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110th Anniversary: Liquid Separation Membranes Based on Nanowire Substrates for Organic Solvent Nanofiltration and Membrane Distillation

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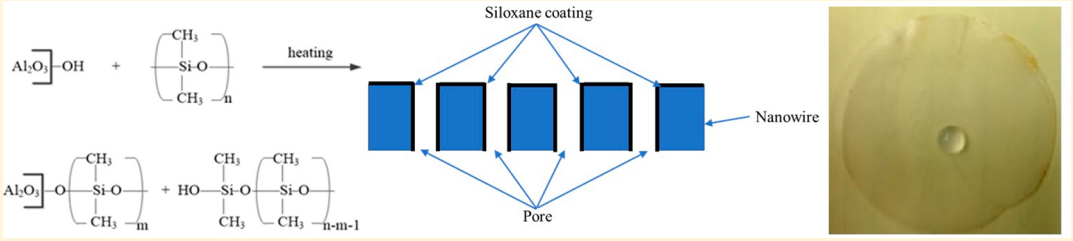
Supporting Information



ABSTRACT: Ceramic nanowire-based flat porous membranes allow development of organic−inorganic membranes. Two types of surface modifications of alumina nanowire-based membranes were implemented. The first one involved reaction of hydroxyl groups on an alumina surface with silicone oil at a higher temperature, developing a grafted coating yielding a nonporous or a porous hydrophobic membrane. The hydrophobicity was verified via a contact angle comparable to that of a porous hydrophobic ethylene chlorotrifluoroethylene membrane. The membrane porosity was demonstrated by running vacuum membrane distillation with a 1 wt % salt-containing brine. The process yielded satisfactory water vapor flux with 98% salt rejection. The silicone oil's reaction with the alumina surface could also block the pores, yielding a nonporous membrane for organic solvent nanofiltration (OSN). Interfacial polymerization was also carried out on the porous nanowire membrane to yield a nonporous polyamide membrane. The developed membrane was tested for OSN using the dyes Safranin O (MW, 351 g/mol) and Brilliant Blue R (MW, 826 g/mol) in methanol. Rejections of 68.1% and 76.7% were achieved for Safranin O and Brilliant Blue R, respectively, at a relatively low pressure of 551 kPag (80 psig). The methanol permeabilities were higher than those of a few nanofiltration membranes described in the literature.

1. INTRODUCTION

New developments in membranes for separation are strongly influenced by breakthroughs in novel materials and structures developed in materials science and engineering. These include carbon nanotubes, graphene, graphene oxide, metal organic frameworks (MOFs), etc. One such development of interest involves ceramic nanowires, which are being investigated as fillers to enhance ionic conductivity of polymer electrolytes.[1] They are also being explored as conducting nanowire bundles in insulating ceramics[2] and as coatings on ceramic foams acting as high-efficiency aerosol filters[3] among many other examples. How such structures could be usefully employed in membranes is of interest.

Most common membranes used for liquid separations employ an integrally asymmetric membrane or a composite membrane. This is also true of membranes for gas separation. Composite membranes allow individual optimization of the selective membrane coating and the substrate supporting the thin selective membrane. For almost all polymeric membranes, the substrate providing mechanical support of the membrane is also polymeric in general. Furthermore, they have to be highly porous. Recently, a series of bendable ceramic nanowire-based porous membranes have become available. The pore size of such membranes varies from 5 to 500 nm; the porosity is ∼70%. These membranes are fabricated using nanowires of titania, alumina, magnesia etc. The fabrication method is described in a patent.[4] Such a nanoporous membrane can be a support for a variety of novel inorganic−organic composite membranes with a polymeric skin which may be nonporous or porous.

The nonporous membranes developed using such a substrate could be designed to separate a variety of mixtures. If the nonporous polymer coating is rubbery, it may be used to separate volatile organic compounds (VOCs) in a gas mixture from inert gases, e.g., nitrogen. If the polymer is appropriate, such a dense membrane may be used to separate organic solvents from larger solutes by nanofiltration. Dutczak et al.[5] developed such a composite capillary membrane by having a polydimethylsiloxane coating on an α-alumina capillary

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support. The bendable nanowire-based substrate of interest is likely to be a useful substrate for that end. While most polymers used as support/substrate undergo swelling from organic solvents to various extents, inorganic supports are unlikely to display such a behavior.

Separation of larger organic solutes from many organic solvents used in pharmaceutical applications can also be implemented by having a polyamide membrane synthesized on the porous support membrane via interfacial polymerization (IP). Kosaraju et al.[6] and Roy et al.[7] implemented interfacial polymerization on porous hydrophilized polypropylene flat/hollow fiber substrates and created efficient solvent-resistant membranes for pharmaceutical applications. Because the nanowire-based support membranes are hydrophilic to start with because of the types of nanowires used, one can implement interfacial polymerization and develop a selective polyamide layer for solvent-resistant nanofiltration without the need for hydrophilizing a hydrophobic polymeric substrate. That is one of the objectives of this study.

A porous membrane developed using a nanowire-based highly porous substrate may have a number of useful applications. In general, the substrate nanowire materials are hydrophilic. If one can hydrophobize the surfaces of the nanowires, then we can have a porous hydrophobic membrane. If the hydrophobizing polymer has high-temperature resistance, then potentially such a porous hydrophobic nanowire-based membrane could function as a battery separator at temperatures as high as 120−150 °C. This would be a considerable improvement over current porous polypropylene membrane (Celgard)-based battery separator membranes during high-temperature excursions. Because these substrates have much higher porosity than Celgard-based substrates, higher transport rates are expected. Further, it could also find useful applications in high-temperature solvent microfiltration applications. An additional application would be high-temperature membrane distillation at temperatures of 120−150+ °C.[8]

A number of strategies have been employed in the literature to develop hydrophobic surfaces on porous hydrophilic ceramic substrates. Gazagnes et al.[9] employed ceramic membranes of zirconia, alumina, and alumino-silicate, with pore diameters of 50, 200, 400, and 800 nm and chemically modified using 1H,1H,2H,2H-perfluorodecyltriethoxysilane, and studied desalination by air gap membrane distillation (AGMD). Koonaphapdeelert and Li[10] hydrophobized a porous alumina hollow fiber surface by grafting using a solution of 2H-perfluorooctylethoxysilane solution. Cerneaux et al.[11] chemically modified the hydrophilic feature of titania and zirconia ceramic substrates into hydrophobic ones by grafting of perfluoroalkylsilane molecules (C8) and compared various membrane distillation methods. Hendren et al.[12] made alumina Anodisc membranes hydrophobic through surface treatments that utilized perfluorodecyltriethoxysilane, trimethylchlorosilane, or trichloromethylsilane and studied direct contact membrane distillation (DCMD). Fang et al.[13] employed fluoroalkylsilane (FAS) to modify porous alumina hollow fiber surface for membrane distillation. Kujawa et al.[14] grafted $C_6F_{13}C_2H_4Si(OC_2H_5)_3$ and $C_{12}F_{25}C_2H_4Si(OC_2H_5)_3$ molecules on titania ceramic membranes (300 kD) and studied desalination by AGMD and DCMD.

Lee et al.[15] studied CO_2 capture in a membrane contactor made of alumina hollow fibers whose surface was hydrophobized by immersion in a hexane solution of a fluoroalkylsilane at room temperature. Yu et al.[16] developed a superhydrophobic surface in a ceramic membrane contactor for CO_2 capture by grafting with a FAS solution on an alumina tube with a ZrO_2 layer. Tao et al.[17] developed an efficient Si_3N_4 ceramic planar membrane for a water desalination process using membrane distillation by the dual-layer phase inversion tape casting and sintering method. We have adopted here a different strategy; it involves using a flat porous ceramic substrate based on ceramic nanowires and then hydrophobizing the ceramic nanowire surface.

The nanowires of interest, for example, those of alumina, TiO_2, etc., have hydroxyl groups on the surface. Bringing pure dry silicone oil of a somewhat higher molecular weight in contact with the substrate and heating it up to 160 °C would cause a cleavage of the Si−O bond of the silicone polymer with recombination on the hydroxylated alumina surface (Leger et al.[18,19]) (Figure 1). Any unbound silicone oil can be extracted

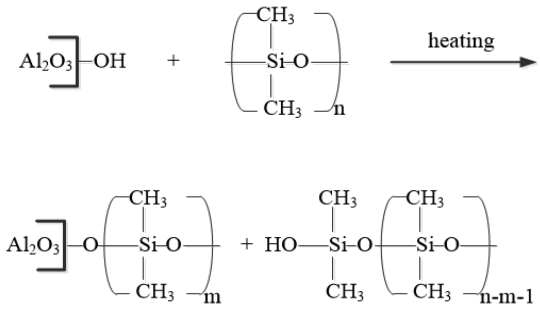

Figure 1. Reaction leading to grafting of silicone oil functionality on porous alumina support membrane surface.

out by using a solvent, for example, hot toluene. Selecting silicone oil of a sufficiently higher molecular weight is likely to decrease the substrate membrane pore size drastically and create an almost dense membrane in the porous region of the nanoporous nanowire-based substrate. A more interesting goal is to create a porous structure.

This has been implemented here by developing first a porous structure with pure dry silicone oil via N_2 blowing and then carrying out heating and surface bonding reactions between the hydroxyl groups with the Si−O bond of the residual silicone polymer clinging to the wall as shown in Figure 1. The success of this approach has been evaluated by carrying out vacuum membrane distillation (VMD) studies. To test the concept, a conventional initially porous alumina (Anodisc) support membrane was used.

From a conceptual point of view, such a strategy can be implemented as well with other inorganic substrates, such as titania, etc. In this communication, we describe these approaches in greater detail with alumina nanowire substrate-based membranes and illustrate the results we have obtained in desalination with vacuum membrane distillation (VMD). We have in addition implemented interfacial polymerization on the hydrophilic ceramic nanowire support and developed a solvent-resistant polyamide nanofiltration membrane.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. The materials and chemicals used included the following: nanowire membrane samples of alumina and titania, size 60 mm (Novarials Corporation (Woburn, MA)); Anodisc 47 (0.02 μm pore size) alumina membrane of 47 mm diameter (Whatman/GE);

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Ind. Eng. Chem. Res. 2019, 58, 14350−14356

hydrophobic ethylene chlorotrifluoroethylene (ECTFE) membrane (3M, St. Paul, MN), nominal pore size of 0.2 μm, thickness of ∼0.005 cm (0.002 in.); silicone oil (poly(methylphenylsiloxane)), viscosity 450−550 cSt (CAS number, 63148-58-3, Sigma-Aldrich); m-phenylenediamine 99% (CAS number, 108-45-2; Sigma-Aldrich); 1,3,5-benzenetricarbonyl trichloride 98% (CAS number, 4422-95-1; Sigma-Aldrich); hexane anhydrous 95% (CAS number, 110-54-3; Sigma-Aldrich); xylene certified ACS (CAS number 1330-20-7; Fisher Scientific); Brilliant Blue R (MW 826 g/mol, dye content 90%, Sigma−Aldrich, St. Louis, MO); Safranin O (MW 351g/mol, dye content 95%, Fisher, Fair Lawn, NJ); sodium carbonate anhydrous power 99% (CAS number, 497-19-8, Sigma-Aldrich); deionized water; ultrahigh purity nitrogen cylinder (NI UHP300, Airgas).

2.2. Experimental Procedure. Before any membrane modifications were carried out, the 25 mm nanowire-based membranes (cut out from 60 mm membranes as described later) were baked in an oven at 200 °C overnight and air cooled to improve its properties; this was implemented per the instructions of the manufacturer.

2.2.1. Membrane Modifications with Silicone Oil. For surface modification with silicone oil, first the Anodisc 47 membrane was used. It was soaked in silicone oil for 12 h, put in a cell and sealed with o-rings. N_2 gas was passed at 1.6 atm pressure (gauge) through the membrane; this process removed the bulk of the silicone oil from the pores of the membrane; the pore surfaces had silicone oil left for grafting/polymerization. The Anodisc membrane surface was then modified with silicone oil left on its pore surfaces at 160 °C for 2 h in an oven. After grafting/polymerization were completed, the membrane was allowed to cool and put back in the cell and toluene was passed through the membrane pores. The idea behind this step was to remove any unbound silicone oil from the membrane surface and from the pores of the membrane. Experiments were also done without passing any N_2 gas at the beginning so that completely nonporous membranes were developed via all other steps identified above.

Because 60 mm size nanowire substrate samples were received from the manufacturer, 25 mm membrane discs were cut out using a 25 mm stainless steel die. Before any modification was implemented, the 25 mm membrane was placed into a Petri dish full of silicone oil. The membrane was soaked for 24 h. The soaked membrane was put in a 25 mm stainless steel holder (Model XX4502500, EMD Millipore Corporation), and both halves of the sample holder were secured. Nitrogen gas was passed through the membrane at ∼138 kPag (20 psig) to remove the bulk of the silicone oil from the pores of the membrane. A layer of silicone oil remained on the pore surfaces and the flat membrane surfaces. The membrane was then put in the oven at 160 °C in N_2 atmosphere for 2 h. After the heat treatment, the membrane was cooled in a N_2 stream. Then toluene was passed through the membrane put in the cell to remove any unbound silicone oil from the membrane surface and pores.

2.2.2. Membrane Modification via Interfacial Polymerization. The solutions used for the IP-based membrane on the inorganic nanowire substrate were as follows: 1 g of trimesoyl chloride (TMC) was dissolved in 49 g of hexane to prepare the organic solution; 1g of m-phenylenediamine (MPD) and 1 g of sodium carbonate were dissolved in 48 g of distilled water to prepare the aqueous solution. Even though the weight-based concentrations of the two reactants are almost identical, their molar concentrations are very different because the molecular weights of the reactants (TMC, 265.47 g/mol; MPD, 108.14 g/mol) are very different; furthermore, this ratio was found to be quite beneficial for similar reactants.[6] A 25 mm ceramic membrane disc (based on alumina nanowires) appropriately heat-treated was placed in a glass Petri dish full of the organic solution for 30 min. Normally a hydrophilic substrate in interfacial polymerization is first wetted with the aqueous phase solution. Here we have instead used the organic solution to avoid the possibility of corrosion of the alumina substrate by the alkali in the aqueous solution. The soaked membrane was next placed on top of a sheet of Kimwipe to get rid of the excess organic solution especially around the edges of the membrane disk. The top side of the membrane disc was then carefully put into another glass Petri dish full of the aqueous solution so that the membrane disc was floating on the surface for 10 min. A thin polyamide film was formed at the aqueous−organic interface. The modified disc was air-dried overnight and then baked at 90 °C for 20 min to complete the reaction from any residual monomers.

The organic solvent nanofiltration studies were conducted in the 25 mm stainless steel filter holder in the dead end mode with the feed liquid solution in a reservoir driven by N_2 gas pressure from a cylinder. The feed liquids were methanol-based solutions of the following dyes: Safranin O (MW, 351 g/mol; maximum absorption, 530 nm) and Brilliant Blue R (MW, 826 g/mol; maximum absorption, 590 nm). The calibration curves for Safranin O and Brilliant Blue R in methanol were obtained by measuring the absorbance of the dyes in methanol solutions at different dye concentrations with a UV−visible spectrophotometer (Cary 50 Bio UV−vis, Varian Inc.). The permeate flux of the solvent and membrane rejections of the dyes Safranin O and Brilliant Blue R in methanol were calculated and reported for each membrane. The membrane rejection R_i of solute species i is defined as

$$R_i = [1 - (C_{ip}/C_{if})] \quad (1)$$

where C_{ip} and C_{if} are the permeate concentration and the feed concentration, respectively, of the dye solute i.

2.2.3. Membrane Characterization. A scanning electron microscope (Model: LEO 1530 VP Gemini (Carl Zeiss Inc., Peabody, MA)) was used to characterize various membranes. An additional scanning electron microscope used to scan the nanowire substrate of this study was JSM 7900F Field Emission SEM (JEOL USA, Peabody, MA). An iPhone was used to take photos of a water droplet on the hydrophobized membrane. The bubble point test was conducted in an EMD Millipore 25 mm filter holder reconfigured to act as a bubble point device. Contact angles of the treated membranes were measured using an optical tensiometer (Model No. A 100, Rame-Hart Inc., Succasunna, NJ). A drop of water was placed onto the surface of the membrane; then the water drop was adjusted so that it was clearly observed under the eye lens.

Vacuum membrane distillation studies were carried out in a preexisting VMD apparatus using 1 wt % NaCl containing solution.[20] The 25 mm stainless steel holder was used here in the dead end mode instead of the regular cross-flow membrane distillation cell in the preexisting membrane distillation apparatus.[20] As a result, temperature polarization was considerable. The solution conductivities were measured using a conductivity meter (Orion 115A+, Thermo Fisher Scientific, Waltham, MA).

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Ind. Eng. Chem. Res. 2019, 58, 14350−14356

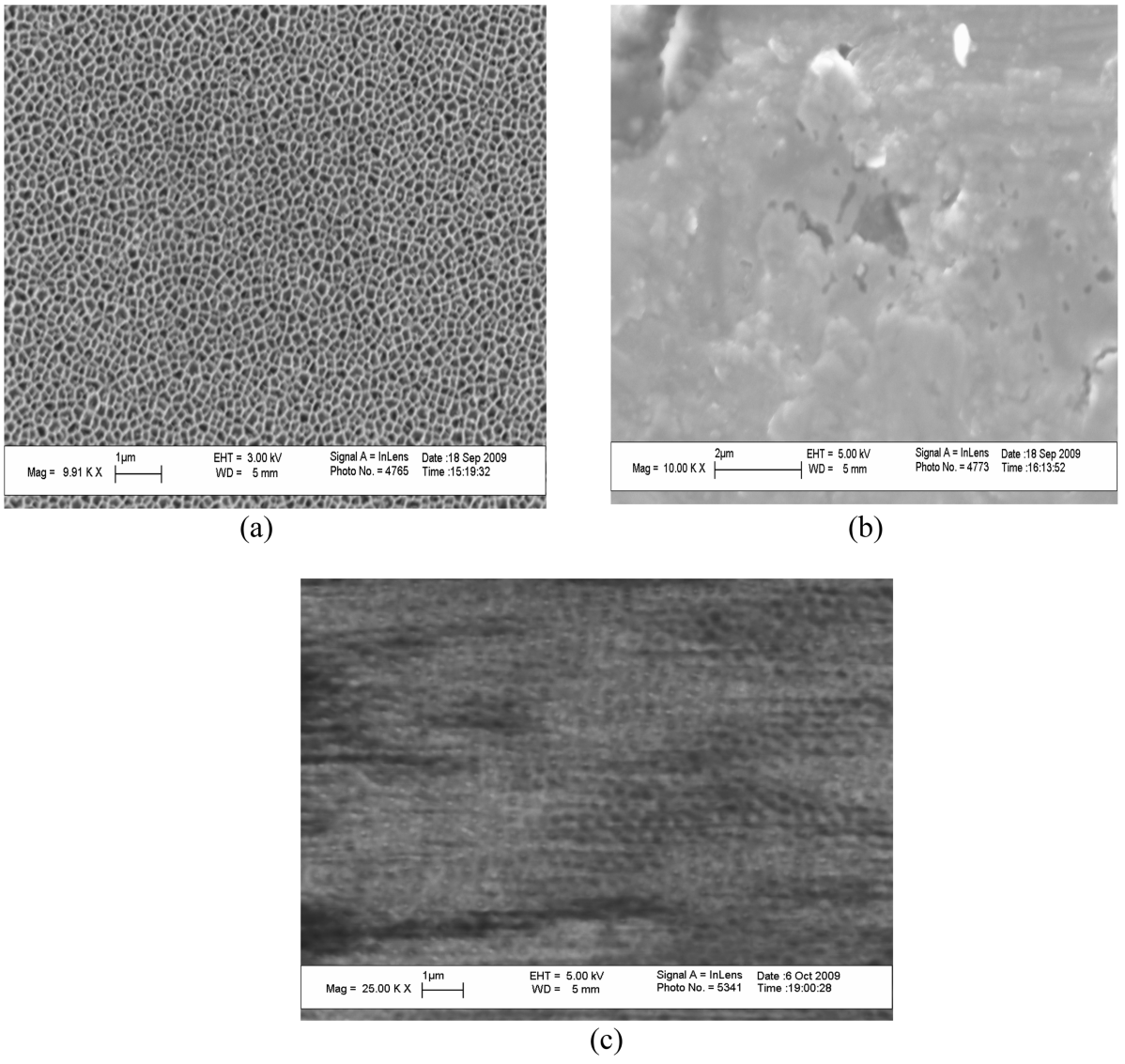

Figure 2. SEM micrographs showing the surfaces of Anodisc 47 modified with silicone oil: (a) unmodified surface; (b) N_2 gas is passed after heating the membrane at 160 °C; (c) N_2 gas is passed before heating the membrane at 160 °C and after polymerization, toluene is passed through the membrane.

3. RESULTS AND DISCUSSION

We first focus on silicone oil-based surface modifications. In scanning electron microscopy (SEM) micrographs, the surface of the unmodified Anodisc 47 membrane has a large number of pores (Figure 2a), which are blocked after the modification process when no N_2 gas-based treatment was implemented before heat treatment in an oven (see Figure 2b). However, before the heating of the membrane at 160 °C, if silicone oil in the pore bulk is blown off by N_2 gas at 138 kPag (20 psig) pressure, pores will be open again. Pores will be more clearly visible if toluene is passed to remove the unbound silicone oil (Figure 2c). Figure 3 provides a conceptual schematic of what happens after blowing off the bulk of the silicone oil in the pores by N_2 gas and then carrying out surface grafting of the residual silicone oil with the porous alumina surface. The schematic shows the hydrophobic coating on the alumina membrane pore surfaces. No data on membrane distillation could be gathered using the modified Anodisc membrane because the membrane was very fragile.

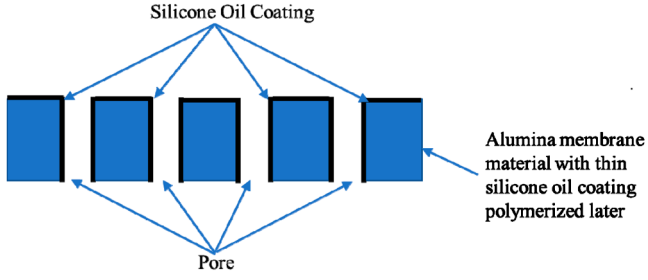

Figure 3. An expanded conceptual schematic of the resulting configuration after the bulk of the silicone oil is blown off the pores in the porous alumina membrane with the pore surface remaining coated with the silicone oil which is polymerized on the alumina surface later by heating.

Having settled the issue of whether the proposed N_2 gas blowing will work, we focused on the ceramic nanowire substrate-based membrane. SEM-based micrographs of the

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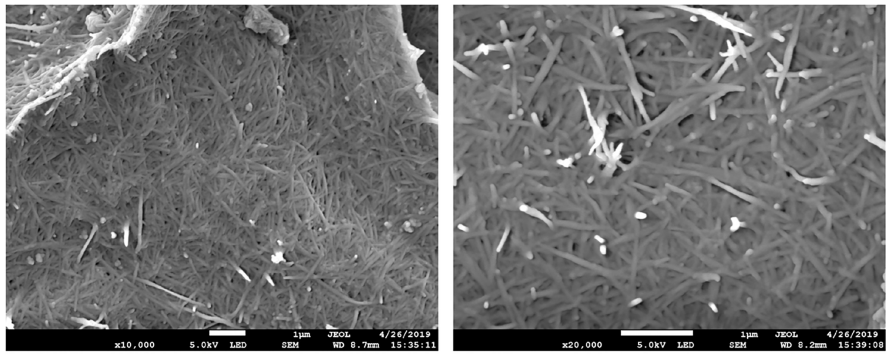

(a) (b)

Figure 4. SEM micrographs of the surface of the nanowire substrate for two different magnifications: (a) ×10 000 and (b) ×20 000.

nanowire substrate of this study for two different magnifications are shown in Figure 4a,b. The nanowires are clearly visible. To develop an estimate of the pore size of the substrate, we focus on the maximum pore size of the virgin membrane. An estimate of the maximum pore size was developed via bubble point tests with toluene. The bubble point pressure of toluene was found to be 138 kPag (20 psig), corresponding to a maximum pore size of 0.8 μm. To develop this estimate, we did not use the form factor usually used in the formula. The surface tension of toluene at 25 °C was taken as 27.3 dyn/cm.

Next, we used an appropriately modified membrane with pores developed by N_2 blowing before polymerization with silicone oil for vacuum membrane distillation studies with 1 wt % salt in water as the feed solution. The vacuum pulled on the other side of the membrane was 91% of full vacuum.[20] The feed solution was imposed on the membrane in the dead end mode without any stirring or flow. The effective diameter of the membrane was 0.015 m. The conductivity of the feed solution was 16.67 mS/m. Water vapor flux values for various brine temperatures are illustrated in Table 1. The conductivity

Table 1. VMD Performance of Hydrophobized Microporous Nanowire Substrate-Based Membrane

feed brine temperature (°C)	water vapor flux (kg/m^2·hr)
65	8.0
75	10.9
85	15.1
95	21.3

of the condensed distillate collected on the other side of the membrane was 350 μS/m. It is expected that the distillate would be free of any salt. The increase in permeate conductivity suggests that there were trace leakages of the feed brine through a few membrane pores. We could have achieved higher water vapor fluxes had it not been for high-temperature polarization on the hot brine side due to a dead-end configuration.

To develop a better understanding of why there was even a trace amount of salt in the condensed permeate, we need to consider the pore size of the membrane and the vacuum level. In the studies on VMD by Li and Sirkar[20] using a variety of membranes, it was found that ePTFE membranes having a nominal pore size of 0.45 μm allowed a small amount of salt leakage from the largest pores resulting in a permeate conductivity of 500−1550 μS as the vacuum level went beyond 88% of full vacuum. Measurements of liquid entry pressure indicated that the largest pore sizes of hydrophobic membranes normally used for membrane distillation will lead to leakage when the vacuum level is high.[20] As indicated earlier, the bubble point pressure measurements of the virgin nanowire-based membrane suggested a maximum pore size of ~0.8 μm. Although pore surface polymerization for hydrophobization will reduce this size, it is still on the high side to allow some salt leakage. However, the salt rejection is very high and is acceptable for most desalination applications.

The hydrophobic nature of the surface-modified microporous membranes can be judged via two additional tests: contact angle measurements and photo of a water drop on the hydrophobized surface. Table S1 illustrates the results of contact angle measurements using optical tensiometry and a comparison with a known microporous hydrophobic membrane of ECTFE (ethylene chlorotrifluoroethylene) of nominal pore size of 0.2 μm.[21] Figure 5 illustrates a single water drop

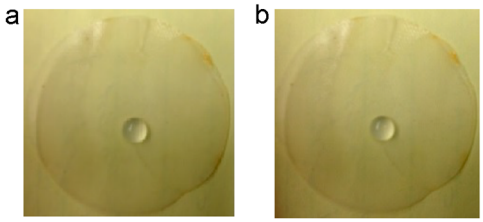

Figure 5. (a) A drop of water on top of the treated alumina membrane disc at t = 0. (b) The same drop of water on top of the treated alumina membrane disc at t = 30 min.

on the surface of the hydrophobized microporous membrane at two different times indicating a stable hydrophobic surface. Tests carried out with hydrophobized porous TiO_2 nanowire-based membranes indicated a similar behavior. Such membranes are likely to be useful for membrane distillation at high temperatures.

We next focus on the performance of interfacially polymerized polyamide membranes on the top surface of the alumina nanowire substrate in solvent-resistant nanofiltration to be identified as organic solvent nanofiltration (OSN). The permeate flux of the solvent methanol and membrane rejections of the dyes Safranin O and Brilliant Blue R in methanol were calculated from the experimental data taken at 25 °C and are shown in Tables S2 and S3, respectively, for two different membranes. At 689 kPag (100 psig), the thin layer formed on top of the ceramic substrate during interfacial

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Ind. Eng. Chem. Res. 2019, 58, 14350−14356

polymerization was destroyed; as a result, the permeate flux was very high. Solute rejection could not be obtained for Safranin O; it was ~8.7% for Brilliant Blue R. At lower pressures, 551 kPag (80 psig) or lower, the membrane performed satisfactorily.

In order to carry out organic solvent nanofiltration at a higher pressure, 620−689 kPag (90−100 psig) and beyond, it is necessary to employ a substrate with a smaller pore size to prevent rupture of the thin polyamide skin. The pore size of the nanowire substrate membranes used here was on the high side (around 0.4−0.8 μm). It is also known that somewhat higher pressure will also significantly enhance the solute rejection.[22]

In addition, the solvent (methanol) fluxes and solute rejections in the fabricated membranes reported in Tables S2 and S3 were compared with some data reported in the literature. The comparison is shown in Table 2 using solvent permeances and solute rejections. Table 2 shows that the interfacially polymerized solvent-resistant polyamide membrane prepared on the support membrane based on the alumina nanowire substrate achieves a reasonable value of normalized methanol flux (or permeance) among the data quoted. The solute rejection, although somewhat on the lower side, is acceptable given the much lower values of feed pressure.

Table 2. Comparison of Methanol Flux of the Modified Membrane with Data from the Literature

membrane	rejection of Safranin O (351 Da) in methanol (%)	rejection of Brilliant Blue R (826 Da) in methanol (%)	methanol flux normalized with pressure ($L/m^2 \cdot hr \cdot bar$)
this study	68.1 at 551 kPa	76.7 at 551 kPa	2.43
interfacially polymerized polyamide membrane on PP support[a,6]	45 at 413 kPa	88 at 413 kPa	1.23
MPF-60 MWCO, 400 Da[22]	86.9 at 3034 kPa	93.8 at 3034 kPa	6.84×10^{-1}
cross-linked polyimide[23]	82.8[b] at 3000 kPa	93.5[c] at 3000 kPa	8.28×10^{-1}

[a]Porous polypropylene (PP) membrane coated with 0.75 wt % poly(ethyleneimine) (PEI) and 0.75 wt % isophthaloyl dichloride (IPD) for 10 min. [b]Rejection of a compound with MW of 350 Da in methanol; extrapolated data. [c]Rejection of a compound with MW of 825 Da in methanol; extrapolated data.

It must be emphasized here that a significant amount of research has been going on in optimizing the OSN membrane. Almost all of the reports have employed polymeric supports. However, Xia et al.[24] have developed a polyamide layer on a tubular ceramic UF membrane and evaluated the resultant membrane for OSN applications after significant optimizations. Quite a few of their membranes (see their Figures 1 and 4) have pure methanol permeances of around 2.5 LMH/bar, which is right around the values that we have obtained (Table 2). However, it needs to be noted that Xia et al.[24] have obtained considerably higher flux values after significant optimization of the interfacial polymerization. To operate organic solvent nanofiltration at a higher pressure using the nanowire substrates, it is necessary to employ a substrate with a smaller pore size to prevent rupture of the thin polyamide skin. One can also optimize the membrane for considerably higher solvent flux in a variety of ways including the chemistry employed in interfacial polymerization.

The dead end configuration of the nanofiltration test cell contributed to concentration polarization and therefore lower solute rejection and lower solvent flux. This aspect was estimated recently during nanofiltration studies with a perfluorodioxole copolymer membrane for nanofiltration[25] in a similar cell and permeation configuration. In ref 25, the flux levels observed were much lower and the level of concentration polarization was therefore quite low. However, here the flux levels are much higher; therefore, the concentration polarization level will be much higher, which explains the observed lower rejection values.

Nonporous silicone membranes were also developed in the alumina nanowire-based support membrane by the procedure described earlier minus the N_2 gas blowing step employed to develop porous hydrophobized nanowire-based membranes. Organic solvent nanofiltration using methanol solutions of the dyes was carried out also with such a nonporous membrane. The solute rejections were considerably lower, primarily because of substantial solvent swelling of the silicone coating. Extensive cross-linking and other strategies are needed to counteract swelling and enhance the selectivity in solvent-resistant nanofiltration membranes based on polydimethylsiloxane and other polymers.[26−28]

4. CONCLUDING REMARKS

A siloxane-based hydrophobized porous alumina nanowire-based membrane was developed successfully on a hydrophilic porous ceramic nanowire substrate. Its hydrophobicity was demonstrated via contact angle studies and tests with vacuum membrane distillation. Wetting angles of the surface-modified membrane were comparable to those of hydrophobic ECTFE membranes. For 1 wt % hot brine solution used as feed in VMD, reasonable water vapor fluxes were obtained; up to ~98% salt rejection was also achieved. Interfacial polymerization was also carried out on such a porous ceramic nanowire substrate to obtain a thin nonporous polyamide film on its surface. Solvent-resistant nanofiltration was successfully carried out using methanol solutions of the dyes Safranin O and Brilliant Blue R. Permeate flux increased with increasing feed pressure. Rejection values of 68.1% and 76.7% were achieved for dye solutions of Safranin O and Brilliant Blue R, respectively, in methanol at a feed pressure of 551 kPag (80 psig). In addition, the interfacially polymerized solvent-resistant polyamide membrane prepared on the porous substrate membrane based on the alumina nanowire substrate achieved a reasonable normalized methanol flux (or permeance) among the data reported in the literature (Table 2). Further investigations are needed using membranes fabricated from nanowire substrates having finer pores. The ceramic nanowire substrate may be used to develop a variety of useful membranes, porous or nonporous, for a variety of applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b02292.

Tables S1−S3 (PDF)

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Notes

The authors declare no competing financial interest.

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