Water Vapor Transport in Carbon Nanotube Membranes and Application in Breathable and Protective Fabrics

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Abstract

Membranes that selectively block or permeate water vapor find application in dehydration of gaseous streams, pervaporation, humidity control in buildings, protection of moisture sensitive electronics, and in breathable fabrics for environmental protective clothing. Many of these application areas could benefit from the incorporation of carbon nanotubes into membrane materials. Recent studies have demonstrated the ability of carbon nanotubes to enable ultrafast water vapor diffusion through their inner volume, as well as to promote dehumidification of gas streams flowing through their interstitial spaces. Membranes with porosity solely made of the inner channels of carbon nanotubes are especially promising for the development of next generation protective garments because enable a long-sought-after combination of outstanding breathability with protection.

Introduction

A wide spectrum of important applications requires membranes that selectively block or permeate water vapor. For example, the removal of water vapor from gaseous streams is critical in industrial processes such as dehydration of natural and flue gases [1], drying of compressed air [2,3], and for harvesting water vapor from the atmosphere. Humidity regulation is important for air conditioning in buildings [4] and repositories for the conservation of art and paper artifacts. Moisture barriers are used for food storage [5] and protection of moisture sensitive electronics such as solar cells and organic light emitting diodes [6]. Breathable membranes, i.e. membranes that permit rapid water vapor permeation, find application in biofuel separation by pervaporation [3] and in water desalination [7] by membrane distillation [8]. Waterproof, but water-vapor-permeable membranes are widely used in the textile industry for weather protective clothing [9-11].

These membranes are designed to allow body-generated moisture to pass through while preventing wind and rain from penetrating the fabric, thus keeping the body dry and warm. Their selective permeability for water vapor is also interesting in medical applications, e.g., for personal cooling garments [12,13], and as components of protective clothing for first responders, military, and medical personnel [10,14].

In many of the listed applications, boosting membrane permeability is very desirable. For example, in flue gas dehydration [1], membrane distillation, and pervaporation processes, a higher membrane flux can result in energy saving and/or decreased capital costs by reducing plant footprint. For apparel use, higher membrane breathability correlates strongly with increased comfort [11,15]. Unfortunately, performances of conventional polymeric membranes are typically limited by a trade-off between flux and selectivity [16]. Recent advances in nanotechnology have enabled the fabrication of novel membranes incorporating nanomaterials that could potentially overcome this shortcoming of polymer films [17]. Among these, carbon nanotubes (CNT) are emerging as exciting building blocks for fabrication of water-vapor selective membranes for several reasons. First and most importantly, the graphitic walls of CNTs are molecularly smooth and slippery [18•], and this property has been linked to CNTs unique ability to sustain fluid transport rates that are several orders of magnitude faster than typically found in other pores of similar sizes [19,20]. Second, while the outer surface of vertically aligned CNT forests is superhydrophobic [21,22], the inner surface of CNT nanopores can be readily wetted by liquid water [23•]. Thus, water (vapor) transport can be either facilitated or hindered by judicious choices of the CNT membrane structure, permeation pathways, and operating conditions. Third, the diameter of CNTs can be synthetically tuned from sub-nanometer to tens of nanometers, and their length can be controlled on the sub-micron to millimeter scale, thus enabling a unique combination of ultrahigh aspect-ratio with small pore opening. Finally, well-defined sites for chemical functionalization at the entrance of an open CNT nanochannel can be easily targeted to create selective gates for molecular transport [24]. This localized functionalization may enable boosting membrane selectivity without a dramatic flux loss.

In this paper, we review studies published in the last five years that have highlighted the CNT potential to either enhance or block water vapor permeation through membranes by exploiting CNT geometry, wetting, and fast flow properties. We describe different types of CNT

membranes that have been fabricated, and their specific use in applications involving water vapor transport. Special attention is given to the field of breathable and protective fabrics.

CNT membrane types

CNT membranes with a variety of structures have been fabricated and investigated for their potential use in a wide class of applications involving selective transport of water vapor. These include membranes with vertically-aligned CNTs (VACNT) working as only through pores in an otherwise impermeable film (type 1 – Figure 1) [25••]; matrix-less membranes made of ultralong, vertically-aligned CNT arrays, in which the flow pathways are the interstices among CNTs (type 2) [26••]; and membranes where CNTs are immobilized in the pores of a polymer film or partially/fully embedded into a polymer matrix (type 3) [27-30]. The permeation behavior of water vapor observed in these membrane types differs both qualitatively and quantitatively depending on the preferential transport pathways (Figure 2).

Water vapor transport through CNT inner channels

The first quantification of water vapor transport rates inside CNT nanochannels under a concentration gradient appeared only recently. Bui et al. [25] prepared type-1 CNT membranes by filling the interstitial spaces between sub-5 nm, vertically-aligned, single-walled nanotubes (SWNTs) with parylene-N. To measure the membrane breathability, a purely diffusive steady-state transport of water vapor was established by exposing each membrane side to a nitrogen gas stream with a different relative humidity (RH). Because water fluxes measured with a constant concentration gradient were independent of the inlet RH in the range of 55% - 85%, water did not condense inside the pores and transported through the CNTs as vapor. Measured water vapor diffusivity in SWNTs was 24 times larger than Knudsen diffusion predictions and comparable to bulk diffusivities ($\approx 0.16 \text{ cm}^2 \text{ s}^{-1}$ in these SWNTs vs $0.26 \text{ cm}^2 \text{ s}^{-1}$ in the bulk) (Figure 3a). The magnitude of this flow enhancement E with respect to Knudsen theory is in excellent agreement with that of pressure-driven nitrogen flow through these ($E=50$) and other type-1 membranes reported in the literature [31•-35]. In analogy with pressure-driven transport of pure gases, water vapor enhanced flow is likely due to the inherent wall smoothness of well-graphitized CNT pores [36•-39].

Water vapor transport through CNT interstitial spaces

A very different water-vapor permeation behavior was found when the interstitial spaces between nanotubes rather than the CNT inner channels were used as gas flow pathways [26,40]. Matrix-less membranes made of closed, 4-mm long, vertically aligned, multi-walled nanotubes (MWNTs) impeded water vapor transport by a combination of capillary condensation, reverse capillary flow, and water rejection/removal at the superhydrophobic MWNT tips [41]. This mechanism of water rejection (shown in Figure 2.B) was supported by the more efficient dehumidification at higher RH of the incoming gas stream [26], at lower temperature of the MWNT membrane [40], and with membranes having a reduced intertube distance (R_1 and R_c in Figure 2) [40,41]. Thanks to a large porosity (98.5%) and a large average distance between the MWNTs (~ 73 nm), the achieved permeability of dry gases ($2.1 \times 10^{-9} - 3.8 \times 10^{-8}$ mol m/m² s Pa) was orders of magnitude greater than the permeability of polymeric membranes typically used for water vapor separation [26]. Selectivity (defined as permeability ratio) for several polar and non-polar gases with respect to water vapor was as high as $\sim 2 \times 10^5$ (Figure 4).

Water vapor transport through CNT-polymer composites

Membranes incorporating randomly-oriented, 30-nm wide MWNTs into super-absorbing polymers were evaluated for their ability to harvest water vapor from the atmosphere [30] (type 3 – Figure 1). In these composite materials, molecular transport occurred through the polymer matrix, the CNT channels, and possibly through (sub-)nanogaps at the interface between nanotubes and polymer [42]. Addition of MWNTs increased water vapor removal from wet air by up to 45%, and this improved performance was attributed to the nanotube slippery walls and to changes in the polymer-water interaction in the presence of MWNTs.

Functionalized CNTs were also immobilized in the pores of hydrophobic membranes (polytetrafluoroethylene, polypropylene) for water desalination by membrane distillation [27-29]. CNT incorporation doubled the water vapor flux and increased salt rejection. The benefit of CNT addition was attributed to the creation of additional pathways for water vapor transport (at the tube outer surface and through the CNT inner volume) and to the increased hydrophobicity of the composite membrane that prevented salty water penetration.

Note that, because the multiple gas permeation pathways in type-3 membranes cannot be decoupled easily, the relative importance of each transport mode to the performance improvement could not be quantified. Nevertheless, since the magnitude of flow enhancement in CNTs typically decays with increasing nanotube diameter [36] and defect density, the water vapor permeation rate through the core of the large diameter, oxidized MWNTs of these studies may be significantly lower than through pristine SWNTs [25].

Application in breathable and protective fabrics

The ability of small-diameter SWNTs to transport rapidly water vapor by diffusion has important implications for the fabrication of protective garments. To minimize physiological burden and prevent the risk of heat stress, a protective ensemble must provide a moisture vapor transport rate (MVTR) $>1500\text{--}2000\text{ gr m}^{-2}\text{ day}^{-1}$ [43], i.e. large enough to allow efficient evaporative cooling of the body through perspiration [9,44]. Unfortunately, achieving both high protection and high breathability in a single material is challenging, and current protective materials sacrifice breathability in order to prevent exposure to harmful agents [44,45].

Sub-5nm SWNT membranes with pore densities of about $5\times 10^{11}\text{ tube/cm}^2$ were demonstrated to exhibit outstanding moisture vapor transport rates approaching $8000\text{ gr m}^{-2}\text{ day}^{-1}$ [25], i.e. 4-fold larger than the breathability target. Notably, these transport rates were comparable or larger than those of conventional breathable fabrics tested at the same conditions (Figure 3b). In addition, the small diameter of the SWNT pores enabled complete rejection of $\geq 5\text{-nm}$ analytes by size exclusion and, thus, provided protection from biological threats [25]. These results showed that, by combining high breathability and protection in a single functional material, CNT pores can effectively overcome the breathability/protection trade-off predicted by conventional diffusion theories (Figure 3a).

Future outlook

The proof-of-concept demonstration [25] of combined bio-protection and outstanding breathability in VACNT membranes has highlighted the potential of CNT nanomaterials for next-generation breathable and protective fabrics. Further development, however, is

required to meet the demand of high comfort, increased protection from a wider spectrum of threats, mechanical robustness for incorporation in garments, and scalability of the fabrication process.

Boosting CNT membrane selectivity is expected to provide the most benefit. VACNTs with the narrowest diameters produced so far [46-48] typically contain a population of sub-nanometer CNTs, but also a tail of larger size nanotubes that extends up to ~2-nm. Thus, membranes made of these state-of-art, narrow VACNTs could easily block the permeation of hazardous species as small as 2-nm by size exclusion. Contrary to biological threats, chemical threats are small enough to permeate even through the narrowest diameter VACNT arrays achieved so far. Fortunately, the entrance of an open CNT nanochannel offers well-defined sites for chemical functionalization that can be easily targeted to create selective gates for molecular transport. Integration of chemical-threat-responsive molecules [49•] at the CNT entrance could greatly improve the membrane protection properties toward chemical hazards.

While membranes with sub-5nm SWNTs at densities of 5×10^{11} tube/cm² display a small resistance to water vapor transport, the overall fabric permeability may be detrimentally reduced if additional layers are coated on the CNT membrane surface or smaller diameter SWNTs are adopted for increased protection. To counteract this potential loss of breathability, it is desirable to increase CNT pore density. Growth of VACNT arrays with $> 10^{13}$ tube/cm² was demonstrated in the literature [46], and their successful integration in flexible films could dramatically enhance the intrinsic CNT membrane breathability.

A unique advantage of the VACNT membrane structure is that transport and mechanical properties are largely decoupled. The former are dictated by the CNT pores, the latter by the impermeable material filling the interstitial gaps between nanotubes. Thus, the filling matrix can be potentially chosen with the sole aim of optimizing mechanical properties such as flexibility, mechanical robustness, tear resistance, etc. Incorporation of barrier polymers typically used in protective garments would be especially beneficial.

Scaling-up fabrication of VACNT membranes remains challenging. VACNT membranes best exploit the transport properties of the CNT inner pores, but so-far have been demonstrated only at cm² scale with a batch process that starts from CVD-grown VACNT forests [32,34,50-53]. Solution based methods have the potential to produce large area

VACNTs and could be integrated in roll-to-roll processes. These methods aim to align solution-dispersed CNTs with an external field and lock the nanomaterial orientation by in-situ polymerization [54]. In spite of considerable progress [55], this fabrication route has not demonstrated yet adequate packing densities of SWNT pores across the membrane thickness to form breathable films.

Conclusions

Among the recently developed types of CNT membranes, those using VACNTs as a building block best exploit the unique nanomaterial wetting and transport properties and have enabled permeation rates that greatly surpass those of competing polymer membranes. The unique geometry and hydrophobicity of matrix-less CNT membranes could offer a low-energy, cost-effective strategy to control humidity in industrial application. The recent demonstration that water-vapor transport driven by a relative humidity gradient is exceptionally fast inside SWNTs has revealed the potential of these nanomaterials for use in breathable and protective fabrics. These quantitative measurements of water vapor diffusion in CNTs have also provided key missing information to design membranes for pervaporation and membrane distillation. Widespread adoption of VACNT membranes by the industry requires resolving challenges related to their large-scale manufacturability at a competitive cost, as well as further enhancing membrane selectivity.

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Figure Captions

Figure 1. Fabrication process for three types of CNT membranes. Type 1: VACNT membranes that transport fluids only through the inner volume of the CNT pores. Type 2: Matrix-less VACNT membranes, where the transport pathways are the interstitial spaces between CNTs. Type 3: Mixed matrix membranes, in which one or both CNT ends are covered by a permeable polymer. A-C: SEM images of the cross-section (A-B) and surface (C) of the three types of membranes. Reproduced with permission from [25] (type 1) - Copyright © 2016, John Wiley and Sons; [26] (type 2) - Copyright © 2012, American Chemical Society; and [29] (type 3) - Copyright © 2011, American Chemical Society.

Figure 2. Mechanism of water vapor transport through (A) the endohedral CNT volume and (B) the interstitial space in-between VACNTs. **A:** Water diffuses through the CNT channels as vapor and with rates that greatly exceed Knudsen predictions [25]. **B:** According to Kelvin equation, water vapor condenses in the gaps between VACNTs. Formation of an asymmetric liquid meniscus originates a large Laplace pressure difference in the fluid that drives liquid water backwards [41]. Q_{Kn} is the volumetric flow rate for Knudsen diffusion; Q the measured volumetric flow rate; M the molecular weight; V_m the molar volume; R_c the capillary radius; T the absolute temperature; R the universal gas constant; E the enhancement factor; μ is the fluid viscosity; L the pore length; L_s the slip length at the pore wall; R_1 and R_2 ($=R_c/\cos \theta$) the radii of curvature of the two menisci; P_{sat}^K and P_{sat} the saturation pressure of water vapor in equilibrium with a curved liquid meniscus and next to a flat interface, respectively; γ the surface tension; θ the contact angle.

Figure 3. Water vapor transport through VACNT membranes, commercial breathable fabrics, and other porous membranes. **A:** Single-pore water vapor diffusivity. The pore size dependences predicted by bulk, transition, and Knudsen diffusion equations are represented by the black dot-dashed line, solid black line, and the blue dashed line, respectively. Points represent experimental results for several porous membranes. Inset: Enhancement factor defined as ratio of measured to predicted diffusivity. PC = polycarbonate; AAO = anodic aluminum oxide. Upper x-axis: Typical dimensions (nm) of biological threats. **B:** MVTR (bars), corresponding total (R_{tot} , circles) and boundary layer resistance (R_{BL} , dashed line) to water vapor transport for CNT membranes and several commercial breathable fabrics based on macroporous films (ePTFE, eVent, NoeShell) or dense polymer laminates (Gore-Tex Pro Shell, Sympatex). Reproduced with permission from [25] - Copyright © 2016, John Wiley and Sons.

Figure 4. Gas transport through matrixless VACNT membranes. **A:** Gas selectivity with respect to water vapor when the inlet gas is at 100% RH. **B:** Permeability comparison. Data for matrixless VACNT membranes are shown as solid squares, while control data from the literature are represented by the open symbols. Red circles = molecular sieves; green diamonds = carbon nanotubes (inner volume); blue stars = polymeric membranes for water vapor separation. Reproduced with permission from [26] - Copyright © 2012, American Chemical Society.

Figure 1. Fabrication process for three types of CNT membranes. Type 1: VACNT membranes that transport fluids only through the inner volume of the CNT pores. Type 2: Matrix-less VACNT membranes, where the transport pathways are the interstitial spaces between CNTs. Type 3: Mixed matrix membranes, in which one or both CNT ends are covered by a permeable polymer. A-C: SEM images of the cross-section (A-B) and surface (C) of the three types of membranes. Reproduced with permission from [25] (type 1) - Copyright © 2016, John Wiley and Sons; [26] (type 2) - Copyright © 2012, American Chemical Society; and [29] (type 3) - Copyright © 2011, American Chemical Society.

<p>A</p>	<p>B</p>
$Q_{Kn} = \frac{2}{3} \sqrt{\frac{8\pi}{MRT}} R_c^3 V_m \frac{\Delta P_{gas}}{L} \quad \text{Knudsen Diffusion}$ $E = \frac{Q}{Q_{Kn}} \quad \text{Enhancement factor}$ $\Delta P_{H2O} = P_{H2O,in} - P_{H2O,out} \quad \text{Driving force}$	$Q_{HP} = \frac{\pi R^4}{8\mu} \frac{\Delta P_T}{L} \left(1 + \frac{4L_s}{R_c}\right) \quad \text{Hagen-Poiseuille}$ $\Delta P_{Laplace} = 2 * \gamma * \left(\frac{1}{R_1} - \frac{1}{R_2}\right) \quad \text{Laplace pressure}$ $\Delta P_T = \Delta P_{Laplace} + \Delta P_{gas} \quad \text{Driving force}$ $RT \ln \frac{P_{sat}^K}{P_{sat}} = -V_m * \left(\frac{2\gamma * \cos \theta}{R_c}\right) \quad \text{Kelvin equation}$

Figure 2. Mechanism of water vapor transport through (A) the endohedral CNT volume and (B) the interstitial space in-between VACNTs. **A:** Water diffuses through the CNT channels as vapor and with rates that greatly exceed Knudsen predictions [25]. **B:** According to Kelvin equation, water vapor condenses in the gaps between VACNTs. Formation of an asymmetric liquid meniscus originates a large Laplace pressure difference in the fluid that drives liquid water backwards [41]. Q_{Kn} is the volumetric flow rate for Knudsen diffusion; Q the measured volumetric flow rate; M the molecular weight; V_m the molar volume; R_c the capillary radius; T the absolute temperature; R the universal gas constant; E the enhancement factor; μ is the fluid viscosity; L the pore length; L_s the slip length at the pore wall; R_1 and R_2 ($= R_c / \cos \theta$) the radii of curvature of the two menisci; P_{sat}^K and P_{sat} the saturation pressure of water vapor in equilibrium with a curved liquid meniscus and next to a flat interface, respectively; γ the surface tension; θ the contact angle.

Figure 3. Water vapor transport through VACNT membranes, commercial breathable fabrics, and other porous membranes. **A:** Single-pore water vapor diffusivity. The pore size dependences predicted by bulk, transition, and Knudsen diffusion equations are represented by the black dot-dashed line, solid black line, and the blue dashed line, respectively. Points represent experimental results for several porous membranes. Inset: Enhancement factor defined as ratio of measured to predicted diffusivity. PC = polycarbonate; AAO = anodic aluminum oxide. Upper x-axis: Typical dimensions (nm) of biological threats. **B:** MVTR (bars), corresponding total (R_{tot} , circles) and boundary layer resistance (R_{BL} , dashed line) to water vapor transport for CNT membranes and several commercial breathable fabrics based on macroporous films (ePTFE, eVent, NoeShell) or dense polymer laminates (Gore-Tex Pro Shell, Sympatex). Reproduced with permission from [25] - Copyright © 2016, John Wiley and Sons.

Figure 4. Gas transport through matrixless VACNT membranes. **A:** Gas selectivity with respect to water vapor when the inlet gas is at 100% RH. **B:** Permeability comparison. Data for matrixless VACNT membranes are shown as solid squares, while control data from the literature are represented by the open symbols. Red circles = molecular sieves; green diamonds = carbon nanotubes (inner volume); blue stars = polymeric membranes for water vapor separation. Reproduced with permission from [26] - Copyright © 2012, American Chemical Society.