Gated Ion Transport through Dense Carbon Nanotube Membranes

Miao Yu, Hans H. Funke, John L. Falconer,* and Richard D. Noble

Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309-0424

Received November 2, 2009; E-mail: john.falconer@colorado.edu

Abstract: Gated ion diffusion is found widely in hydrophobic biological nanopores, upon changes in ligand binding, temperature, transmembrane voltage, and mechanical stress. Because water is the main media for ion diffusion in these hydrophobic biological pores, ion diffusion behavior through these nanochannels is expected to be influenced significantly when water wettability in hydrophobic biological nanopores is sensitive and changes upon small external changes. Here, we report for the first time that ion diffusion through highly hydrophobic nanopores (~3 nm) showed a gated behavior due to change of water wettability on hydrophobic surface upon small temperature change or ultrasound. Dense carbon nanotube (CNT) membranes with both 3-nm CNTs and 3-nm interstitial pores were prepared by a solvent evaporation process and used as a model system to investigate ion diffusion behavior. Ion diffusion through these membranes exhibited a gated behavior. The ion flux was turned on and off, apparently because the water wettability of CNTs changed. At 298 K, ion diffusion through dense CNT membranes stopped after a few hours, but it dramatically increased when the temperature was increased 20 K or the membrane was subjected to ultrasound. Likewise, water adsorption on dense CNT membranes increased dramatically at a water activity of 0.53 when the temperature increased from 293 to 306 K, indicating capillary condensation. Water adsorption isotherms of dense CNT membranes suggest that the adsorbed water forms a discontinuous phase at 293 K, but it probably forms a continuous layer, probably in the interstitial CNT regions, at higher temperatures. When the ion diffusion channel was opened by a temperature increase or ultrasound, ions diffused through the CNT membranes at a rate similar to bulk diffusion in water. This finding may have implications for using CNT membrane for desalination and water treatment.

Introduction

Hydrophobic carbon nanotubes (CNTs) may serve as a simplified model to mimic biological pores and reveal properties of these hydrophobic nanochannels. For example, the potassium channel from *Streptomyces lividans* (KcsA) preferentially filters K^+ over Na^+,[1] whereas aquaporins allow water to permeate through freely, but block permeation of ions and protons.[2] Another significant feature of these pores is their high transport rate, which is comparable to bulk diffusion. Ion diffusion also switched between ion conduction and exclusion (i.e., gated transport) upon changes in ligand binding, temperature, transmembrane voltage, and mechanical stress.[3−5]

One common feature of these functional membranes in living cells is the channels with nano-sized constrictions from hydrophobic residues. These channels, combined with functional chemical groups, result in high water fluxes, high water selectivity over ions, or ion selectivity. Carbon nanotubes, due to their high hydrophobicity and structural simplicity, have been considered as a model system to study water conduction, ion permeation, and ion/water interactions in a nano-confined hydrophobic environment.[6,7]

Hummer et al.[8] used molecular dynamics simulations to study water conduction in a CNT with a diameter of 0.81 nm. They found rapid, pulse-like conduction of water through the axis of the CNT, and when attraction between water and the CNT wall was reduced slightly, water in CNTs changed from a filled state to an empty state. Water adsorption isotherms measured by Wang et al.[9] using NMR changed from convex to concave as the temperature increased from 281 to 295 K, indicating that the single-walled CNTs (~1.4 nm diameter) changed from hydrophilic to hydrophobic. Li et al.[10] used simulations to observe an electrostatic gating of water transport through single-

(1) Doyle, D. A.; Cabral, J. M.; Pfuetzner, R. A.; Kuo, A. L.; Gulbis, J. M.; Cohen, S. L.; Chait, B. T.; MacKinnon, R. *Science* **1998**, *280*, 69–77.

(2) Murata, K.; Mitsuoka, K.; Hirai, T.; Walz, T.; Agre, P.; Heymann, J. B.; Engel, A.; Fujiyoshi, Y. *Nature* **2000**, *407*, 599–605.

(3) Voets, T.; Droogmans, G.; Wissenbach, U.; Janssens, A.; Flockerzi, V.; Nilius, B. *Nature* **2004**, *430*, 748–754.

(4) Chang, G.; Spencer, R. H.; Lee, A. T.; Barclay, M. T.; Rees, D. C. *Science* **1998**, *282*, 2220–2226.

(5) Bass, R. B.; Strop, P.; Barclay, M.; Rees, D. C. *Science* **2002**, *298*, 1582–1587.

(6) Holt, J. K.; Park, H. G.; Wang, Y. M.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Science* **2006**, *312*, 1034–1037.

(7) Fornasiero, F.; Park, H. G.; Holt, J. K.; Stadermann, M.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 17250–17255.

(8) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188–190.

(9) Wang, H. J.; Xi, X. K.; Kleinhammes, A.; Wu, Y. *Science* **2008**, *322*, 80–83.

(10) Li, J. Y.; Gong, X. J.; Lu, H. J.; Li, D.; Fang, H. P.; Zhou, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 3687–3692.

walled CNTs (0.81 nm). The water flux decreased 90% when an external charge attached tightly to the CNT wall, as opposed to when the charge distance to the CNT wall was 0.85 nm. High water flux in CNTs was reported by Majumder et al.[11] using aligned, multiwalled CNT membranes; the water flux was 4−5 orders of magnitude higher in CNTs with a diameter of approximately 7 nm than Hagen−Poiseuille hydrodynamic flow theory predicted. Holt et al.[6] also reported high fluxes for aligned CNT membranes with sub-2 nm pores.

Fornasiero et al.[7] negatively charged the pore entrance of sub-2 nm CNT membranes by plasma treatment and found significant ion exclusion when aqueous electrolyte solution moved through their membranes because of a pressure drop. Because their ion rejection was more sensitive to solution pH and electrostatic screening length, but less to steric configurations of ions, they suggested a Donnan-type ion rejection mechanism, which is dominated by electrostatic interactions between membrane charges at the CNT pore mouth and moving ions.

In a previous study, we prepared dense, vertically aligned CNT membranes by capillary-force driven shrinkage of CNT arrays grown by chemical vapor deposition (CVD).[12] The volume fraction of CNT pores in the dense CNT membranes was approximately 20%, as calculated from N_2 adsorption, whereas it was only 1.3% for the as-grown CNT array. The average pore diameters of the CNTs and the interstitial pores in the dense CNTs membranes were approximately 3 nm, as determined by N_2 adsorption at 77 K, TEM, and nanogold filtration.[12] The dense CNT membranes had gas fluxes that were approximately 450 times that calculated for Knudsen diffusion, and this observation is consistent with previous findings for CNT membrane studies.[6] Because of the much denser packing of CNTs and because of the additional transport pathway between CNTs, the gas permeability of the dense CNT membrane was more than 4 orders of magnitude higher than permeabilities for previous CNT membranes.[6,13,14]

In the current study, ion diffusion through dense CNT membranes was studied. Ions diffused through both the CNT pores and the interstitial regions, and diffusion had a gated behavior that depended on the ions, temperature, and ultrasonication. At room temperature, the gate for ion transport closed, probably because water does not wet CNTs well, and thus did not form a continuous water layer for ion diffusion. The gate was opened by ultrasonication or by a 20-K temperature increase. When the ion diffusion channel was opened, ions diffused at rates similar to their bulk diffusion rates in water. Water adsorption isotherms showed that these CNTs became more hydrophilic as the temperature increased, and thus, the CNT membranes were more likely to be filled at higher temperature. Water adsorption isotherms also showed that at 306 K, water appeared to fill interstitial pores in dense membranes at an activity (partial pressure/saturation pressure) of ~0.53, but it did not condense inside CNT pores.

Experimental Methods

Preparation of Dense CNT Membranes. The preparation of dense VA-CNT membranes was described previously.[12] Vertically aligned carbon nanotube arrays were grown by water-assisted chemical vapor deposition (CVD)[15] and the arrays were collapsed into a dense membrane by capillary forces resulting from solvent evaporation.[16] A horizontal quartz tube housed in a furnace was used for CVD. Catalyst thin films (1-nm Fe/10-nm Al_2O_3) were deposited by sequential e-beam evaporation onto silicon wafers that had a 500-nm oxide layer. The wafers were placed into the quartz tube, the tube purged with Ar, and then temperature was increased. At 623 K, hydrogen (400 sccm) was introduced, and after 20 min (933 K), an argon stream (30 sccm) that bubbled through a water bubbler was used to introduce water (~730 ppm) to the reactor. After another 10 min, at 1023 K, ethylene (100 sccm) was introduced. After CVD, the VA-CNT array was detached from the substrate by water etching, as suggested by Ci et al.[17] The array was then soaked in *n*-hexane for 30 min and dried at room temperature to collapse the CNTs into a dense membrane. The membranes were stored in a vacuum oven at 343 K for 24 h. A membrane was used in this form for adsorption measurements. A membrane was glued onto a porous filter (5 μm pores) using epoxy for permeation measurements. Characterization by N_2 adsorption at 77 K indicated that the average CNT pore diameter was 3 nm and the interstitial pores between CNTs were approximately 3 nm. Nanogold filtration indicated an average membrane cutoff size of ~3 nm.

Ion Diffusion. Dense CNT membranes were also glued onto the bottom of a polyethylene tube. Before each ion diffusion measurement, membranes were placed in DI water in an ultrasonic bath for 2−4 h and then dried overnight in a vacuum oven at 60 °C. Typically, 200 mL of concentrated solution, prepared by boiling DI water for 30 min to remove dissolved gases and then dissolving an appropriate amount of salt, was placed in a beaker. The plastic tube with the membrane and 12 mL of DI water inside was immersed in the solution. Because the membrane areas was small, the permeate concentration was less than 1% of the feed concentration for all measurements. The height of the tube was adjusted so the two liquid levels were the same to eliminate hydrostatic gradients. Both feed and permeate solutions were stirred using stir bars to minimize concentration polarization. A conductivity meter immersed in the permeate solution measured the conductivity. A water bath was used to control the solution temperature. The feed and permeate liquids were preheated when measurements were made above room temperature. To determine the effect of ultrasound, the system was placed in an ultrasonic water bath (Branson 3510, 40 kHz). To avoid ultrasound heating of the feed or permeate solutions, the ultrasonic bath was filled with 1 L of water and the ultrasonication time was usually shorter than 5 min.

Adsorption Measurements. Adsorption isotherms of water and *n*-hexane on dense CNT membranes and as-grown CNTs were measured by a volumetric method, and the amounts adsorbed in repeat isotherms were within 5% of each other. Approximately 30 mg of as-grown or shrunk VA-CNT arrays was used for adsorption measurements in an Autosorb-1 (Quantachrome Corp) system. The samples were outgassed in vacuum at 473 K for about 6 h. Water and hexane vapor adsorption measurements were performed at 293−306 K, and N_2 adsorption/desorption was conducted at 77 K.

Zero Current Potential Measurements. The zero current potential across membranes was measured using two Ag/AgCl (KCl saturated) electrodes through agar salt bridges in the feed and permeate solutions, following Nishizawa et al.[18] The offset potential of the electrodes due to different electrolyte concentrations on feed and permeate sides was eliminated, and the zero current potential

(11) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. *Nature* **2005**, *438*, 44–44.

(12) Yu, M.; Funke, H. H.; Falconer, J. L.; Noble, R. D. *Nano Lett.* **2009**, *9*, 225–229.

(13) Hinds, B. J.; Chopra, N.; Rantell, T.; Andrews, R.; Gavalas, V.; Bachas, L. G. *Science* **2004**, *303*, 62–65.

(14) Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E. *Nano Lett.* **2007**, *7*, 2806–2811.

(15) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362–1364.

(16) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987–994.

(17) Ci, L. J.; Manikoth, S. M.; Li, X. S.; Vajtai, R.; Ajayan, P. M. *Adv. Mater.* **2007**, *19*, 3300–+.

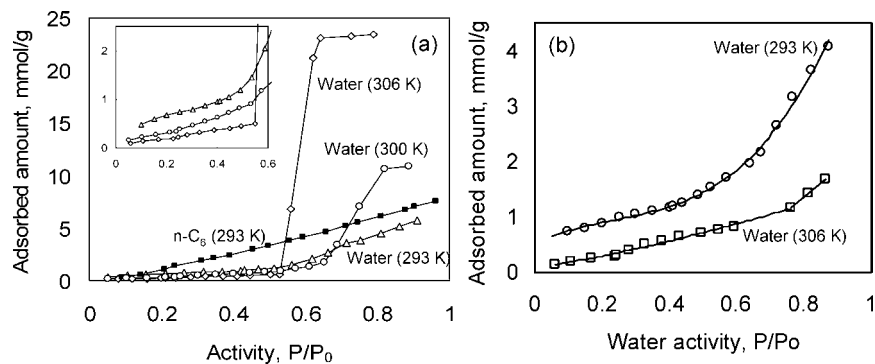(18) Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700–702.

Figure 1. (a) Water and *n*-hexane vapor adsorption isotherms on dense CNT membranes (inset is the water adsorption isotherms at low activity); (b) water adsorption isotherms on as-grown CNTs.

Table 1. Pore volume of as-grown and dense CNT arrays

	pore volume, mL/g			
morphology	N_2 at 77 K		*n*-hexane	water
As-grown	0.19 (2.0−5.0 nm)	14.4 (>5.0 nm)	—	~0.1 (293 K)
dense	0.76 (1.5−8.5 nm)	0.04 (>10.0 nm)	0.82 (293 K)	~0.1 (293 K)
				~0.42 (306 K)

was the potential across the membranes. The potential was measured typically after ion diffusion stopped, but it was also measured by replacing the permeate solution with different concentrations of electrolyte solution.

Results and Discussion

Adsorption Isotherms. An adsorption isotherm for *n*-hexane adsorption on dense CNT membranes was measured at 293 K in an effort to estimate the available pore volume of the membrane and to determine if *n*-hexane adsorption differed significantly from water. As shown in Figure 1a, the amount of *n*-hexane adsorbed increased linearly with *n*-hexane pressure, and at an activity of 0.96, *n*-hexane occupied 0.82 mL/g of the dense CNT membranes (Table 1). The density of *n*-hexane adsorbed in CNT membranes was assumed to be the same as its liquid density. This pore volume is almost the same as that obtained by N_2 adsorption at 77 K (Table 1), and indicates that *n*-hexane completely wetted the CNTs and interstitials.

The water adsorption isotherm on dense CNT membranes at 293 K was concave (Figure 1a), a type III isotherm, indicating the CNTs were hydrophobic. At the highest water activity used (0.91), approximately 0.10 mL/g CNT adsorbed in the dense CNT membranes (Table 1, Figure 1a). Since the water adsorption isotherms were similar at low activities for the dense membrane and the as-formed CNTs at 293 K, the distribution of water between the interior and the interstitial CNT pore surfaces could not be determined. Mao et al.,[19] who measured water adsorption isotherms at room temperature on single-walled CNTs (SWNT) by NMR, found that even at an activity of one, the amount of water adsorbed was only 25% of the theoretical saturation value, and most of the water accumulated near the CNT opening. They concluded that defects in their CNTs may have strongly affected water adsorption and prevented its diffusion into the CNTs. Our CNTs are also expected to have defects, which may limit water adsorption at room temperature.

Water adsorption isotherms at 306 K were also similar on dense CNT membranes (Figure 1a inset) and as-grown CNTs

(Figure 1b) at low activities. At low activities, when the temperature was increased from 293 to 306 K, the amount of adsorbed water decreased, as expected, since desorption is faster at the higher temperature. The shape of isotherms at low activities changed from concave to almost linear as the temperature increased, which may indicate a start of transition from hydrophobic to hydrophilic.[9]

At higher activities, the water adsorption isotherms at 300 and 306 K on dense CNT membranes were dramatically different from the isotherm at 293 K. Over a narrow activity range (0.53−0.64) at 306 K, *the amount of water adsorbed increased approximately by a factor of 40*. Thus, at an activity of 0.64, the CNTs adsorbed 10 times as much water as they did at 293 K. Since the amount of water adsorbed in the as-grown CNTs decreased as the temperature increased from 293 to 306 K (Figure 1b), the sharp increase in adsorbed water in the dense membranes at 306 K indicates that the additional water adsorbed and perhaps condensed in the interstitial pores. That is, increasing the temperature by 13 K apparently caused water to wet the outside of the CNTs much better at higher activities. As the water activity increased further, the amount of water adsorbed was essentially constant. At 300 K, the water adsorption isotherm on dense CNT membranes exhibited similar behavior to that at 306 K, but the increase in adsorption was over a wider activity range (0.64−0.82), and the amount adsorbed only increased a factor of 5 in that activity range.

The water saturation loading on dense membranes at 306 K was about 4 times that at 293 K. As shown in Table 1, the saturation loading at 306 K was about 50% of the total dense CNT membrane volume, whereas the loading was only 10% at 293 K. The large increase in the amount of water adsorbed in dense CNT membranes, for only a 13 K increase in temperature, may result because a continuous water phase formed in the interstitials.

Striolo et al.[20] simulated adsorption on single-walled carbon nanotubes (SWCNT) with sizes from 0.8 to 2.7 nm and found negligible water adsorption at low activity and a sharp increase

(19) Mao, S. H.; Kleinhammes, A.; Wu, Y. *Chem. Phys. Lett.* **2006**, *421*, 513–517.

(20) Striolo, A.; Chialvo, A. A.; Gubbins, K. E.; Cummings, P. T. *J. Chem. Phys.* **2005**, *122*, 234712.
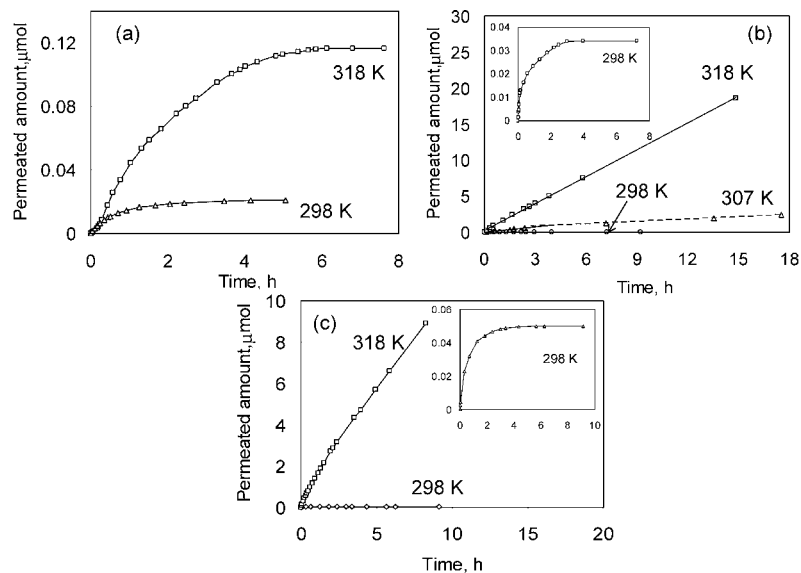
Figure 2. Amounts of salts or acid that permeated through a dense CNT membrane as a function of time. (a) HCl with feed concentration of 1 mM, (b) Na_2SO_4 with feed concentration of 10 mM (inset is Na_2SO_4 amount at 298 K with the same units for the *x* and *y* axes), (c) KCl with feed concentration of 10 mM (inset is KCl amount at 298 K with the same units for the *x* and *y* axes).

to complete filling at a threshold activity. The shapes of their simulated isotherms are similar to those measured for our dense CNT membranes at 306 K (Figure 1), but their simulations were for water condensation in the CNTs instead of the interstitials pores. If we assume interstitial pores in dense CNT membranes have similar surface properties as interior CNT pores in Striolo's simulation, we could estimate, using the Kelvin equation, that water condensation at an activity of 0.53 at 306 K corresponds to a pore size of 4.0 nm based on Striolo et al.'s adsorption data. This pore size is similar to the interstitial pore sizes in the dense membranes from N_2 porosimetry measurement.[12]

Wang et al.[9] found that SWCNTs with 1.4-nm diameter changed from hydrophobic to hydrophilic when the temperature decreased from 295 to 281 K. The shape of their water adsorption isotherms, therefore, was different from Striolo et al.'s simulation,[20] which predicted strong hydrophobicity of SWCNTs. Interstitial pores of our dense CNT membranes behave more like CNTs in simulations at 306 K, and is different from water adsorption behavior in CNT pores in Wang et al.'s study.[9] Our CNTs may have a different number of defects or different distribution of defects from those of Wang et al., and thus, temperature may affect water adsorption differently. Although the shape of the water adsorption isotherms in the above studies is different, water reached saturation loading at the highest activity in ideal CNTs (interior pores) in simulation[20] and in CNTs (interior pores) with fewer defects;[9] water adsorption in CNTs (interior pores) with many defects did not reach saturation even at an activity of one, as pointed out by Mao et al.[19] Water adsorption isotherms on as-grown CNTs (Figure 1b) showed that defects on CNTs suppressed water adsorption in interior CNT pores over the entire temperature range. This is consistent with Mao et al.'s finding.[19] However, defects had much smaller effects on water adsorption in interstitial CNT pores at higher temperature (Figure 1a). We do not have an explanation for the smaller effect of defects at higher temperatures, and we are not aware of experimental or simulation results on water adsorption in 3-nm interstitial CNT pores.

Ion Transport. Even though water did not appear to wet the CNTs at 293 K, ions transported across the membrane initially

at 298 K. As shown in Figure 2a, HCl diffused through the CNT membrane initially at 298 K, but after 3.5 h, its diffusion stopped and the HCl concentration on the permeate side did not change for the next 3.5 h. At 298 K, Na_2SO_4 and KCl diffusion exhibited similar behavior; the ion flux for both stopped after about 3 h as shown in Figure 2b. The Na_2SO_4 and KCl feed concentrations were 10 times higher than the HCl feed concentration, but the Na_2SO_4 and KCl concentrations were only 1.7 and 2.4 times higher in the permeate when ion diffusion stopped (Figure 2b,c insets). These permeate concentrations were less than 0.1% of the feed concentrations, so the driving force remained essentially constant during these measurements. Diffusion measurements were made for different feed concentrations of Na_2SO_4, HCl, and KCl, and for a second membrane, and the behavior was similar.

Majumder et al.[11] found that the pure water flux through interior CNT pores in multiwalled CNT membranes (~7-nm CNT pores) decreased approximately 80% in 20 min, but the water flux was constant for 20 min after adding 17 mM KCl to the feed. This suggests that salts in CNT pores may facilitate wetting of CNTs by water. In contrast, Li et al.[10] found an electrostatic gating of water transport through single-walled CNTs (0.81 nm); the water flux decreased 90% when an external charge attached tightly to the CNT exterior wall, as opposed to when the charge distance to the CNT wall was 0.85 nm. Thus, the mechanism by which adsorbed ions affect flow through the CNTs is probably complicated. Pure water permeation through dense CNT membranes showed behavior similar to ion diffusion. At room temperature, the water flux decreased more than 3 orders of magnitude with time, but the steady-state water flux then increased approximately a factor of 30 when the temperature was increased to 333 K. Although more water adsorbs at higher temperature, sparsely distributed voids could still generate large transport resistance, but less than at lower temperatures. In addition, water clusters associated with defects may have lower mobility and thus inhibit water transport, and higher temperature may facilitate their dissociation from defects and thus increase the water flux.

Ion diffusion through a membrane is determined by concentration gradients and by the electrical potential across the
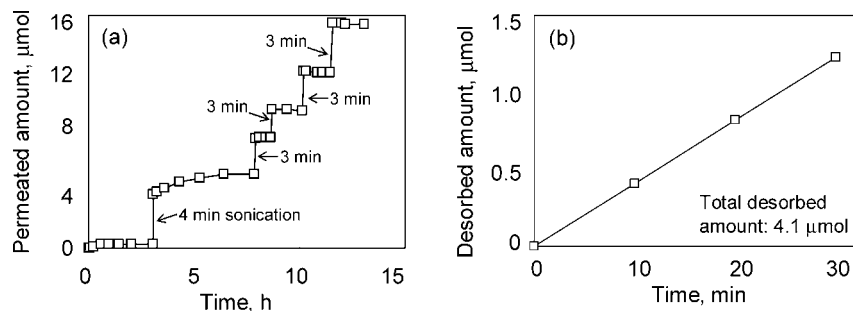
Figure 3. (a) Amounts of HCl that permeated through a dense CNT membrane at 298 K for a 50 mM HCl feed. Ultrasound was turned on for the indicated times; b) after the measurements in (a), the membrane was placed in 500-mL DI water, and the amount of HCl that desorbed is shown as a function of ultrasonication time.

membrane (or the net charges on each side). If both cations and anions transport through the membranes at their stoichiometric ratios, no charge should accumulate on either side of the membrane, no electric field should form across the membrane, and the feed and permeate should eventually reach the same concentration. If the membrane allows only cations or only anions to diffuse, charge will accumulate on both sides and an electric field will form. This would prevent further diffusion of ions and create a concentration gradient at equilibrium.

For the dense CNT membranes, the zero-current potential across the membrane was almost zero before and after ion diffusion stopped, and the feed concentration was at least 100 times the permeate concentration. The permeate solution was replaced with solutions whose concentrations were 1%, 5%, and 10% of the feed concentration, but the zero-current potential was also near zero after ion diffusion stopped. This means that the membrane is not selective for cations or anions, and no net charge accumulated on either side. Also, the dense CNT membranes have an average pore size of approximately 3 nm, which is much larger than the sizes of the hydrated ions, so the membranes are not expected to preferentially allow cations or anions to permeate. In studies by Fornasiero et al.,[7] 2-nm pores in CNT membranes did not selectively transport cations or anions.[7] Our ion diffusion results, the zero-current potential measurements, and the water adsorption isotherms suggest that water may not be in a continuous phase in dense CNT membranes at 298 K when ion diffusion stopped and feed and permeate solution were not connected by free moving ions (Figure 1).

At 318 K, HCl diffusion through a dense CNT membrane was similar to diffusion at 298 K (Figure 2a), but diffusion stopped after 6 h instead of 3.5 h. In contrast, the Na_2SO_4 and KCl fluxes at 318 K were constant for at least 15 and 8 h, respectively, as shown in Figure 2b,c. At 307 K, the Na_2SO_4 diffusion rate decreased after 3.5 h to half its initial value and was then constant. When the temperature decreased to 298 K from either 307 or 318 K, ion diffusion stopped, indicating reversible behavior. The steady-state diffusion rate of Na_2SO_4 at 318 K was 12 times the rate at 307 K and was similar to the KCl rate at 318 K. These ion diffusion measurements were performed at least twice and the temperature sequence was different, but the results were reproducible. As suggested by the water adsorption isotherms (Figure 1), higher temperature may allow the interstitial CNT pores to fill with water and form a continuous ion diffusion channel. The ions in water may affect how water wets the CNTs, so that the differences between HCl and the Na_2SO_4 and KCl salts may be due to this difference in wetting.

When 50 mM HCl was used as a feed instead of 1 mM, diffusion at 298 K stopped after less than 6 h instead of 3.5 h. The permeate solution was then replaced by fresh DI water, and after ~0.5 h, the flux was again zero. The HCl in the new permeate water may be HCl that desorbed from the membrane surface. The system (the membrane and the feed and permeate solutions) was then placed in an ultrasonic water bath, which was turned on for short times. As shown in Figure 3a, ultrasonication for 3 or 4 min increased the HCl permeate concentrations dramatically. The first time, for 4 min, increased the HCl permeate concentration a factor of 13, and subsequent times for 3 min increased the HCl amount by 2.5−3.5 μmol; the initial 4 min of ultrasound increased the HCl amount by 3.6 μmol. These increases correspond to ion diffusion rates that were at least 20 times the initial rates at 298 K. Approximately 3 h was required, after the ultrasound was turned off the first time, for the permeate concentration to reach a constant value. In a subsequent ultrasonication for 3 min, the permeated amount increased, but it did not change when the ultrasound was turned off. Short ultrasound exposures with long times between were used so that the membrane and solutions did not heat up. Ultrasonication may provide additional kinetic energy to water molecules in the membranes. Discontinuous water clusters, which contain ions, may temporarily contact with neighboring water clusters so that ions transfer to the low concentration side.

Because ultrasonication might also desorb HCl from the membrane, at the end of the ultrasonication treatment in Figure 3a, the membrane was taken out of solution and placed in 500 mL of DI water. It was then exposed to ultrasound and HCl desorbed at a constant rate for 30 min, as shown in Figure 3b. The slope corresponds to a desorption rate that is less than 5% of the HCl permeation rates during ultrasonication. The total amount of HCl desorbed after ~4 h of ultrasonication was 4.1 μmol, whereas the total amount that permeated through the membrane during 16 min of ultrasonication was approximately 15 μmol. Thus, the increase in permeate concentration during ultrasonication was due to diffusion through, not desorption from, the membrane.

The high diffusion rates of ions through the CNT membranes, at elevated temperature or during ultrasonication, are similar to their bulk diffusion rates in water. The HCl diffusion rate through the membrane at 298 K during ultrasonication was 5.0×10^{-4} mol/(m²·s), for a feed concentration of 50 mM, a membrane thickness of ~500 μm and a membrane area of 0.3 cm². The diffusion rate of HCl in water at 298 K is 3.2×10^{-4}

mol/(m^2·s).[21] The diffusion rate of Na$_2$SO$_4$ through the membrane at 318 K was 1.2×10^{-5} mol/(m^2·s) for a feed concentration of 10 mM, and the diffusion rate of Na$_2$SO$_4$ in water at 298 K is 2.4×10^{-5} mol/(m^2·s).[22] The diffusion rate of KCl at 318 K is also similar to its diffusion rate in water at 298 K.

Conclusions

In summary, ion diffusion through dense CNT membranes showed a gated behavior, which may be due to the poor water wettability in dense CNT membranes at room temperature, but better wetting in the interstitial CNT pores at higher temperature, as suggested by the water adsorption isotherms. The ions were trapped in dense CNT membranes at 298 K, possibly due to the discontinuity of water clusters in the membrane, and did not diffuse through dense CNT membranes at steady state. Ion diffusion rates increased significantly when the temperature increased or when the membranes were exposed to ultrasound. Water condensed in the interstitial CNT pores and filled ~70% of the interstitial CNT pore volume at 306 K, but less than 17% of interstitial CNT pore volume at 293 K. More water in the pores at higher temperature increases the likelihood of forming continuous water channels in dense CNT membranes for ion diffusion. Although water did not wet dense CNT membranes at room temperature, ultrasound may facilitate the formation of temporary continuous water channels for ion diffusion.

Supporting Information Available: Additional figures of pressure-driven water permeation results. This material is available free of charge via the Internet at http://pubs.acs.org.

JA9091769

(21) Harpst, J. A.; Holt, E.; Lyons, P. A. *J. Phys. Chem.* **1965**, *69*, 2333-&.
(22) Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*; Cambridge University Press: New York, 1984.