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Evaluating the Potential of Superhydrophobic Nanoporous Alumina Membranes for Direct Contact Membrane Distillation

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hydrodynamics; membrane distillation; temperature polarization

Abstract*Hypothesis:*

Direct contact membrane distillation (DCMD) processes exploit water-repellant membranes to desalt warm seawaters by allowing only water vapor to transport across. While perfluorinated membranes/coatings are routinely used for DCMD, their vulnerability to abrasion, heat, and harsh chemicals necessitates alternatives, such as ceramics. Herein, we systematically assess the potential of ceramic membranes consisting of anodized aluminum oxide (AAO) for DCMD.

Experiments:

We rendered AAO membranes superhydrophobic to accomplish the separation of hot salty water (343 K, 0.7 M NaCl) and cold deionized water (292 K) and quantified vapor transport. We also developed a multiscale model based on computational fluid dynamics, conjugate heat transfer, and the kinetic theory of gases to gain insights into our experiments.

Findings:

The average vapor fluxes, J , across three sets of AAO membranes with average nanochannel diameters (and porosities) centered at 80 nm (32%), 100 nm (37%), and 160 nm (57%) varied by $< 25\%$, while we had expected them to scale with the porosities. Our multiscale simulations unveiled how the high thermal conductivity of the AAO membranes reduced the effective temperature drive for the mass transfer. Our results highlight the limitations of AAO membranes for DCMD and might advance the rational development of desalination membranes.

1. INTRODUCTION

Mass transfer of water vapor across porous media regulates the behavior of numerous natural and applied systems including soils¹⁻², transpiration²⁻³, crushed ores, food processing⁴, leaks and cracks in construction⁵⁻⁷, electronic packaging⁶, membrane extractions of water vapor⁸ and other chemicals⁹, and micro- and nano-fluidics¹⁰⁻¹⁷. Of those systems, we are interested in extracting desalted water from the oceans through membrane distillation (MD), wherein water vapor from hot salty streams is transferred through porous hydrophobic membranes to condense on the other side^{9, 18-21}. If the other side comprises a stream of cold deionized water, the process is known as the direct contact membrane distillation (DCMD; Figure 1); or if the other side comprises air at low pressure, the process is known as the air gap MD²². In comparison to reverse osmosis (RO), an energy intensive yet common desalination technique²³, MD processes can be designed with lower carbon footprint because the latter can utilize low-grade waste heat from industrial and natural sources, such as low-enthalpy geothermal or solar-thermal^{20, 24}. However, fluxes from the MD-based-approaches have been limiting in comparison to RO, prompting research in innovating approaches towards novel materials and processes.

The flux of desalted water and energy efficiency in DCMD process crucially depend on the thermal gradients across the membranes; other membrane characteristics, including the hydrophobicity, porosity, thermal and chemical stability, and resistance to biofouling determine the long-term functionality^{19-22, 25-26}. Thus, ideal membranes should be water-repellent, bad conductor of heat, mechanically robust, and inert to chemical and biological fouling. To this end, a variety of materials have been explored for scalability, efficiency, and durability, including polytetrafluoroethylene (PTFE)²⁶, polyvinylidene fluoride (PVDF)²⁷, graphene oxide²⁸, carbon nanotubes⁸, buckypapers²⁹, and organosilica infused PVDF³⁰. In fact, commercial MD membranes extensively exploit PTFE, which offers excellent thermal, chemical, and hydrophobic characteristics²⁵⁻²⁶. However, PTFE has poor mechanical properties and researchers have explored the addition of fillers comprising alumina and titania to boost the durability, strength, and abrasion resistance³¹. Porous ceramic membranes have also been investigated for MD^{20, 25, 32-34}. In fact, anodized aluminum oxide (AAO) membranes are of particular interest as they provide (i) a light, lithography-free platform comprising vertically-aligned nanochannels of tunable

diameters with ultrahigh packing densities ($\sigma \geq 10^{13}$ channels- m^{-2}), (ii) ease of surface modification³⁵, and (iii) amenability to theoretical modeling due to their geometrical simplicity to gain insights into mass transport^{4, 6}. For instance, AAO membranes with nanochannels of diameters ranging from 10-120 nm were used to investigate the transport of water (vapor and liquid)^{4, 6} and noble gases³⁶ at 295 K and 1 atm and compared with continuum models for mass transport; others deposited amorphous carbon³⁷⁻³⁸ onto AAO membranes by chemical vapor deposition to render them hydrophobic and observed 45-times higher mass transfer of liquid water in comparison to the predictions of the Hagen-Poiseuille theory of Newtonian liquids and ascribed it to the hydrodynamic slip at water-hydrophobe interfaces³⁷. Recently, researchers have employed silanation reactions to hydrophobize AAO membranes and investigated osmotic mass transfer of water vapor under isothermal conditions¹⁰ and thermal gradients³². While the focus of most of those approaches has been on the surface functionalization of AAO membranes, effects of their thermal conductivity on mass transfer in DCMD are not entirely clear. In fact, a known sink for the energy efficiency in DCMD is the drop in the temperatures between the liquid-vapor interfaces and the bulk liquids due to the formation of thermal boundary layers—also known as temperature polarization²⁰. Indeed, temperature polarization is primarily influenced by the thermal conductivity of membranes. For instance, thermal conductivities of commercial PVDF/PTFE membranes range within 0.04-0.08 W- m^{-1} -K⁻¹ and researchers have simulated the effects of temperature polarization by incorporating extant experimental correlations of Nusselt numbers across a wide range of flow conditions^{20, 39-45}. However, for AAO and other ceramic membranes, such experimental data do not exist preventing clear insights into mass transport. To clarify this matter, we present experimental results on the mass transport of water vapor across nanoporous AAO membranes in DCMD along with a multiscale theoretical model explaining our observations.

Figure 1. Schematic of a typical direct contact membrane distillation (DCMD) setup - a hydrophobic membrane separates a salty stream (hot) of water from a deionized (cold) stream, flowing in opposite directions. Only water vapor transports across from the hot to the cold side.

2. MATERIALS CHARACTERIZATION

We investigated three types of coin-shaped AAO membranes (Synkera Tech., USA) with average nanochannel diameters, D , centered at 80 nm, 100 nm, and 160 nm (Figure 2, S1-3), with the macroscopic diameter of 2.5 cm and thickness, $\delta \approx 100 \mu\text{m}$. Their porosities, defined as the fraction of the entrapped air to the membrane volume, were 32% (80 nm), 37% (100 nm), and 57% (160 nm), respectively. The surface density of holes on the top sides of the membranes were similar across the membranes, whereas the numbers on the undersides varied in the ratio $\sigma_1 : \sigma_2 : \sigma_3 :: 2.9 : 2.3 : 2.0$ (Table 1). The variation in the surface density of pores on the underside was due to branching of some nanochannels (Figure 2D₃-D₄). The as-received membranes were unfit for DCMD due to their hydrophilicity - the advancing and receding contact angles of deionized water under normal temperature and pressure (NTP: 293.15 K, 1 atm) conditions on smooth and flat alumina in air were $\theta_A \approx 40^\circ$ and $\theta_R \approx 0^\circ$, respectively, and when drops of water were placed on as-received AAO membranes, they spontaneously imbibed into the nanochannels underneath, as observed by others⁴⁶⁻⁴⁸ (Figure 3A). Further, those membranes exhibited mechanical fragility and chemical reactivity towards hot water. To overcome those challenges, we annealed the AAO membranes in air in a muffle furnace to render them polycrystalline. During annealing, the temperature was ramped from the room temperature to 773 K at 10 K-min⁻¹, from 773 to 923 K at 5 K-min⁻¹, and from 923

to 1273 K at 2 K-min⁻¹; subsequently, the dwell time at 1273 K was 2 h. After annealing, cooling was performed at 2 K-min⁻¹ from 1273 K to 873 K, and at 5 K-min⁻¹ until 303 K. To prevent the bending and buckling of the membranes during annealing, they were sandwiched between smooth alumina plates of 1.5 mm thickness and a ceramic plate of mass 0.3 kg was placed on top. The resulting membranes were polycrystalline, primarily comprising γ - and δ -alumina phases¹⁰, and exhibited mechanical and chemical robustness, though with higher surface roughness (Figure 2).

Figure 2. (A-C) Representative scanning electron micrographs of the top and bottom sides of pristine and annealed AAO membranes with an average channel diameter of 80 nm (A₁-A₄), 100 nm (B₁-B₄), and 160 nm (C₁-C₄) respectively, demonstrating that annealing at 1273 K for 2 h in air did not lead to physical damage. (D) Representative cross-sectional TEM images of the as-received AAO films of average channel diameter, $D = 80$ nm. After the heat-treatment, crystalline grains and pits appeared on the AAO nanochannels, which increased their roughness. Channels are characterized by the darker contrast in the images.

The selected area electron diffraction (SAED) patterns of the as-received AAO membranes, observed during transmission electron microscopy, comprised a single broad ring confirming the amorphous phase (Figure 3A-C). On the other hand, the heat-treated AAO membranes exhibited spot and ring patterns in the SAED patterns and lattice fringes in the TEM images, confirming the polycrystallinity (Figure 3B-D).

Figure 3. High magnification TEM images of pristine (A and C); and annealed AAO membranes (B and D) of average channel diameter $D = 80$ nm. Insets in images (A) and (D) are SAED patterns collected on the respective AAO membranes.

We further confirmed those observations with x-ray diffraction (XRD) - the XRD patterns of the pristine AAO membranes showed broad humps centered at the 2θ values 28° and 64° , implying that the as-received AAO membranes were amorphous (Figure 4A-C). In contrast, the XRD patterns from the heat-treated (annealed) AAO membranes showed diffraction peaks corresponding to δ - and γ -alumina (JCPDS files numbers 00-010-0425 and 00-046-1131, respectively) (Figure 4A-C).⁴⁹ No noteworthy differences between the top and bottom sides of the AAO membranes were observed.

Figure 4. XRD patterns of pristine, annealed, and FDTS-coated AAO membranes with average nanochannel diameters of (A) 80 nm, (B) 100 nm, and (C) 160 nm. Patterns (a) and (b) correspond to the top and bottom sides of pristine AAO membranes, patterns (c) and (d) correspond to the top and bottom sides of annealed AAO membranes, and patterns (e) and (f) correspond to the top and bottom sides of FDTS-coated AAO membranes. Symbols ‘ δ ’ and ‘ γ ’ in the graphs indicate the phases of Al_2O_3 .

Subsequently, to render the alumina surface hydrophobic, characterized by apparent contact angles of water in air, $\theta_r > 90^\circ$, we chemically grafted perfluorodecyltrichlorosilane (FDTS) molecules onto alumina through a molecular vapor deposition technique (Figure 5, SI Section S2). The absence of any extra peak in the XRD pattern of the FDTS-coated AAO membranes, in comparison to annealed AAO, confirmed that no solid impurity was introduced. Due to the combination of surface chemistry and nanoscale roughness, the resulting FDTS-coated annealed AAO membranes exhibited superhydrophobicity, characterized by advancing and receding contact angles of water droplets in air $\theta_A > 160^\circ$ and $\theta_R > 150^\circ$ (Table 1). The contact angles were measured using the Kruss Drop Shape Analyzer (DSA100) interfaced with the Advance software; sessile drops of volume 4 μL were deposited onto several locations on the membranes at the rate of 0.2 $\mu\text{L/s}$ and contact angles were estimated by fitting tangents at the solid-liquid-vapor interface as well as fitting circles to the shape of drops. FDTS-coated AAO membranes *repelled* water drops falling from a height of $\sim 1\text{cm}$ (Figure 5).

Table 1. The summary of contact angles of water on all the AAO membranes investigated in this work before and after silanation with FDTS. (Section S3 explains image analysis employed to obtain surface pore densities listed below)

Surface treatments of AAO membranes	Apparent contact angles, θ_r , for deionized water		Topside pores		Underside pores	
	Top	Bottom	Dia (nm) ($\pm$ std. dev.)	Pore density ($\#/m^2$) $\times 10^{13}$	Dia (nm) ($\pm$ std. dev.)	Pore density ($\#/m^2$) $\times 10^{13}$
80 nm (pristine)	38°	41°	77 $\pm$ 18	1.8	65 $\pm$ 22	2.9
80 nm (annealed)	0°	0°				
80 nm (FDTS)	162°	150°				
100 nm (pristine)	69°	38°	97 $\pm$ 19	1.6	91 $\pm$ 26	2.3
100 nm (annealed)	0	0				
100 nm (FDTS)	152°	151°				
160 nm (pristine)	17°	20°	176 $\pm$ 33	1.8	185 $\pm$ 34	2.0
160 nm (annealed)	0	0				
160 nm (FDTS)	151°	161°				

We estimated the maximum pressure that our superhydrophobic membranes could withstand against water infiltration, also known as the liquid entry pressure or the breakthrough pressure, as $P_L = 2\gamma_{LV} \cos \theta_o / r$, where $\gamma_{LV} = 72$ mN/m is the surface tension of the water at the normal temperature and pressure (NTP: 293 K, 1 atm), θ_o is the intrinsic contact angle of water on a smooth surface of identical chemical composition as the membrane, and r is the radius of the channel (Figure 5A-B)⁵⁰. For example, for the FDTS-coated AAO membranes with $D = 80$ nm, the liquid entry pressure was $P_L \approx 12$ atm, which ensured that liquid water would not penetrate them under the mild application of pressure in our DCMD experiments; only water vapor would. Therefore, we considered our membranes to be suitable for the investigation of mass transfer of water vapor in the DCMD configuration (Figure 1).

Figure 5. (A) A schematic of liquid water penetrating a superhydrophilic anodized aluminum oxide (AAO) membrane, driven by the curvature of the liquid (the intrinsic angle of the air-water system, $\theta_o \approx 20^\circ$). (B) AAO membranes with covalently grafted perfluorodecyltrichlorosilane (FDTs) molecules. The intrinsic angle of the air-water system on smooth alumina increased to $\theta_o \approx 110^\circ$, and the membrane exhibited superhydrophobicity. If water was forced inward, the curvature of the air-water interface prevented intrusion (shown by dotted lines); the maximum pressure, known as the liquid entry pressure, $P_L = 4\gamma_{LV} \cos \theta_o / D$, where $\gamma_{LV} = 72 \text{ mN/m}$ and other variables are shown. (C) A ball and stick representation of a perfluorodecyltrichlorosilane molecule with gray, light-green, purple and dark-green balls representing carbon, fluorine, silicon and chlorine atoms, respectively. (D) A representative high-speed image sequence of a water droplet bouncing on a superhydrophobic AAO membrane with nanochannels of average diameter $D = 80 \text{ nm}$.

3. EXPERIMENTAL SETUP

We used a custom-built DCMD module⁸ to measure the flux of water vapor across our superhydrophobic AAO membranes (Figure 6). The membranes separated a hot stream of water from the Red Sea ($\sim 0.7 \text{ M NaCl}$) at 343 K (which we refer to as the feed side), from a cold stream of deionized water at 292 K (the permeate side). The feed- and permeate flows were opposite in direction and maintained at 100 ml/min ($\sim 0.2 \text{ m/s}$). The undersides of the membranes were in contact with the feed side (Figure 2, Table 1). The flux of the water vapor from the feed to the permeate was measured by monitoring the increasing mass of the latter over time using a precision balance (resolution: 0.01 g).

Figure 6. (A) Schematic of direct contact membrane distillation (DCMD) setup used to quantify the flux of water vapor transported across superhydrophobic AAO membranes. (B) Photograph of the module with FDTs-coated AAO membrane installed in the DCMD setup. Inside the module, a polydimethylsiloxane (PDMS) o-ring prevents mechanical damage to the membrane

4. RESULTS AND DISCUSSION:

Under our experimental conditions, the volumetric flux of the AAO membranes of average nanochannel diameters 80 nm, 100 nm, and 160 nm ranged within $7.2 \leq J \leq 8.9 \text{ L m}^{-2} \text{ h}^{-1}$ over a span of 20 hrs of operation. The salt rejection rate in the DCMD process was $\approx 99.9\%$, measured through the electrical conductivity of the permeate solutions. Contrary to our expectation, the fluxes did not scale with the porosities of the membranes – while the porosities, ζ , varied by $\sim 80\%$ across our membranes, the flux, J , varied only by $< 25\%$. To understand the mass transport at the pore-scale, we exploited the simple geometry of our AAO membranes (Table 1) and converted the membrane fluxes into the rate of transport of water molecules passing through the inlets to the nanochannels as, $\dot{n} \approx 3.34 \times 10^9 \text{ s}^{-1}$, $\dot{n} \approx 3.72 \times 10^9 \text{ s}^{-1}$, and $\dot{n} \approx 4.13 \times 10^9 \text{ s}^{-1}$. To gain insight into the factors controlling the mass transport, including membrane porosity, thermal conductivity, fluid dynamics, and heat and mass transfer, a new multiscale simulation framework was implemented.

4.1 Multiscale Model

The predictive power of models based on the kinetic theory of gases⁵¹, the Navier-Stokes equation⁵², and the Boltzmann equation⁵³ has been realized^{4, 54}. Since liquid water did not penetrate into our superhydrophobic AAO membranes, we could quantify heat transfer across them by approximating them as rigid solids sandwiched between the feed and permeate (Figure 7). To capture the steady-state temperature profiles, we employed computational fluid dynamics (CFD) coupled with conjugate heat transfer. Considering the steady-state temperatures and latent heat of the feed, vapor fluxes were estimated using the kinetic theory of gases. This multiscale approach captured our experimental conditions and results within reasonable accuracy. Below, we introduce the modeling approach in the following three sub-sections:

4.1.1 Pore Flow

We estimated the mass transfer of water vapor through vertically-aligned pores of our AAO membranes by assuming it to be an ideal gas⁵⁵⁻⁵⁶. For an ideal gas diffusing across a channel of macroscopic dimensions, the number of molecular collisions with the walls is insignificant in comparison to the collisions between the gas molecules and their effects can be ignored. However, as the size of the channel, D , becomes comparable to the average distance traveled by the gas molecules between successive collisions, also known as the mean free path, the collisions with the walls become important. The mean free path of an ideal gas is given by, $\lambda = \frac{k_B T}{\sqrt{2} n d^2 P}$, where P , T , and d are the pressure, temperature, and molecular size of the gas⁵⁵. The gas rarefaction can be described by the Knudsen number defined as $Kn = \frac{\lambda}{D}$. Thus, based on the Knudsen number, Kn , flows inside channels are classified into three regimes: (i) continuous or hydrodynamic flow ($Kn < 0.01$), where the frequency of gas-gas collisions is much higher than frequency of gas-surface collision, (ii) transitional flow ($0.01 < Kn < 10$), where the frequency of collisions with the walls is similar to the gas-gas collisions, and (iii) free-molecular or Knudsen flow ($Kn > 10$), where collisions with the walls dominate the diffusion rates^{4, 55-56}. We estimated the mean free path of water vapor under our experimental conditions to be $\lambda \approx 100$ nm that was commensurate with the average diameter of the nanochannels in

our membranes. Thus, the mass transfers through our AAO membranes were governed by the transitional (or interdiffusive) range, where the collisions of water vapor with both channel walls and gas molecules should be considered. Under such conditions, the mass flux, J , is related to the molar flow rate, M_{II} , as⁵⁷⁻⁵⁸

$$J = \frac{M_{II}}{\pi r_c^2} = \frac{D_{II} \Delta P}{R_o T_m L}, \quad (1a)$$

$$D_{II} = 1 / \left(\frac{1}{D_{KI}} + \frac{1}{D_{CI}} \right), \quad (1b)$$

$$D_{KI} = \frac{4r_c}{3} \sqrt{\frac{2k_B T_m}{\pi m}}, \quad (1c)$$

$$D_{CI} = \frac{3}{8P_T d_m^2} \sqrt{\frac{(k_B T_m)^3}{2\pi} \left(\frac{1}{m_1} + \frac{1}{m_2} \right)}, \quad (1d)$$

$$d_m = \frac{(d_{m1} + d_{m2})}{2}, \quad (1e)$$

where D_{II} is the intermediate interdiffusive constant, D_{KI} is the Knudsen diffusion constant (considering collisions with the wall), D_{CI} is the classical interdiffusive constant (considering collisions between gas molecules), r_c is the radius of the channel, ΔP is the vapor pressure difference at the edges of the nanochannels in contact with the feed and permeate respectively, R_o is the universal gas constant, T_m is the mean temperature at the two ends of channel (317.5 K)⁵⁹, L is the channel length, k_B is the Boltzmann constant, m is the molecular mass, d_{m1} and d_{m2} are the molecular diameters of the two components (water vapor and N_2), d_m is the mean molecular diameter of the interdiffusive gas, and P_T is the pressure inside the nanochannel.

4.1.2 Conjugate Heat Transfer

Assuming the feed and permeate to be incompressible, we used the following governing equations to simulate heat transfer at solid-liquid interfaces⁶⁰:

Mass Conservation:

$$\nabla \cdot \rho \mathbf{u} = 0 \quad (2)$$

Momentum Conservation:

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla(\rho \mathbf{u} \cdot \mathbf{u}) = -\nabla P + \nabla \cdot \mu [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] + \rho \mathbf{g} \quad (3)$$

Energy Conservation:

$$\frac{\partial(\rho E)}{\partial t} + \nabla \cdot [\mathbf{u} (\rho E + P)] = \nabla \cdot [K \nabla T + \bar{\mathbf{t}} \cdot \mathbf{u}] \quad (4)$$

where $\mathbf{u}$ represented the velocity vector, P was the hydrodynamic pressure, $\bar{\tau}$ was the stress tensor, $\mathbf{g}$ represented the acceleration due to gravity, E was the total energy, K was the liquid thermal conductivity, ρ and μ were the fluid density and viscosity. The stress tensor and total energy were estimated as,

$$\bar{\tau} = [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \quad (5)$$

$$E = h - \frac{P}{\rho} + \frac{|\mathbf{u}|^2}{2} \quad (6)$$

where h was the sensible enthalpy represented by

$$h = \int_{T_{ref}}^T C_{p,j} dT \quad (7)$$

Under our experimental conditions the flows were laminar (~ 0.2 m/s), so we ignored the effects of turbulence in our model. Subsequently, heat transfer through the solid AAO membrane was simulated by the following energy equation:

$$\frac{\partial(\rho h)}{\partial t} = \nabla \cdot [k_m \nabla T] \quad (8)$$

where k_m was the thermal conductivity of the AAO membrane. We approximated the heat transfer from the hot to the cold sides to comprise heat conduction and the latent heat of evaporation at the feed-side as:

$$\mathbf{Q}_m = k_m \nabla T + J \Delta H_v \quad (9)$$

where k_m was the thermal conductivity of the AAO membrane, J was the vapor flux (Eq. 1a), and ΔH_v was the latent heat of vaporization of seawater (2258 kJ/kg). The contributions of conduction and latent heats, the first and second terms in equation (9), were estimated by equations (2-8) and a boundary condition on the feed-side respectively. The thermal conductivity of the AAO membranes, k_m , was estimated as a function of porosity, ζ (percentage), based on the empirical relationship developed by Abad and co-workers⁶¹ using a photoacoustic technique, as

$$k_m = 1.32 - 0.01 \times \zeta \quad (10)$$

As the porosity of the membranes increased from 32% to 35% and 57% for membranes with average nanochannel diameters 80 nm, 100 nm, and 160 nm, the thermal conductivities were estimated to be $1.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $0.95 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and $0.75 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively.

Figure 7. Schematic of an AAO membrane with the feed-side (Red Sea water ~0.7 M NaCl at 343 K at 100 ml/min) and permeate-side (deionized water at 292 K) streams flowing in opposite directions on either side. Thermophysical properties of the feed and permeate are also listed: U denotes the flow speed, T is the temperature, ρ is the density, μ is the viscosity, and γ is the surface tension.⁶²

4.1.3 Multiscale Coupling

The coupling between the feed, permeate, and vapor transport was simulated by solving equations Eq. 1-9. At each time-step, the numerical framework (Eq. 2-8) yielded distributions of temperature and flow-velocity and hydrodynamic pressure in the simulation box (Figures 6B, 7, 8). Temperature-dependent vapor pressures at the feed- and permeate-side were estimated through the empirical Antoine equation⁶³⁻⁶⁵. Based on the pressure difference across the membrane pores, ΔP , vapor flux, J , was computed at each time step (Eq. 1a) and the updated value of flux was passed to the conservation equations solver through Eq. 9. This procedure was repeated until the steady state was reached using the ANSYS-Fluent software (Version 17.2) using a second-order time and space control volume discretization.

4.2 Theoretical Predictions:

Using the above-mentioned multiscale framework, we simulated the steady-state hydrodynamic (gauge) pressures, liquid velocity contours, and temperature distributions in the feed-membrane-permeate system subjected to our experimental conditions. The model confirmed that the hydrodynamic pressure drops along the superhydrophobic membrane surface were negligible (Figure 8A), perhaps due to the entrapment of air at the solid-liquid interface rendering slippage^{12, 17, 66}. The velocity profiles were symmetric on either side with minor flow constriction effects at the inlets (Figure 8B). The temperature profiles across the membranes were found to be linear (Figures 8C-D).

Figure 8. Representative predicted spatial contours for AAO membranes ($D = 100$ nm, $\delta \approx 100$ μ m) separating the feed and permeate flows under our experimental conditions. (A) Hydrodynamic pressure distribution; (B) Fluid velocity distribution; (C) Temperature distribution; (D) Zoom-in view of the temperature distribution.

Most notably, we found that the temperature differences of the air-water interfaces at the feed and permeate sides of the membrane pores of diameters 80 nm, 100 nm, and 160 nm were 37%, 38%, and 46% lower respectively, in comparison to the difference in the temperatures of the bulk streams (Figure 9A). As a result of this temperature polarization, the vapor fluxes across the AAO membranes did not vary proportionally with the

porosity, as would have been the case if the interfacial temperature profiles were the same (Eq. 1A).

Figure 9. (A) Thermal boundary layer profiles for AAO membranes with average nanochannel diameters, D , 80 nm, 100 nm, and 160 nm under cross-flow configuration. The feed-side comprised water from the Red Sea (~ 0.7 M NaCl) at 343 K and the permeate side comprised of deionized water at 292 K, both flowing at 0.2 m/s, in opposite directions. (B) Temperature profiles along the whole lateral dimension of the AAO membrane with nanochannel diameter, $D = 100$ nm.

Our multiscale model predicted the pore-level fluxes across the nanochannels of diameters 100 nm and 160 nm to be $\approx 4\%$ and $\approx 23\%$ higher than that through the 80 nm channels respectively, which was in agreement with the experimental results (Figure 10). The simulated lateral temperature distributions are presented in Figure 9B. The model also predicted that the mass transport could be enhanced by reducing the thermal conductivity (Figures S4-5) and increasing the feed-side temperature (Figure S6).

Figure 10. Experimental (red) and simulated (blue) flow rates of water vapor across hydrophobic nanochannels of AAO membranes with average channel diameters 80 nm, 100 nm, and 160 nm. Theoretical predictions without considering temperature polarization across membranes are presented as green circles. Lines have been drawn to facilitate viewing.

Below, we briefly discuss potential sources of error in our predictions due to the lack of consideration of concentration polarization, capillary condensation, gas-mixtures, and multiphase flows. Due to the evaporation of water at the feed-side, the salt concentration rises affecting the vapor pressure, known as concentration polarization²², but these effects were not considered in our model. Capillary condensation of water inside nanochannels leading to water plugs is also possible^{4, 6, 48, 67-68}, but assumed to be negligible in this work. The application of the kinetic theory of gases to simulate mixtures of real gases in confinement could also lead to errors and researchers have proposed more rigorous methods^{55, 69}, which were not considered here. We also note that multiphase simulations explicitly considering membrane porosity could yield more accurate description of the physics^{4, 70} also falls beyond the scope of this work.

5. Conclusion and Outlook:

We investigated the mass transport of water vapor across nanoporous ceramic membranes composed of AAO for potential application in DCMD, a low carbon footprint technology for desalination. While ceramic membranes could offer superior abrasion-resistance in comparison to the PTFE counterparts in DCMD, the influence of their thermal conductivity on the vapor transport has not been entirely clear. In response, we compared the performance of AAO membranes comprising vertically aligned nanochannels with average diameters centered at 80 nm, 100 nm, and 160 nm. To render the membranes suitable for DCMD, we annealed them at 1273 K for 2 hrs, followed by chemically grafting hydrophobic coatings onto them. The efficacy of the resulting superhydrophobic AAO membranes for DCMD was evaluated through a custom-built set up, where the membranes separated counter-flowing streams (0.2 m/s) of hot salty water (343 K, 0.7 M NaCl) and cold deionized water (292 K). Interestingly, we found that the difference in the fluxes of vapor across the membranes comprising of nanochannels of average diameters 80 nm and 160 nm was 25%, $7.2 \leq J \leq 8.9 \text{ Lm}^{-2}\text{h}^{-1}$, whereas we expected a doubling in proportion to the porosities. To understand the factors and mechanisms underlying this observation, we employed a multiscale model based on computational fluid dynamics and kinetic theory of gases to predict fluxes across those membranes while capturing the hydrodynamics and heat transfer in our experiments. Our

simulations demonstrated that the high thermal conductivity of the AAO ceramic membranes led to severe temperature polarization, such that the temperature differences between the apposing air-water interfaces inside the nanochannels, driving the mass transport, were significantly lower than that of the bulk liquids. Specifically, the temperature differences between the liquid-vapor interfaces under our experimental conditions were predicted to be 37%, 38%, and 46% lower for the AAO nanochannels of diameters 80 nm, 100 nm, and 160 nm respectively. The pore-level predictions of flux of water vapor were in reasonable agreement with our experimental results. Thus, our report explains the mechanisms and factors underlying the limited scope of AAO membranes for DCMD, as suggested by others³². To compare with typical PVDF, PTFE, and polypropylene membranes employed in DCMD, with cumulative thermal conductivities, $k_m \approx 0.07 \text{ Wm}^{-1}\text{K}^{-1}$, considering the polymer conductivity, $k_m \approx 0.26 \text{ Wm}^{-1}\text{K}^{-1}$ and 80% porosity^{19, 26}, the thermal conductivities of typical AAO membranes are nearly an order of magnitude higher. Thus, for AAO membranes to be employed in DCMD, strategies for lowering the thermal conductivity should be explored. For instance, it might be worth exploring thermally insulating materials to coat AAO membranes, without clogging the nanochannels, before rendering them superhydrophobic⁷¹. New approaches in designing thermoelectric materials, where the reduction of thermal conductivity is also crucial, might be insightful⁷²⁻⁷⁴. Alternatively, superhydrophobic AAO membranes should be tested in the air gap MD and vacuum MD configurations that are less vulnerable to temperature polarization⁷⁵. This work might advance the rational design of materials and processes for DCMD and thermally driven liquid-vapor extraction, in general.

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ACCEPTED MANUSCRIPT

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Graphical abstract