitrogen (DPN) curves of TiO_2 membranes prepared in this study. The pore size distributions of porous membranes were evaluated using the nanopermporometry technique, the principle of which is based on the capillary condensation of vapors inside pores and subsequent blocking of permeation of a noncondensable gas (nitrogen). Water was used as a condensable gas. Nanopermporometry characterization reveals that nano-sized porous titania top-layer having average pore size of about 3.5 nm, which were defined at 50% of DPN, was successfully prepared.

Table 2
Graded support membrane performances (($P = 0.05$ *MPa, 298 K*)

Test piece No.	Sintering temp.[K]	Minimum pore size [μm]	Maximum pore size [μm]	MFP pore size [μm]	Pure water flux [m^3/m^2 d]
1	1,488	0.129	0.520	0.407	5.43
2	1,473	0.201	1.340	0.585	39.9

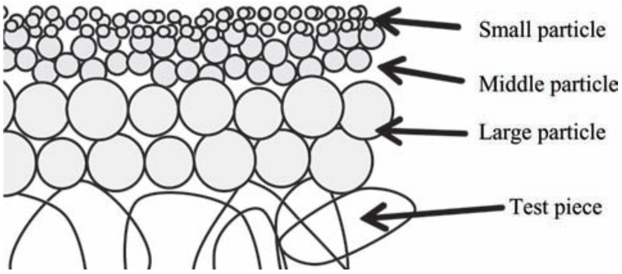

Fig. 8. Schematic image of orderly EPD.

Table 3
Pencil hardness test of the EPD coating

Sintering temp.[K]	1,273	1,373	1,473	1,523	1,573	1,673
Pencil hardness	<6B	<6B	<B	>9H	>9H	>9H

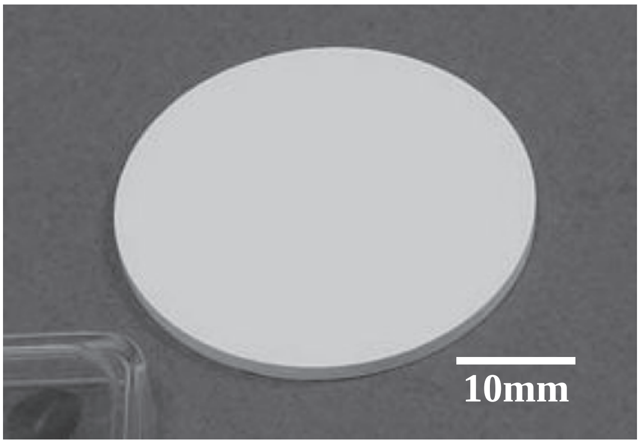

Fig. 9. Photograph of the surface modified support disc by EPD.

4. Conclusions

We have developed pore-size-graded inorganic supports and applied them to the supports of nanosized porous inorganic membranes. First, crushed AMAKUSA china stone (distributed in the range of ca. 10 nm to 100 μm) was used as raw materials of support discs. The green support disc was prepared by sedimentation method in the powder dispersed suspension, followed by firing at 1,473 K. The sintered support disc has graded structures and the pore size was less than 2.0 μm. Then three types of Al_2O_3 particles, the average diameters of 0.7, 0.4 and 0.08 μm, were orderly deposited by EPD on the above support disc and/or commercial support discs having pore size of less than 0.7 μm. The deposited support disc was sintered at 1,523 K and the average pore size of the surface was about 0.1 μm. Finally, TiO_2 colloidal sols were coated on the deposited support disc, and subsequently sintered at 723 K. As a result, nano-sized porous TiO_2 top-layer having average pore size of about 3.5 nm was successfully prepared.

Table 4
Membrane performance of EPD support disc

EPD layer	Particle diameter [μm]	Minimum pore size [μm]	Flux (bubble point method) [L/min]
Large particle	0.7	0.20	0.21
Large particle + Middle particle	0.7 + 0.4	0.17	0.087
Large particle + Middle particle + Small particle	0.7 + 0.4 + 0.08	0.10	0.044

Table 5
Permeance of the various disc membranes

Disc membrane	Permeance [10^{-6} mol/m^2 s Pa]
Sample 1 (Alumina disc + EPD)	15.8
Sample 2 (Alumina disc + EPD)	15.0
Sample 3 (Test peace + EPD)	9.4
Sample 4 (Test peace + EPD + sol–gel)	4.8

Acknowledgement

This study was supported by the Research and Development Grant Program of the Kanto Bureau of

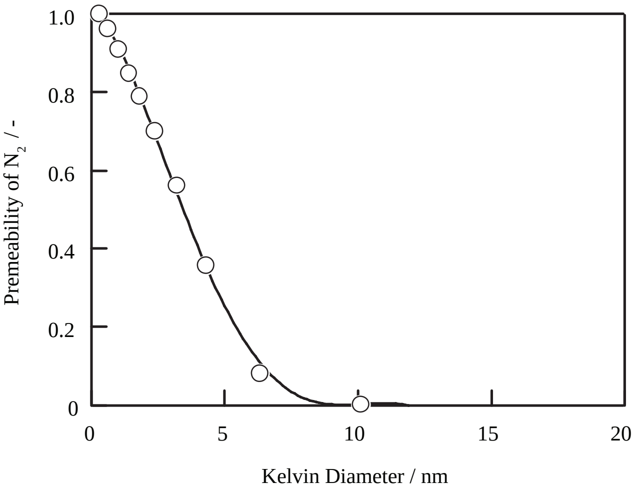

Fig. 10. Dimensionless permeability of nitrogen of TiO_2 membranes determined by nanopermporometry. (condensable vapor: water).

Economy, Trade and Industry, Ministry of Economy, Trade and Industry (METI) of Japan.

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