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Current Opinion in Chemical Engineering

Water vapor transport in carbon nanotube membranes and application in breathable and protective fabrics

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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.

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Current Opinion in Chemical Engineering 2017, **16**:1–8

This review comes from a themed issue on **Separation engineering**

Edited by **Mainak Majumder**

http://dx.doi.org/10.1016/j.coche.2017.02.001

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, that is, 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, for example, 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 subnanometer to tens of nanometers, and their length can be controlled on the submicron 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 ($\approx 0.16\ cm^2\ s^{-1}$ in these SWNTs vs. $0.26\ cm^2\ s^{-1}$ 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•,32–35]. 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••,37–39].

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 super-hydrophobic MWNT tips [41]. This mechanism of water rejection (shown in Figure 2b) 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 (2.1×19^{-9}–3.8×10^{-8} mol m/m^2 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 superabsorbing 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 (polytetrafluoroethyelene, 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.