Aligned Small Diameter Single-Walled Carbon Nanotube Membranes for Reverse Osmosis Desalination

Qualifying Examination

Department of Chemistry

The University of Texas at Dallas

Blake Wilson

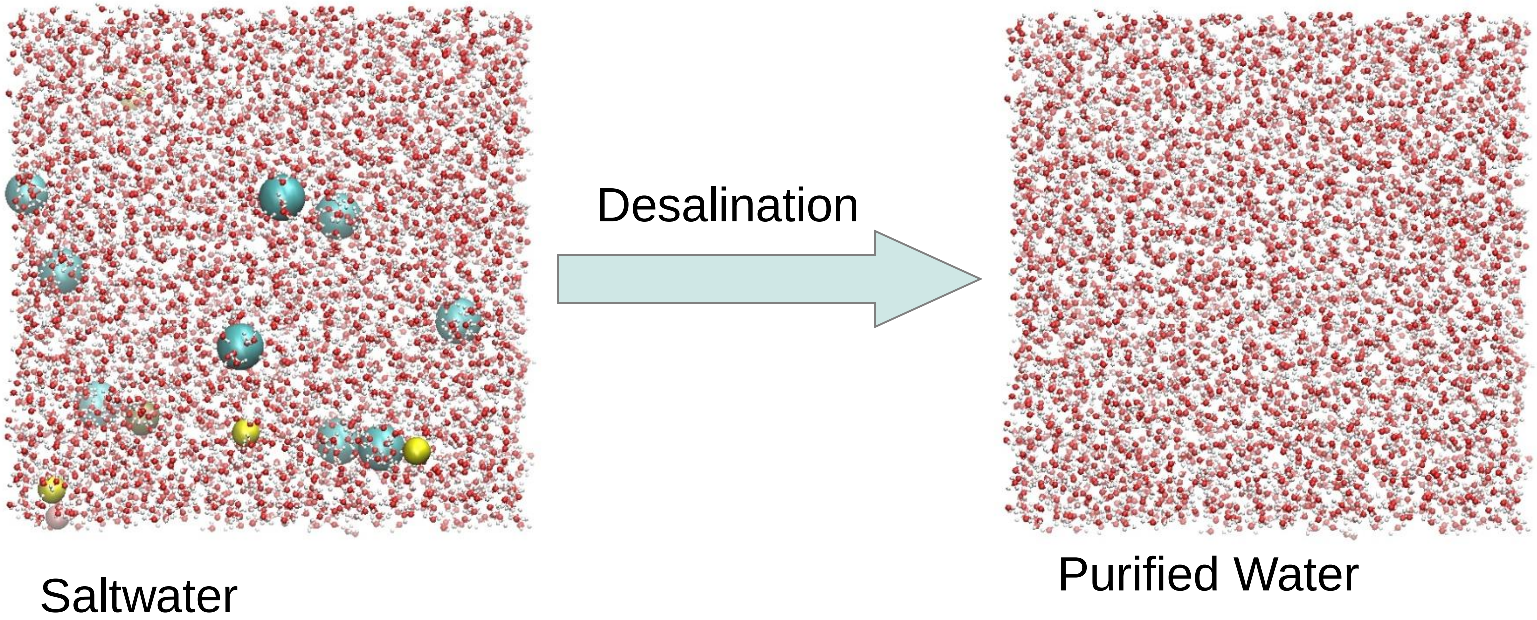
January 31st 2013

Outline

- Background
  - Desalination
  - Carbon Nanotubes (CNTs)
  - CNTs for Desalination
- Methods
  - Membrane Fabrication
  - Characterization
  - Additional Studies
- Intellectual Merit

Water Desalination

- Water purification technique
- Removes dissolved salts from water
- Early example was reported in CE 200



Kalogirou, S. A. Progress in Energy and Combustion Science **2005**, *31*, 242 – 281
Al-Karaghouli, A.; Renne, D.; Kazmerski, L. L. Renewable and Sustainable Energy Reviews **2009**,
El-Dessouky, H. J Pak Matr Soc **2007**, *1*, 34–35

Water Content

- ~70% of earth's surface is covered with water
- ~97% of the earth's water supply is composed of salt water
- ~3% of the earth's water supply is fresh water
- Only about 0.25% of the fresh water supply is readily available for use

El-Dessouky, H. J Pak Matr Soc **2007**, *1*, 34–35.
Karagiannis, I. C.; Soldatos, P. G. Desalination **2008**, *223*, 448 – 456
Kalogirou, S. A. Progress in Energy and Combustion Science **2005**, *31*, 242 – 281.

http://static.guim.co.uk/sys-images/Guardian/Pix/pictures/2012/9/26/1348685373327/Southern-Ocean-010.jpg
http://img1.findthebest.com/sites/default/files/600/media/images/Earth.jpg

Salinity of Water

Types of Saltwater and typical concentration of total dissolved salts (TDS):

- Brine
  - > 50,000 ppm
- Sea Water
  - 30,000 – 50,000 ppm (Average ~35,000 ppm)
- Brackish Water
  - 1000 – 30,000 ppm
- Fresh Water
  - < 1000 ppm

http://www.engineeringtoolbox.com/water-salinity-d_1251.html
http://www.cc.gatech.edu/cpl/projects/graphcuttextures/data/interaction/LittleRiver.jpg

Major Desalination Techniques

Phase-change Processes

1. Multi-stage flash (MSF)

2. Multiple effect boiling (MEB)

3. Vapour compression (VC)

Membrane Processes

1. Reverse Osmosis (RO)

2. Electrodialysis (ED)

- MSF constitutes ~44% of worldwide production
- RO constitutes ~42% of worldwide production

Al-Karaghouli, A.; Renne, D.; Kazmerski, L. L. Renewable and Sustainable Energy Reviews **2009**, 1
Kalogirou, S. A. Progress in Energy and Combustion Science **2005**, *31*, 242 – 281

Reverse Osmosis Membranes

- RO membrane first demonstrated in the 1950's by Reid
- Development of RO membranes with feasible flux values in the 1960's Loeb and Sourirajan.

Loeb　　　　　　　　　　Sourirajan

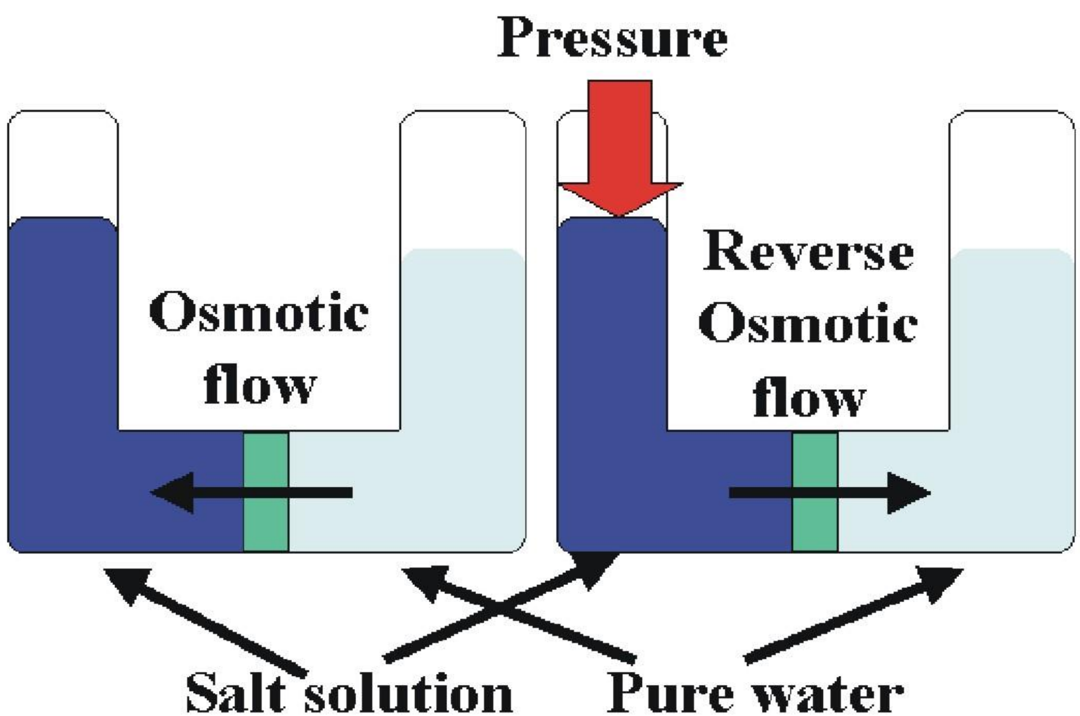
Williams, M. EET Corporation and Williams Engineering Services Company **2003**, *1*, 1–29

http://www.desalination.com/sites/default/files/Museum_veteran/LoebSidney.JPG?1311772740

http://www.greentechmedia.com/images/wysiwyg/News/hall-of-fame/loeb.jpg

Reverse Osmosis Membranes

- What is Osmosis?
  - What is Reverse Osmosis (RO)?



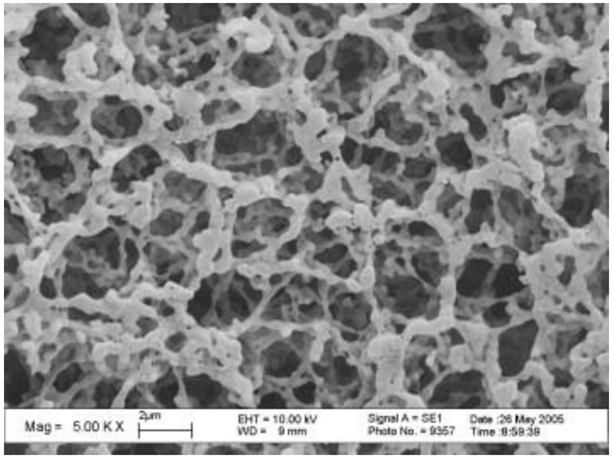
Dark Blue = Salt water

Light Blue = Pure water

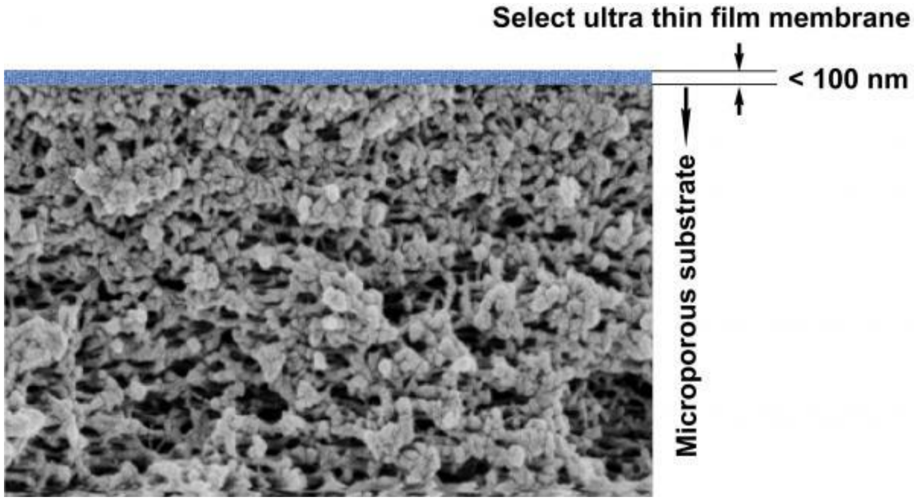
Reverse Osmosis. http://library.thinkquest.org/C0131200/Osmosis.htm.

Reverse Osmosis Membranes

- Current commercially available RO membranes can be broken into two categories:
  - Cellulose acetate (CA) membranes
  - Thin film (TF) membranes



SEM micrograph of CA membrane



Representation of TF membrane

Williams, M. EET Corporation and Williams Engineering Services Company 2003, 1, 1–29
http://www.advantecmfs.com/filtration/membranes/img/cace.jpg
http://apps.eng.unimelb.edu.au/research-projects/images/web_resize/proj120-Nanometer%20Image%201.jpg

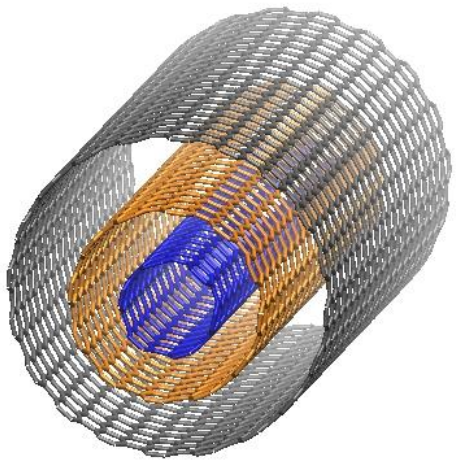
Advantages of RO Membranes

- No energy intensive phase-changes
- No costly solvents or adsorbents
- Can be used for desalination of brackish and sea water
- Simple to design and run
- Easily integrated into hybrid desalination systems

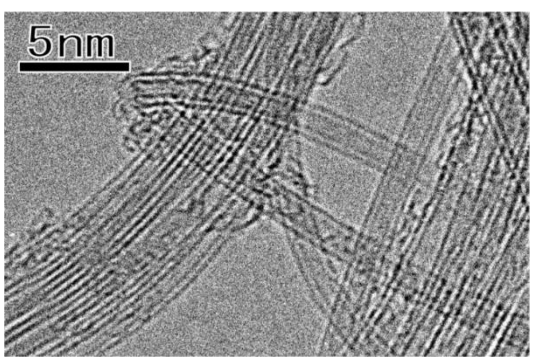
Williams, M. EET Corporation and Williams Engineering Services Company 2003, 1, 1–29
http://www.sciencephoto.com/image/3353/350wm/A3000063-Boiling_water_showing_bubbles-SPL.jpg

Carbon Nanotubes (CNTs)

- Multi-walled carbon nanotubes (MWCNTs) reported in 1991 by Iijima
- First single-walled carbon nanotubes reported in 1993.



- Show many remarkable properties including:
  - Electronic
  - Mechanical
  - Thermal
  - Transport

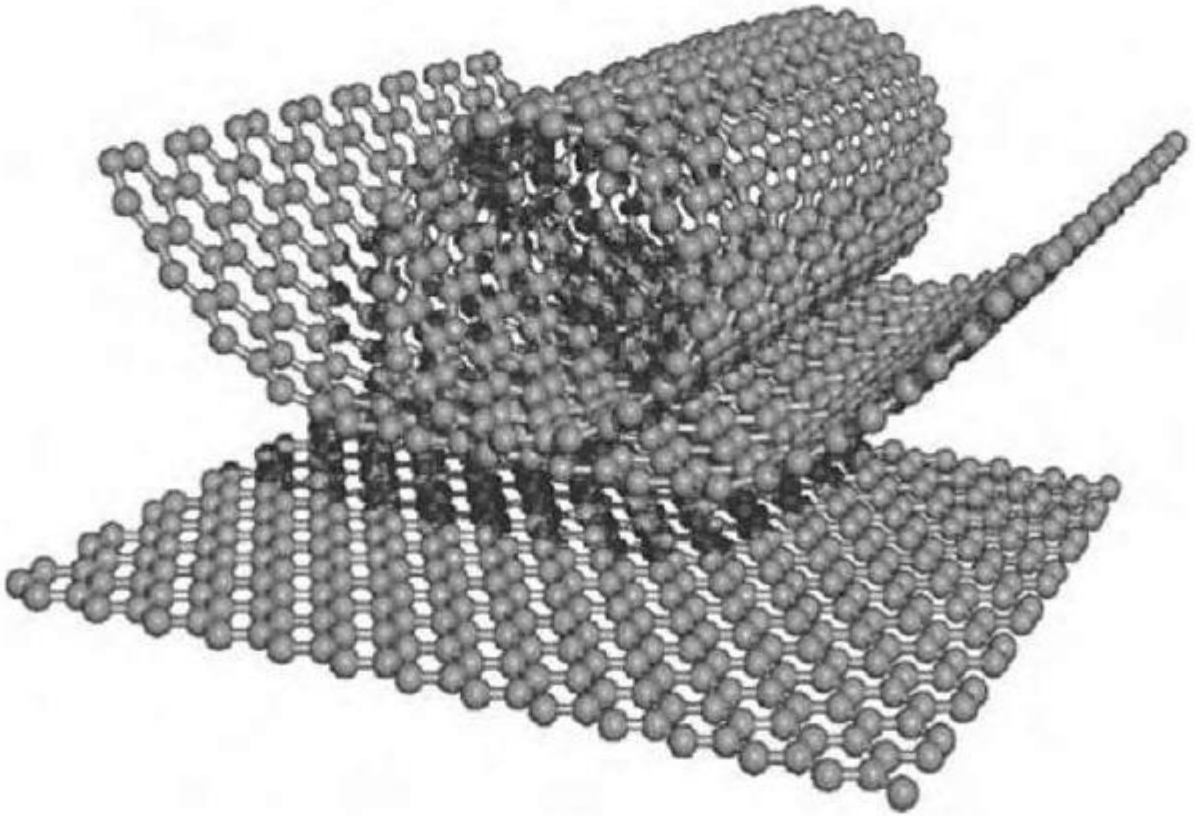


TEM image of Double-walled Carbon Nanotubes (DWCNTs)

Majumder, M.; Ajayan, P. Comprehensive membrane science and engineering 2010, 1, 291–310.
Khare, R.; Bose, S. Journal of Minerals & Materials Characterization & Engineering 2005, 4 , 31–46.
http://www.wakayama-u.ac.jp/~kisoda/int/researchactivity.html

Carbon Nanotubes (CNTs)

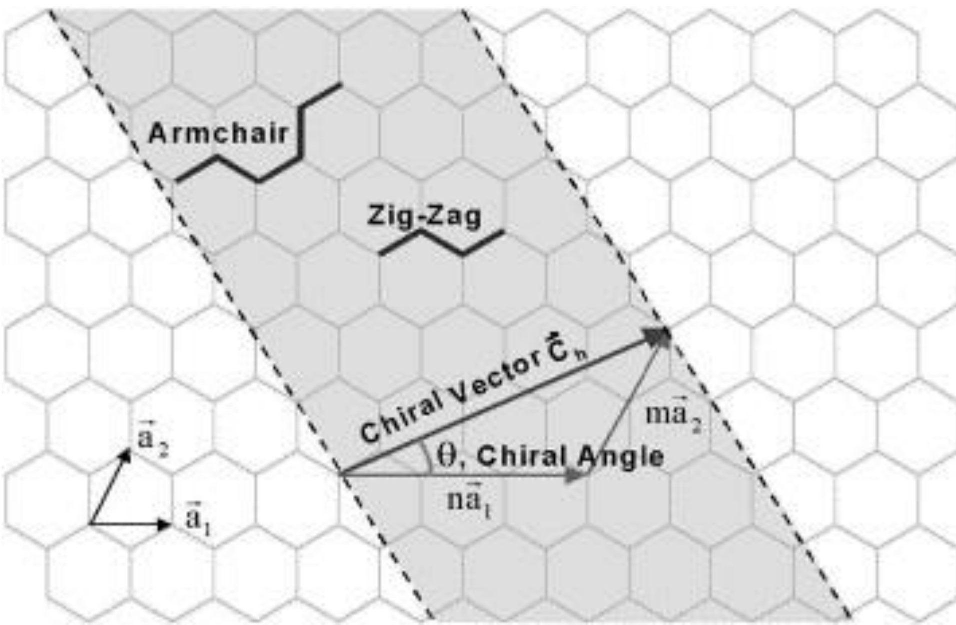
- Cylindrical tubes composed of sp^2 hybridized carbon
- Rolled up sheets of graphene

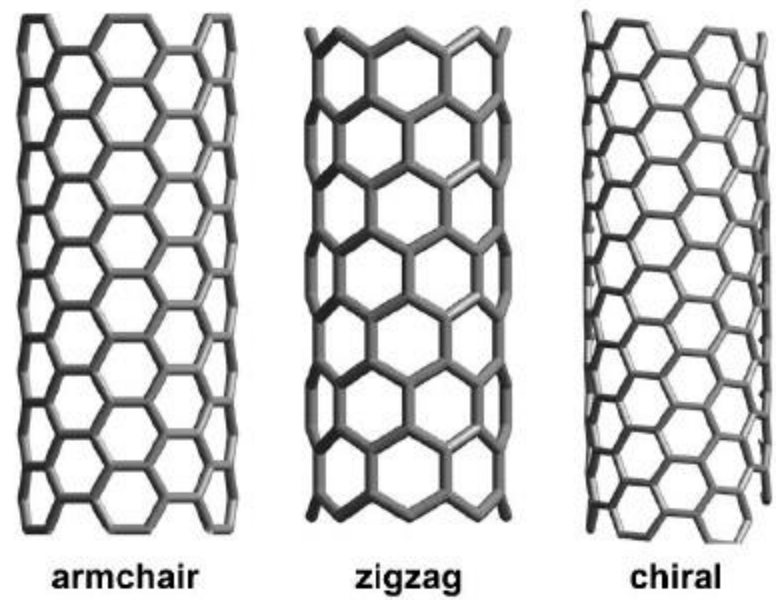


.
http://what-when-how.com/nanoscience-and-nanotechnology/carbon-nanotubes-

Chirality and Types

- Characterized by chiral indices n and m, (n,m)

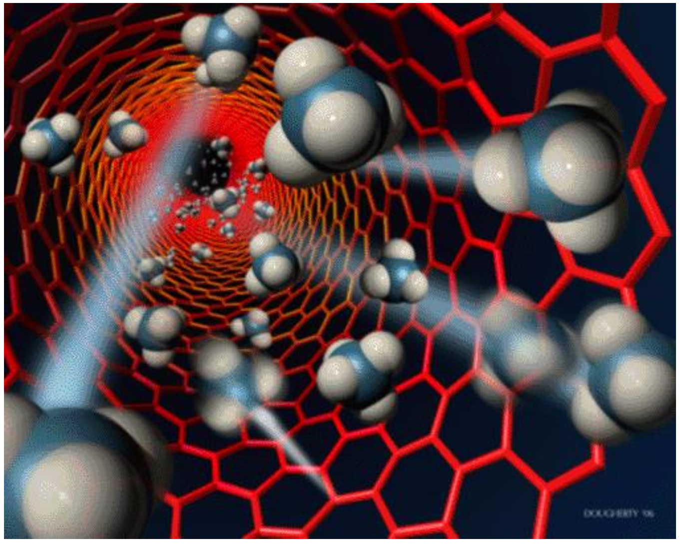




$$D = \frac{a}{n} \times \sqrt{n^2 + m^2 + mn}$$, a=0.246 nm

- Armchair: m = n
- Zigzag: (n,0)
- Chiral: n>m>0

Terrones, M. Annual Review of Materials Research 2003, 33, 419–501
Thostenson, E. T.; Ren, Z.; Chou, T.-W. Composites Science and Technology 2001, 61, 1899– 1912.
Prasek, J.; Drbohlavova, J.; Chomoucka, J.; Hubalek, J.; Jasek, O.; Adam, V.; Kizek, R. J.Mater. Chem. 2011, 21, 15872–15884
Carbon Nanotube Composites. http://coecs.ou.edu/Brian.P.Grady/nanotube.html



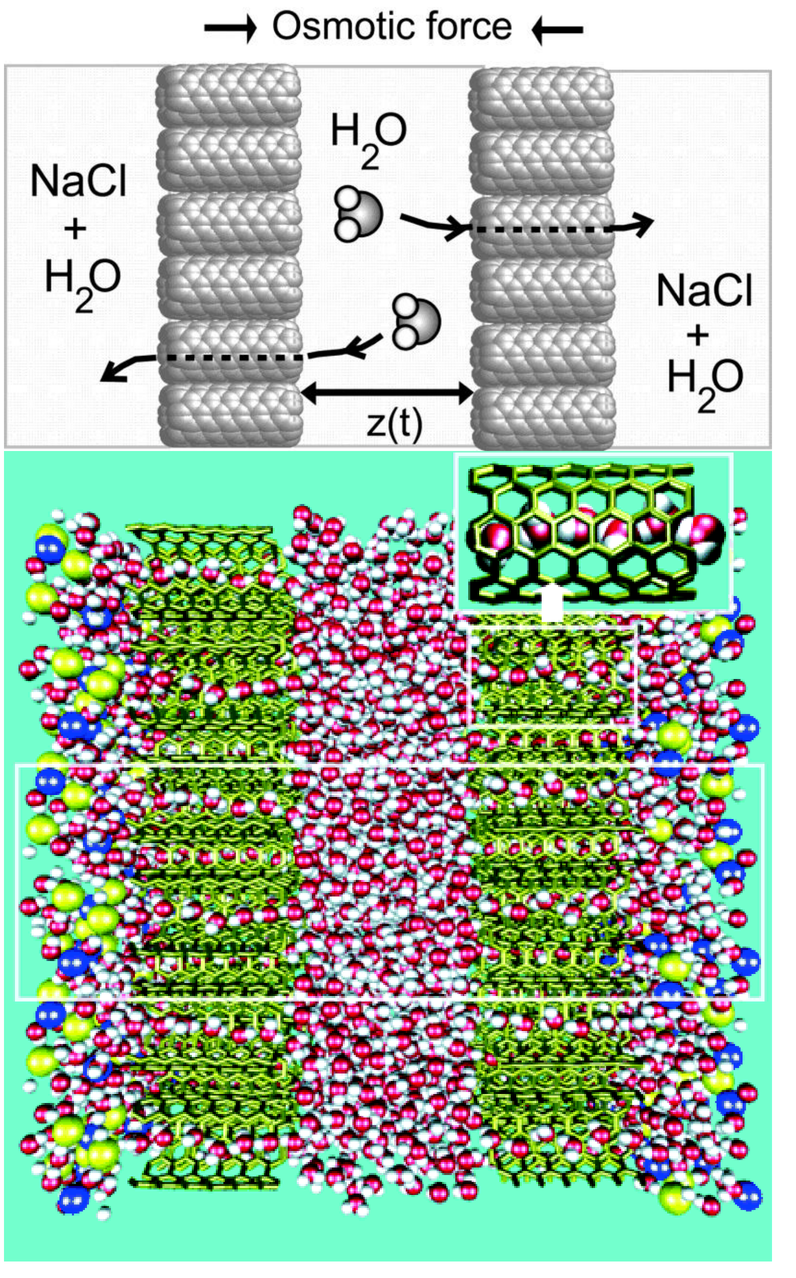
Mass Transport through CNTs

- Fast mass transport of several gases and water through the interior of CNTs has been observed
    - Flux values for gases orders of magnitude greater than equivalent zeolite pores
    - Water transport rates more than 3 orders of magnitude greater than those predicted by bulk water transport models

Altalhi, T.; Ginic-Markovic, M.; Han, N.; Clarke, S.; Losic, D. Membranes 2010, 1, 37–47
Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.;Noy, A.; Bakajin, O. Science 2006, 312, 1034–1037.
https://www.llnl.gov/news/newsreleases/2006/images/membrane_big.jpg

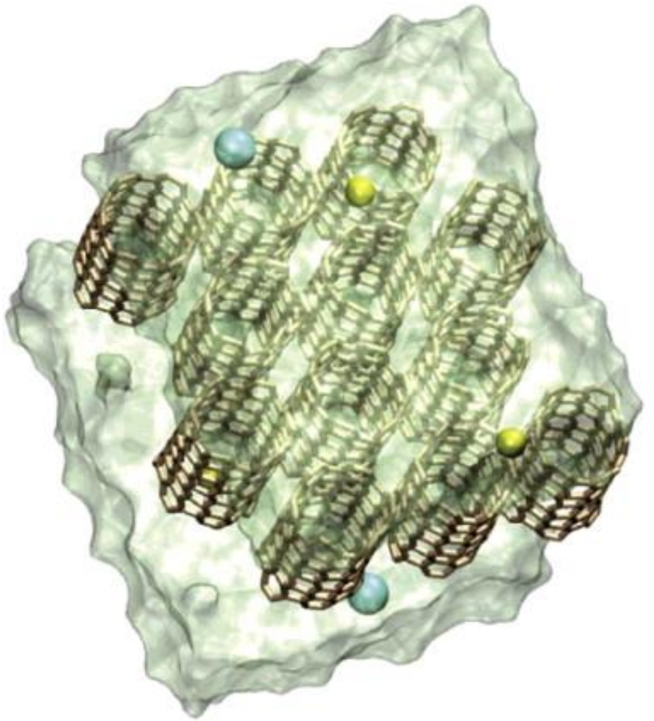
CNTs for Desalination of Water

- Kalra et al. (2003)
  - Showed water molecules travel with almost no friction through the interior of CNTs
  - Main energy barriers are entrance and exit of the tube
  - Observed water transport rates up to 5.8 water molecules per ns per nanotube under large osmotic gradient (0.0173 mL/(s*cm^2) assuming pore density of 10^{11} nt/cm^2)



Kalra, A.; Garde, S.; Hummer, G. Proceedings of the National Academy of Sciences 2003, 100, 10175–10180.

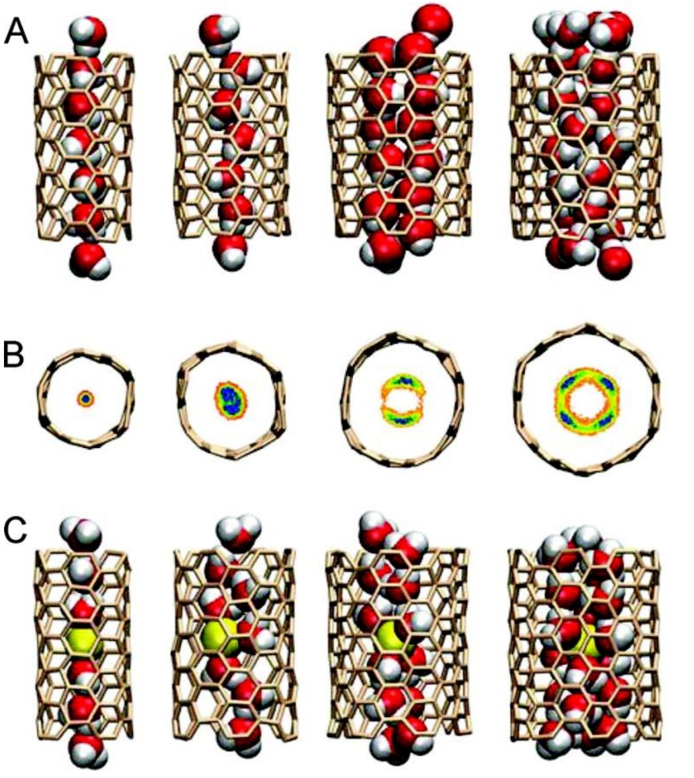
CNTs for Desalination of Water



- Corry (2008)
  - Examined four different diameter tubes
  - Calculated PMFs for water and ion permeation
  - Calculated desalination efficiency

Corry, B. The Journal of Physical Chemistry B 2008, 112, 1427–1434; PMID: 18163610

Ion Rejection and Water Conductance



Under 208 MPa and 250 mM NaCl

Chirality (n,m)	Diameter (nm)	Ion Rejection (%)	Water Conductance (pt pns)
(5,5)	0.66	100	10.4
(6,6)	0.81	100	23.3
(7,7)	0.93	95	43.7
(8,8)	1.09	58	81.5

Corry, B. The Journal of Physical Chemistry B 2008, 112, 1427–1434; PMID: 18163610

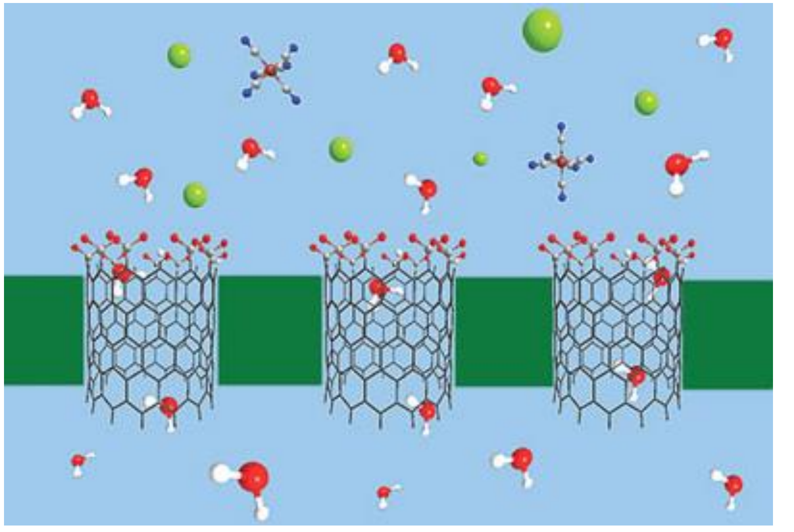
Seawater Desalination Simulation

Chirality (n,m)	Diameter (nm)	Flow Rate ($L/(cm^2*day)$)	Improvement (over FILMTEC SW30HR-380)
(5,5)	0.66	0.16	2.42
(6,6)	0.81	0.27	4.21
(7,7)	0.93	0.42	6.39
(8,8)	1.09	0.65	9.76

Operating pressure of 5.5 MPa and Osmotic pressure of 2.4 MPa . Flow rate calculated assuming pore density of 2.5×10^{11} pores per cm^2

Corry, B. The Journal of Physical Chemistry B 2008, 112, 1427–1434; PMID: 18163610

CNTs for Desalination



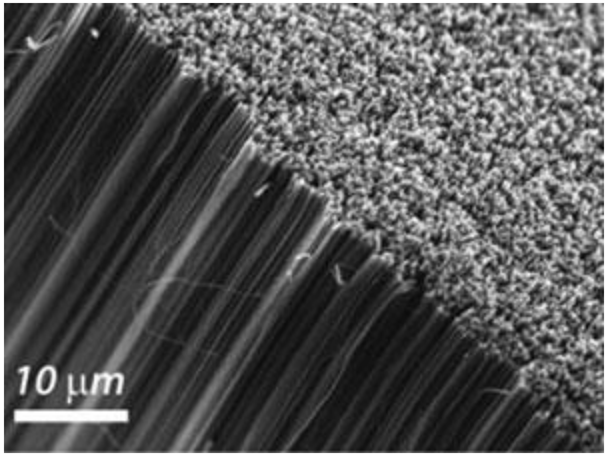
- Fornasiero et al. (2008)
  - Fabricated an aligned DWCNT membrane
  - Average inner tube diameter was 1.6 nm
  - Showed that addition of charged groups to CNT tips increased ion rejection up to 98% under some conditions
  - Show maximum rejections of K^+ and Cl^- of ~ 54% and 41 % respectively

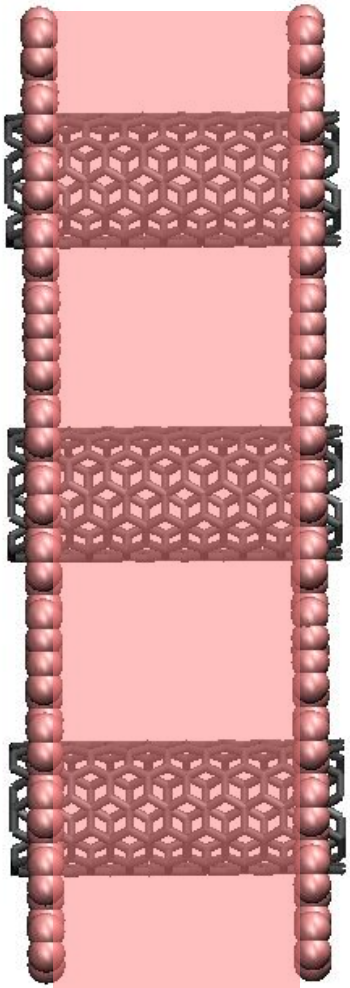
Fornasiero, F.; Park, H. G.; Holt, J. K.; Stadermann, M.; Grigoropoulos, C. P.; Noy, A.;Bakajin, O. Proc of the Nat Acad of Sci 2008, 105, 17250–17255

Methods and Design

- Fabricate the membrane

- Characterize the membrane



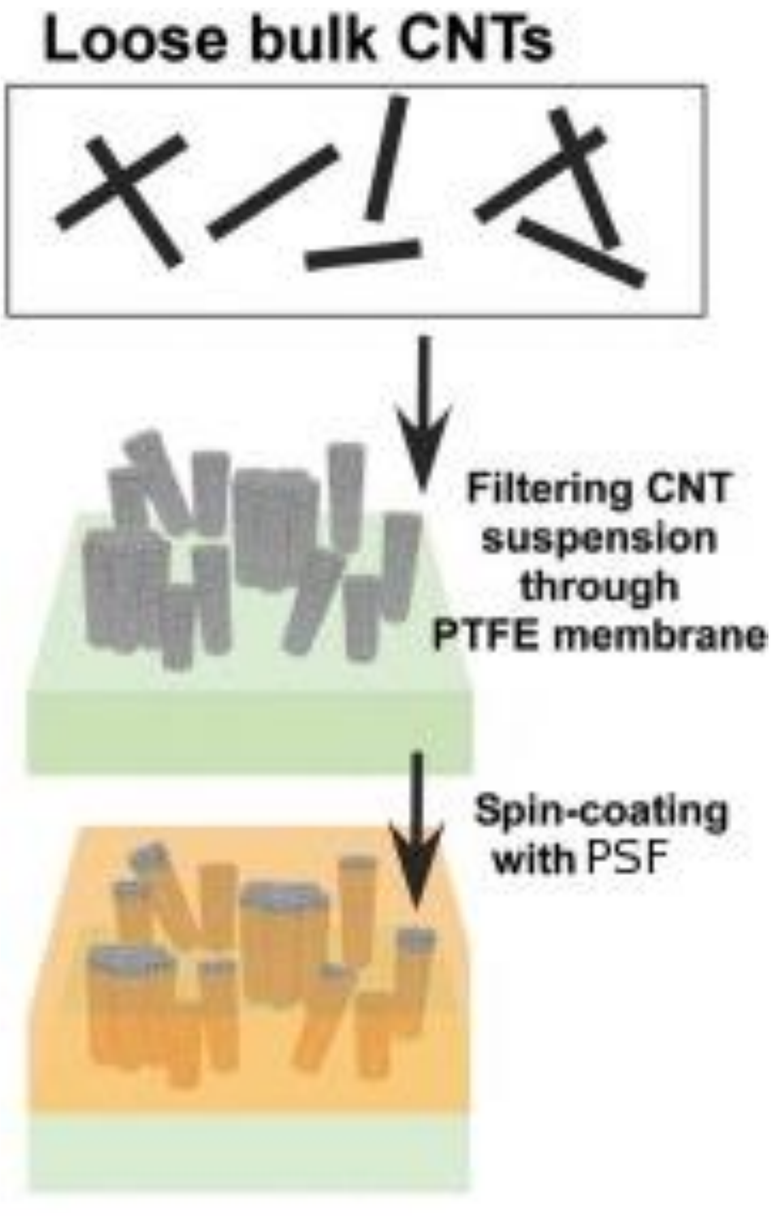


Fabricate the Membrane

- Approach 1: Sub-nm SWCNTs
    - Sub-approach 1: alignment by vacuum filtration
    - Sub-approach 2: shear force and magnetic alignment
- Approach 2: Ultra-dense SWCNT forest

Approach 1: Sub-approach 1

- Synthesize sub-nm diameter SWCNTs by the method of Loebick et al. (2010)
- Treat the tubes with acid to transform into MWCNTs
- Vacuum filter over PTFE membrane
- Spin coat with polysulfone (PSF)



Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E. Nano Letters 2007, 7, 2806–2811
De Heer, W.; Bacsa, W.; Chatelain, A.; Gerfin, T.; Humphrey-Baker, R.; Forro, L.; Ugarte, D. Science 1995, 268, 845–846
Zoican Loebick, C.; Podila, R.; Reppert, J.; Chudow, J.; Ren, F.; Haller, G. L.; Rao, A. M.;Pfefferle, L. D. J Am Chem Soc 2010, 132, 11125–11131

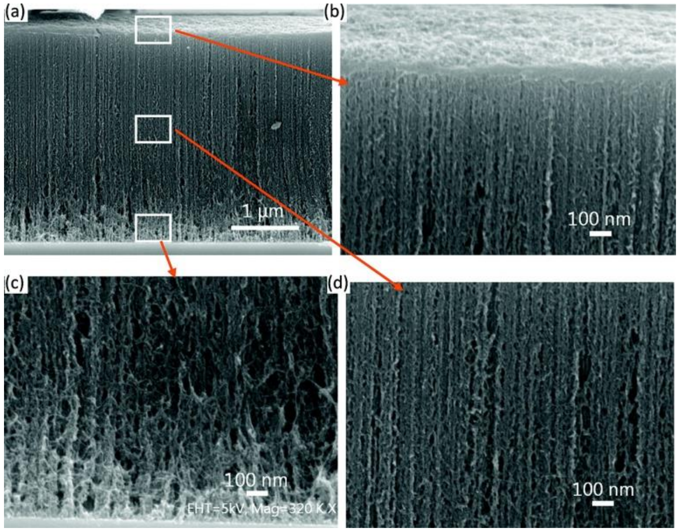
Approach 2: Sub-approach 2

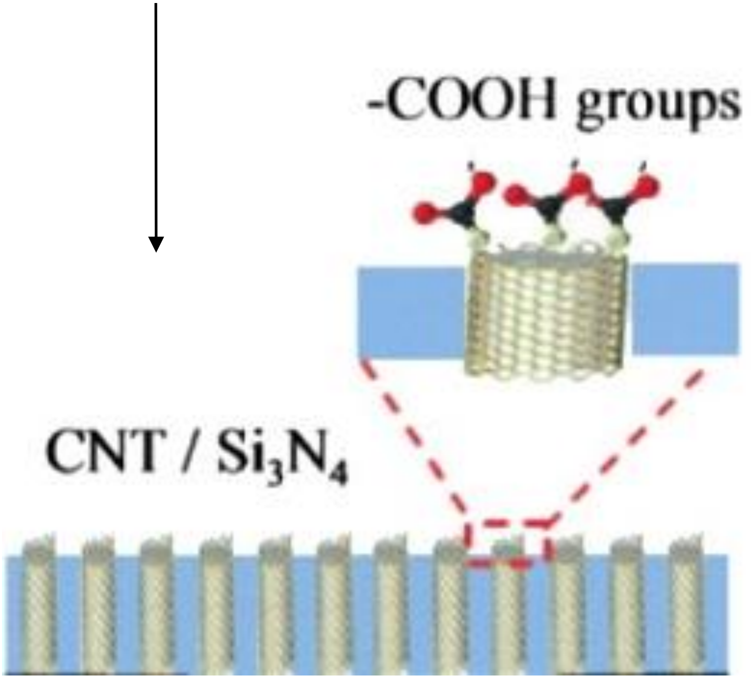
- Synthesize sub-nm diameter SWCNTs
- Disperse SWCNTs in Epoxy Resin and mix with a centrifugal shear mixer
- Cure the CNT/Epoxy composite under high magnetic field
- Microtome composite to desired thickness

Wu, J.; Gerstandt, K.; Zhang, H.; Liu, J.; Hinds, B. J. Nat Nano 2012, 7, 133–139
Xie, X.-L.; Mai, Y.-W.; Zhou, X.-P. Materials Science and Engineering: R: Reports 2005, 49, 89 – 112
Compneschi, E. L.; Ph.D. thesis; Georgia Institute of Technology; 2007

Approach 2

- Synthesize ultra dense SWCNT forest using the method of Zhong et al. (2012)
- Deposit Si_3N_4 to fill the gaps between SWCNTs
- Functionalize the SWCNT tips by water plasma oxidation





Zhong, G.; Warner, J. H.; Fouquet, M.; Robertson, A. W.; Chen, B.; Robertson, J. ACS Nano 2012, 6, 2893–2903
Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.;Noy, A.; Bakajin, O. Science 2006, 312, 1034–1037

Method Analysis: Pore Diameter and Density

- Approach 1
  - Variable SWCNT average diameter ranging from ~0.76-0.93 nm
  - Pore densities on the order of 10^{10}-10^{11} pores per cm^2
- Approach 2
  - Average SWCNT diameter of 1.2 nm
  - Pore density of ~1.5 x 10^{13} pores per cm^2

Wu, J.; Gerstandt, K.; Zhang, H.; Liu, J.; Hinds, B. J. Nat Nano 2012, 7, 133–139

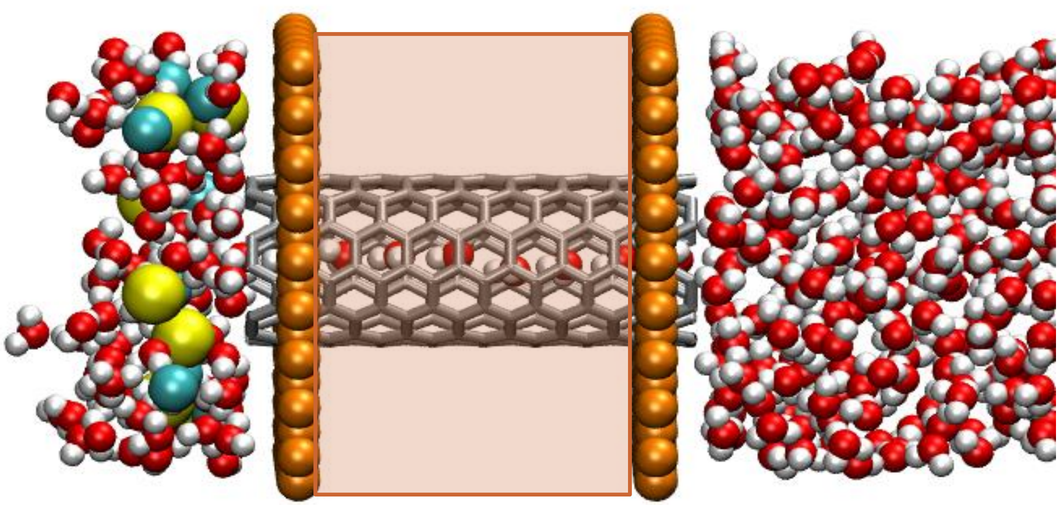
Xie, X.-L.; Mai, Y.-W.; Zhou, X.-P. Materials Science and Engineering: R: Reports 2005

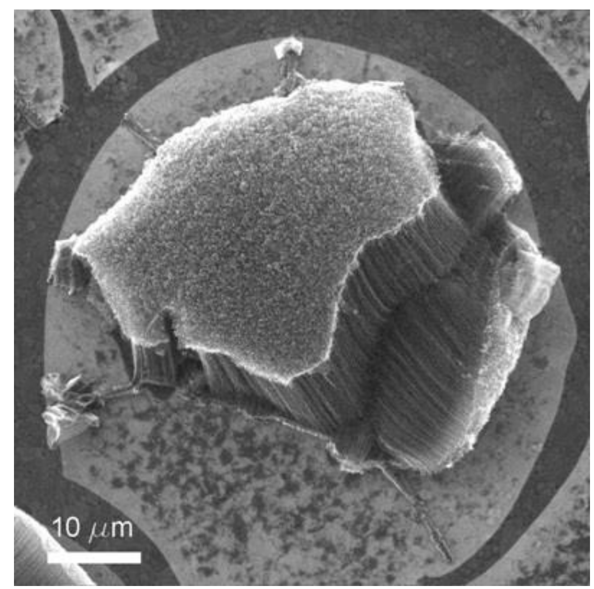
Zhong, G.; Warner, J. H.; Fouquet, M.; Robertson, A. W.; Chen, B.; Robertson, J. ACS Nano 2012, 6, 2893–2903

Zoican Loebick, C.; Podila, R.; Reppert, J.; Chudow, J.; Ren, F.; Haller, G. L.; Rao, A. M.;Pfefferle, L. D. Journal of the American Chemical Society 2010

Characterize the Membrane

- Determine integrity of membrane (check for micro fractures and voids with SEM)
- Confirm average pore diameters and pore densities (TEM and Raman)
- Determine bulk modulus of the membrane and high pressure performance
- Determine flux values of water and ion rejection under various operating pressures and osmotic gradients





http://www.extremetech.com/wp-content/uploads/2012/11/1130_NANOTUBE-5-WEB-640x640.jpg

RO Activity Characterization

For each average tube size: 0.76, 0.86, 0.93, and 1.2 nm study RO induced flux using NaCl

M_{NaCl} (mol/L)	Osmotic Pressure, π (atm)	Operating Pressure (atm)
0.1	4.8	10.0
0.2	9.8	20.0
0.3	14.7	30.0
0.4	19.6	40.0
0.5	24.5	50.0
0.6	29.3	60.0
0.7	34.2	70.0
0.8	39.1	80.0
0.9	44.0	90.0
1.0	48.9	100.0

T= 298 K

Additional Studies

- Characterize and compare the RO activity across different average pore size at constant osmotic pressure and operating pressure for both
  - Unfunctionalized CNT tips
  - Functionalized CNT tips
- Characterize the effects of pore density on activity at constant pore size, osmotic pressure, and operating pressure
- Single pore membrane studies for a range of CNT diameters
- Test ion rejection for other various salts

Intellectual Merit

- Can investigate the effects of pore density and diameter on the flux of water and ion rejection
- Can further investigate the effects of nanotube diameter and tip functionalization on flux of water and ion rejection
- Can compare experimental results to theoretical predictions
- Can gain greater insight into the underlying fundamental processes of water and ion conductance through the interior of CNTs

Summary

- Salt water is a largely untapped resource for the generation of drinkable water
- More efficient RO membranes could have a large impact on the desalination industry; potentially lowering costs and raising output
- CNTs show remarkable mass transport properties; including high water transport rates
- SWCNTs could serve as the pores in highly efficient composite RO membranes
- A multi-pronged set of methods has been devised that will allow thorough investigation of pore size, pore density, and tip functionality on the efficiency of CNT RO membranes; and could lead to RO membranes with greater efficiency than current technology

Thank You.

Questions?

Additional/ Supplemental Slides

Method Analysis: Pros and Cons

Approach 1

Pros:

- Can achieve high selectivity (high ion rejection)

Cons:

- Lower pore density and diameters limits flow rates

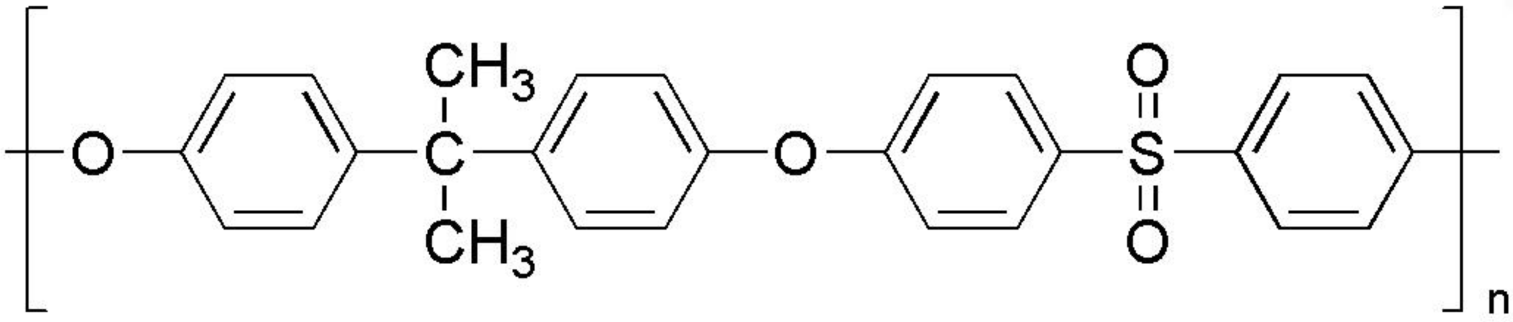
Approach 2

Pros:

- Large pore density and larger pore diameter will lead to significant gains in flow rates

Cons:

- Larger average pore diameter may lead to lack in selectivity (lower ion rejection)

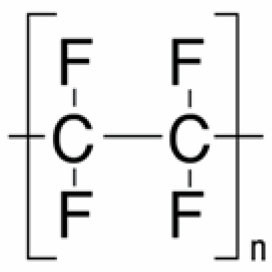


PSF unit structure

- High wettability with CNTs
- Resistant to:
  - Mineral acids
  - alkali
  - Electrolytes
  - Surfactants
  - Hydrocarbon oils
- High compaction resistance (can withstand high pressure)
- Stable over large pH range (2-13)
- Stable in aqueous acids and bases

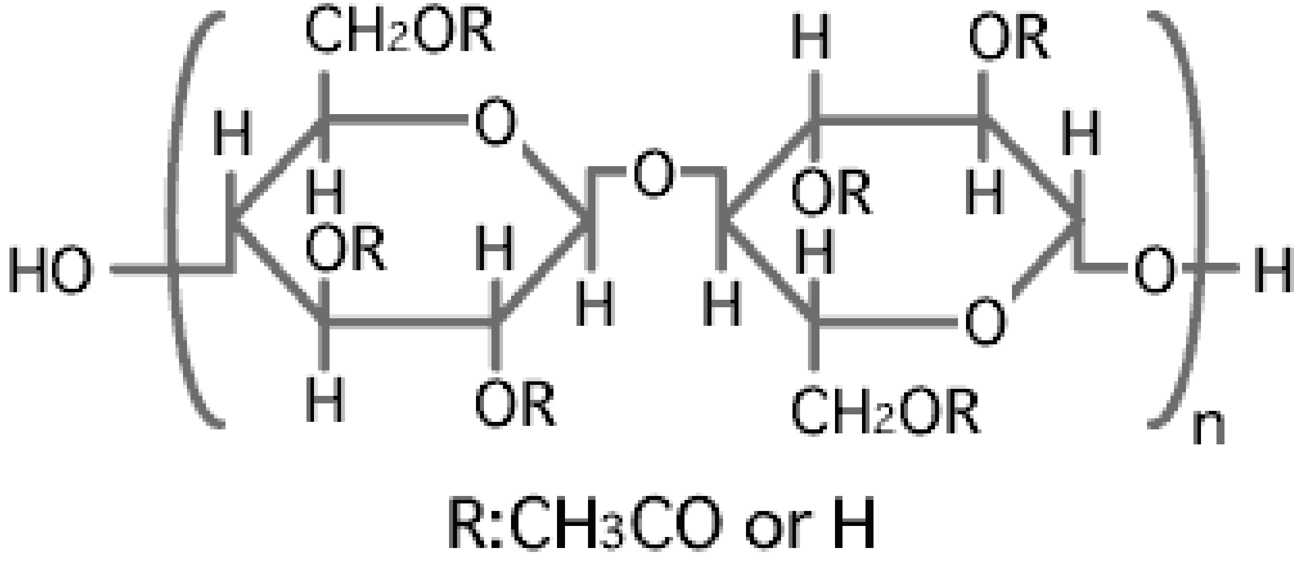
Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E. Nano Letters 2007, 7, 2806–2811

http://en.wikipedia.org/wiki/File:Polysulfone_repeating_unit.png



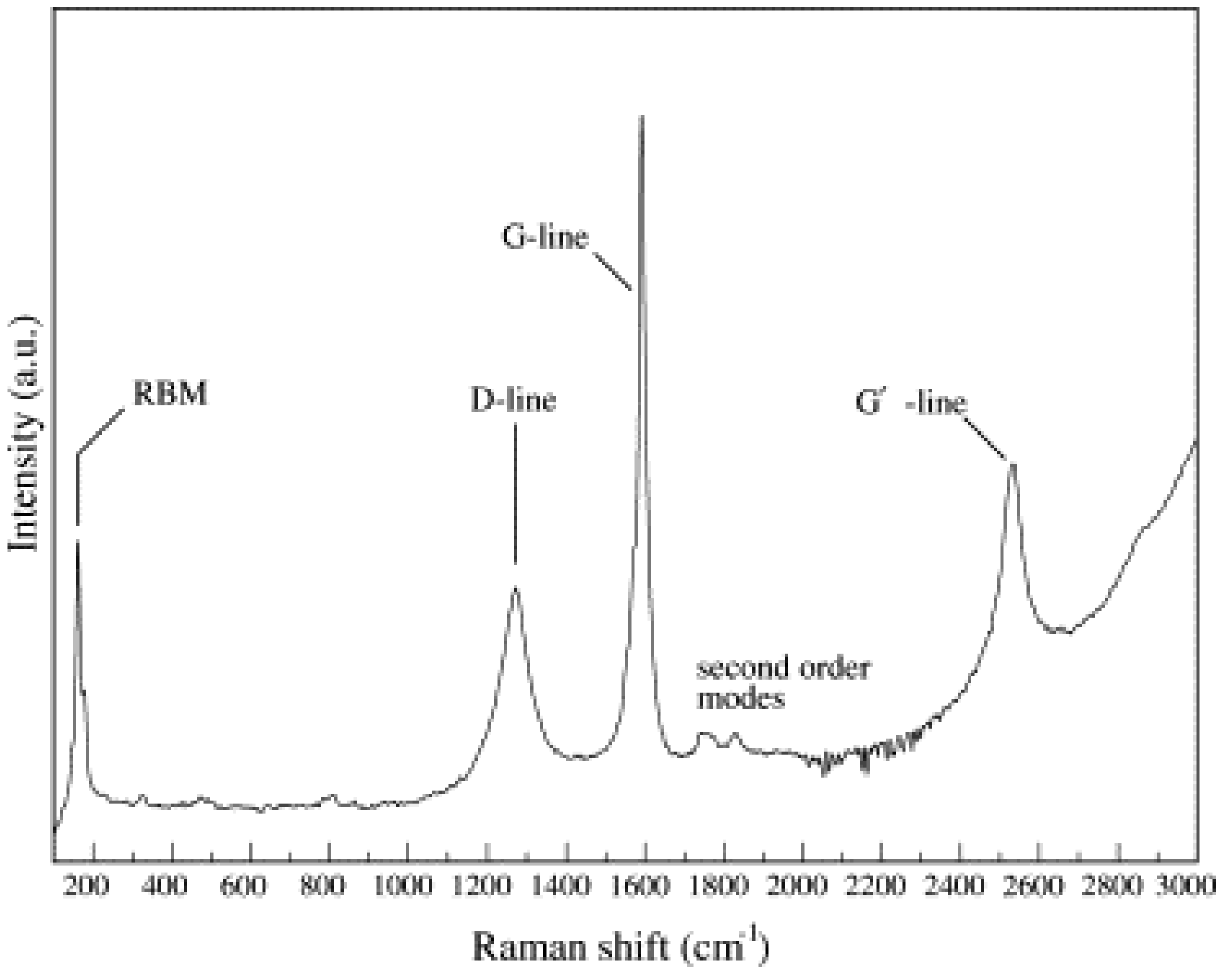
Polytetrafluoroethylene (PTFE)

Pore size ~ 0.2 micron



General Structure for Cellulose Acetate (CA)

http://www.daicel.com/cell_ac/en/common/img/img_what01.gif

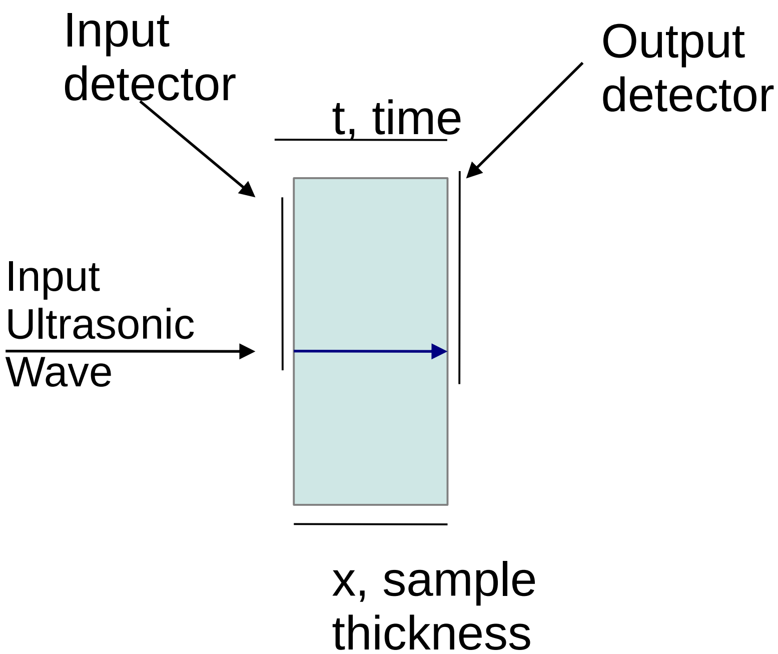


$$\omega_{RBM} = A/d + B$$

Raman spectrum showing the most characteristic features of CNTs: radial breathing mode (RBM), the D band, G band and G′ band. Second order modes are also observed. Spectrum obtained from SWNTs sample (diameter of about 1.07 nm) mixed with KBr using a Elaser=1.16 eV (λ=1064.5 nm) excitation. This sample is produced by electric arc-discharge method followed by air oxidation at CSIC laboratory.

Epron, T. Mat. Sci. And Eng.:B 2005, 119, 105-118

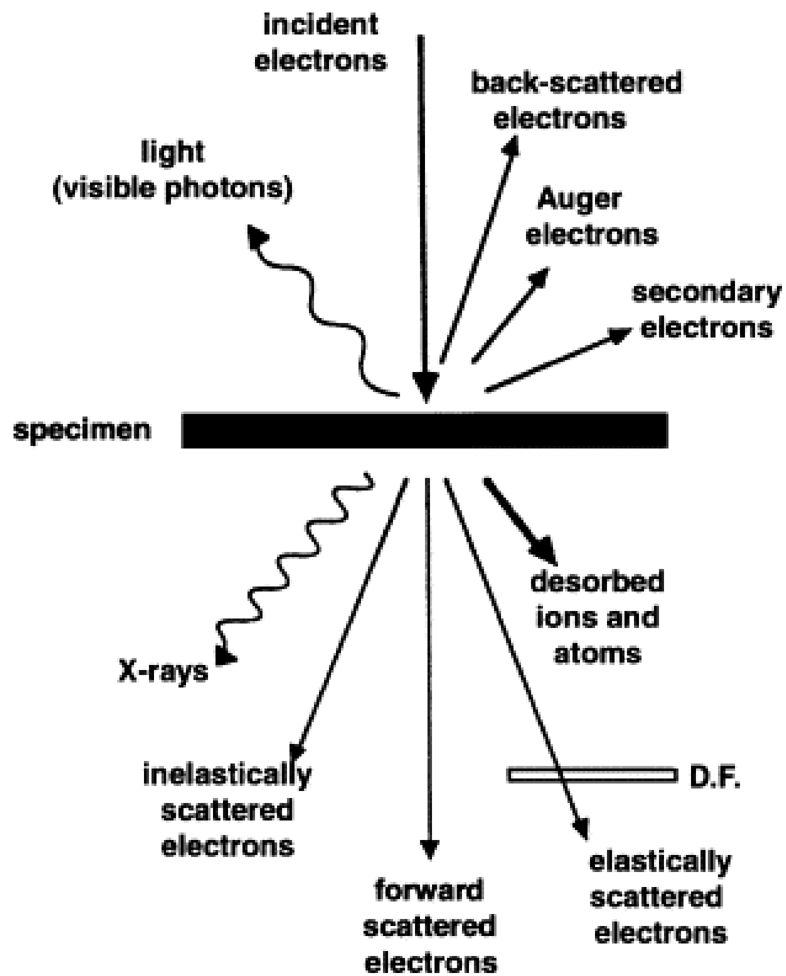
Ultrasonic Measurement of Bulk Modulus



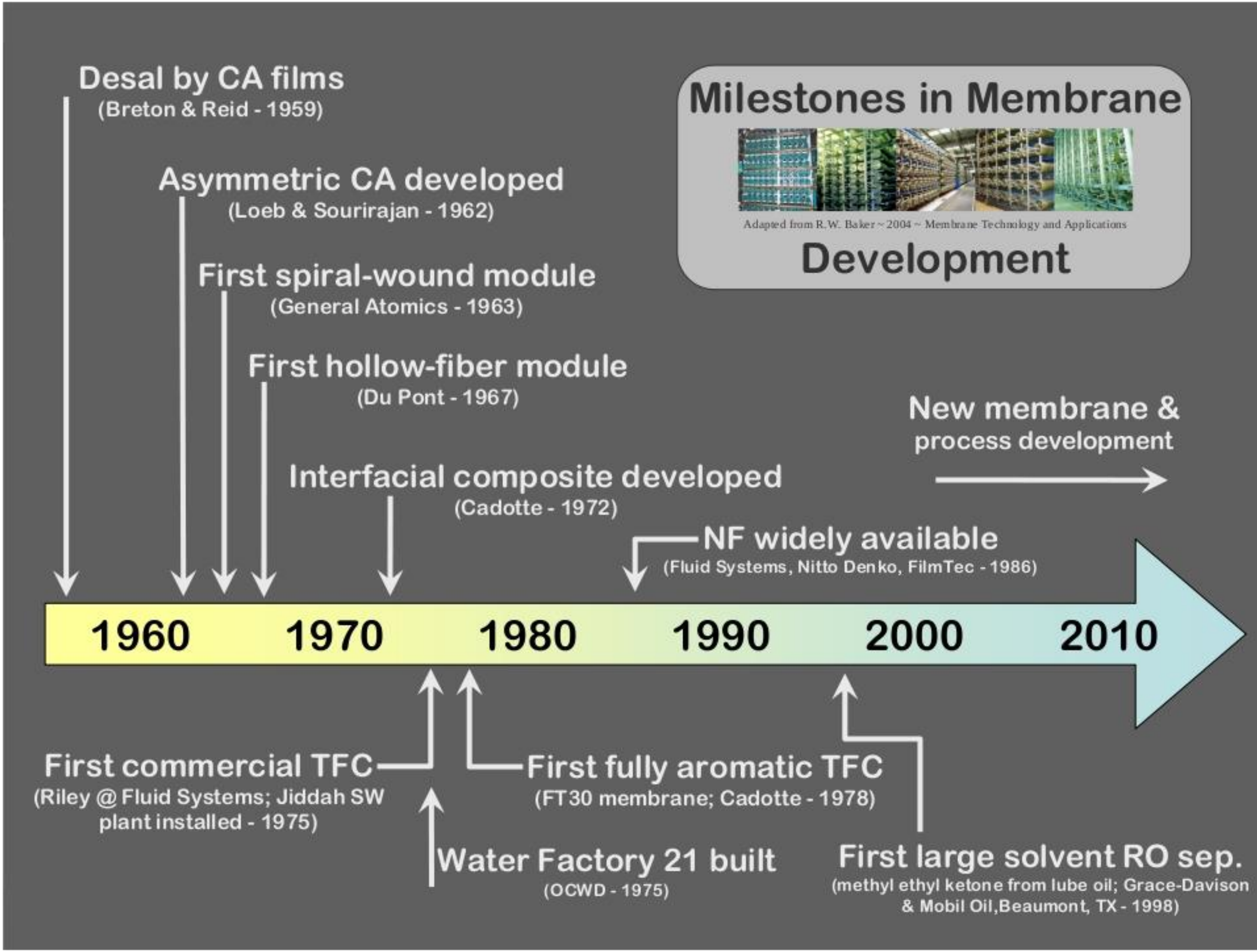
$v = x/t$, v is utrasonic wave velocity

$B = \rho v^2$, B is the bulk modulus and ρ is the sample density

Kadem, B. European Journal of Scientific Research 2012, 72, 414-422

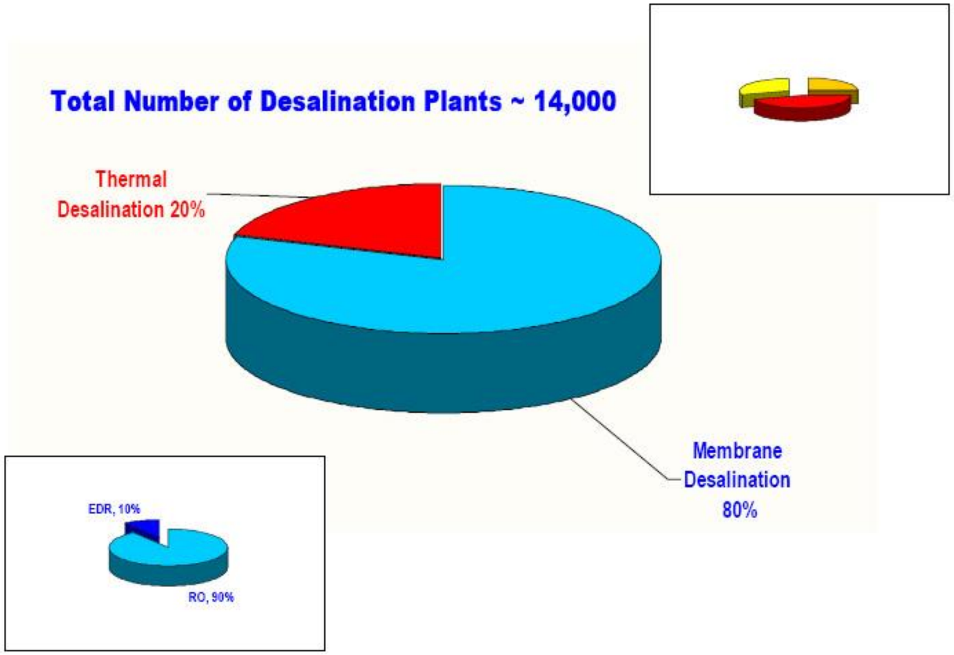


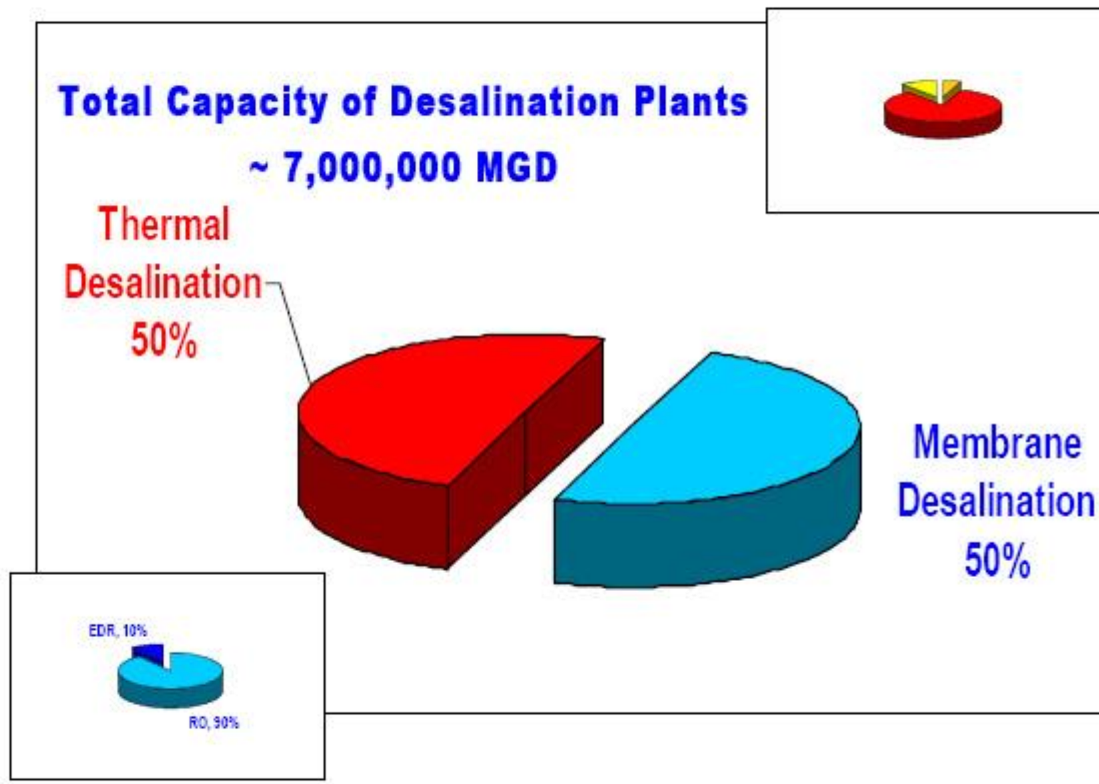
http://ars.els-cdn.com/content/image/1-s2.0-S036005640448002X-gr1.gif



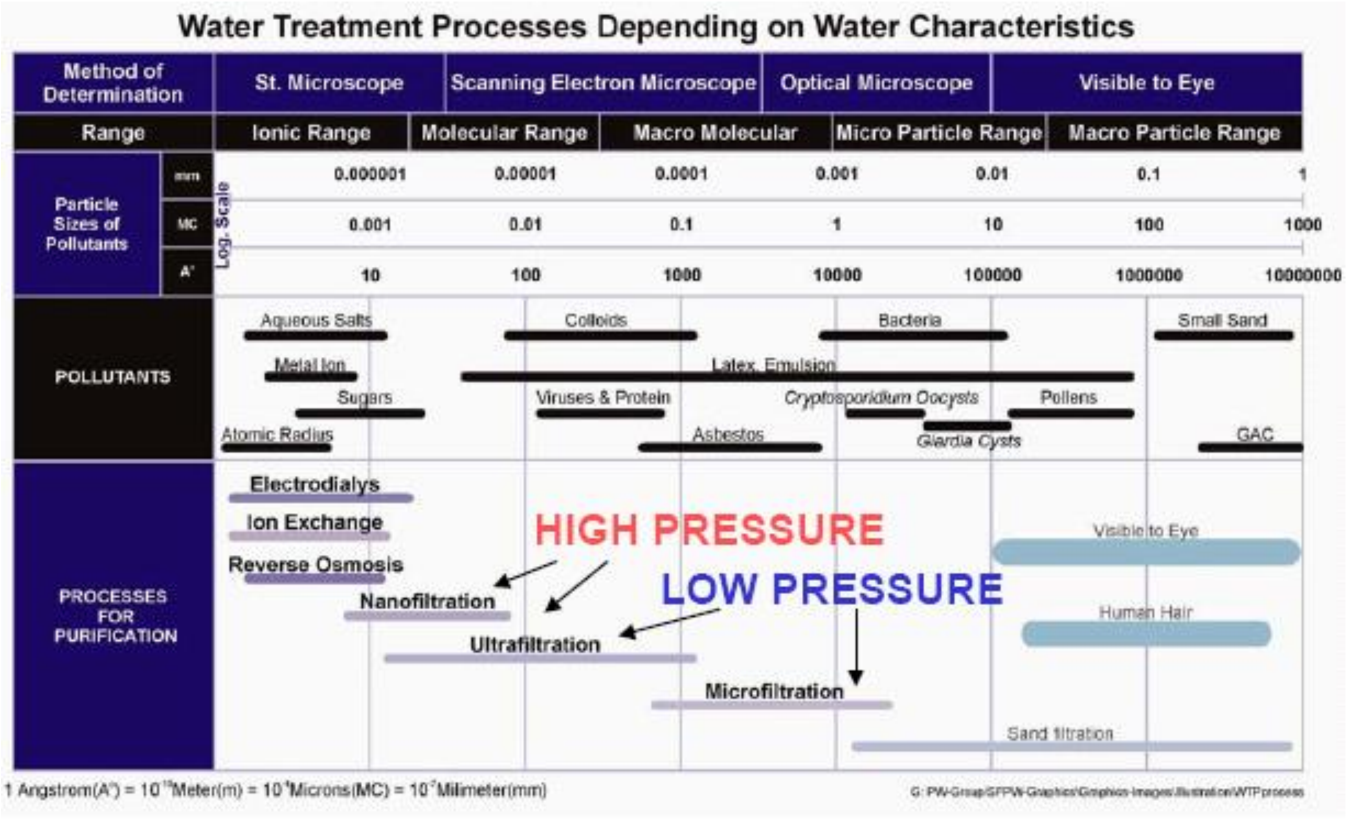
Ridgway, H. Advanced Membrane Technologies 2008

Commercial Desalination



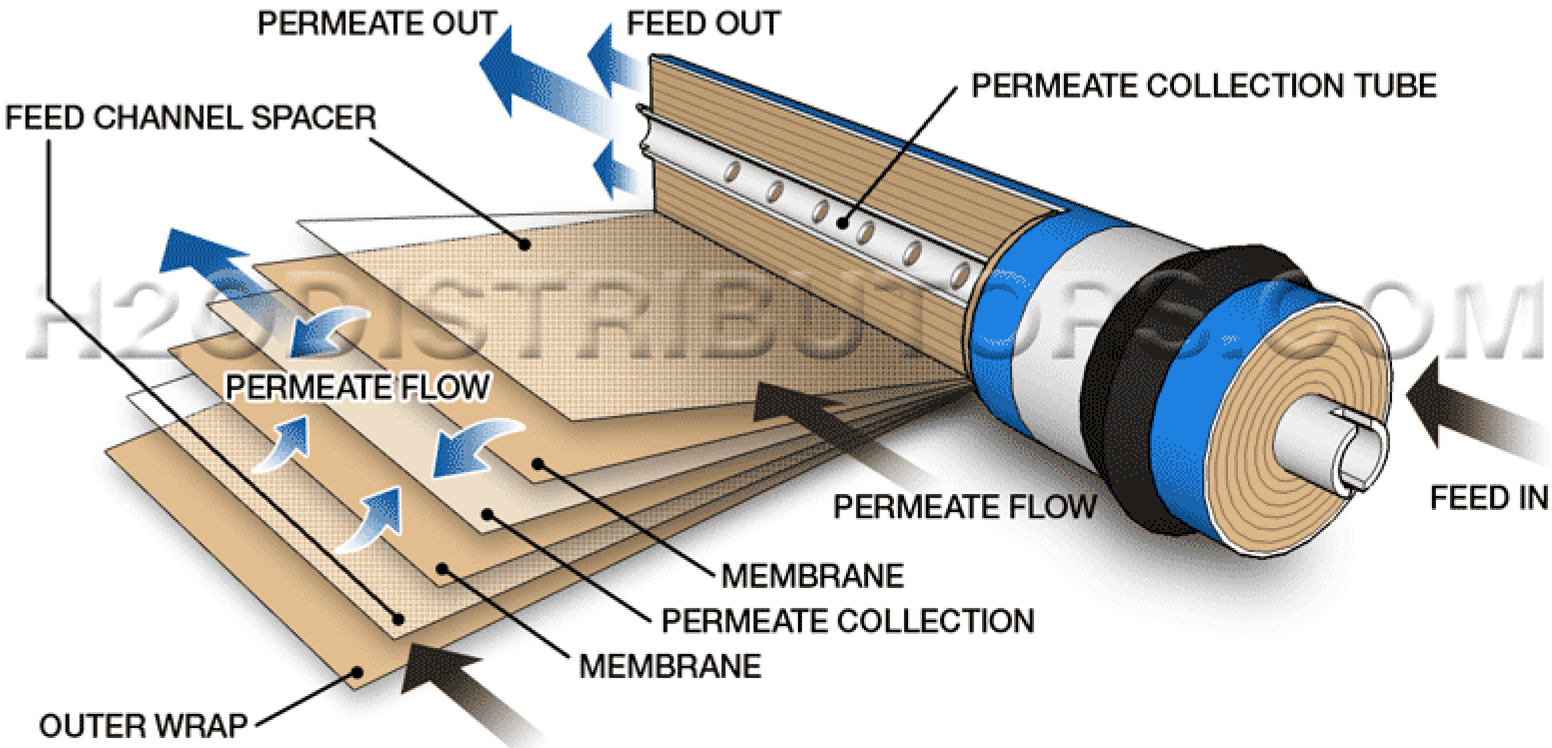


http://www.idswater.com/common/paper/paper_90/desalination%20methods,%20technology,%20and%20economics1.htm

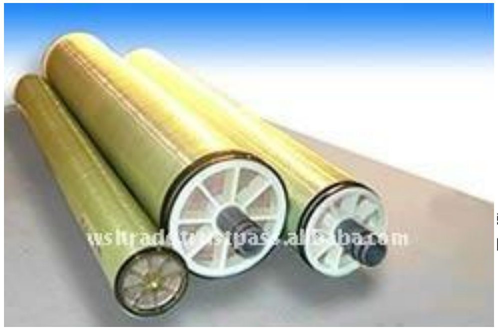


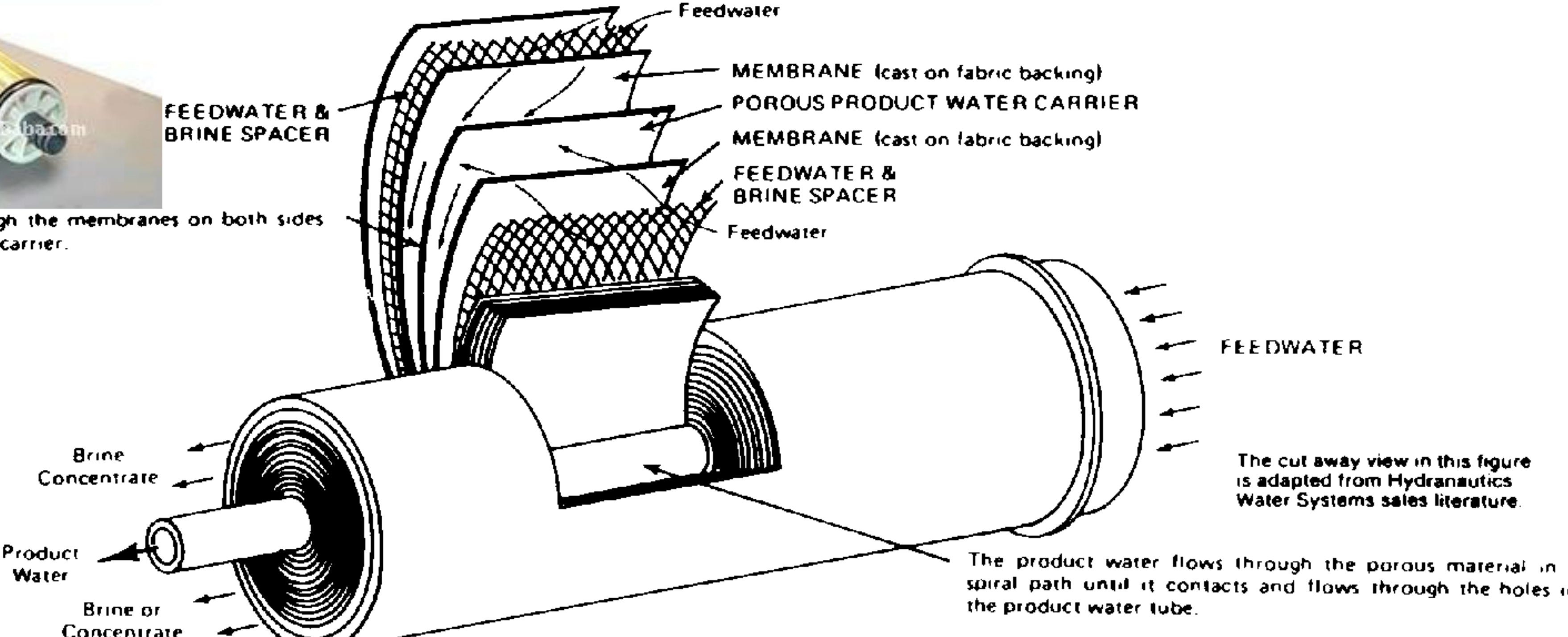
http://www.idswater.com/common/paper/paper_90/desalination%20methods,%20technology,%20and%20economics1.htm

Typical spiral wound RO membrane setup

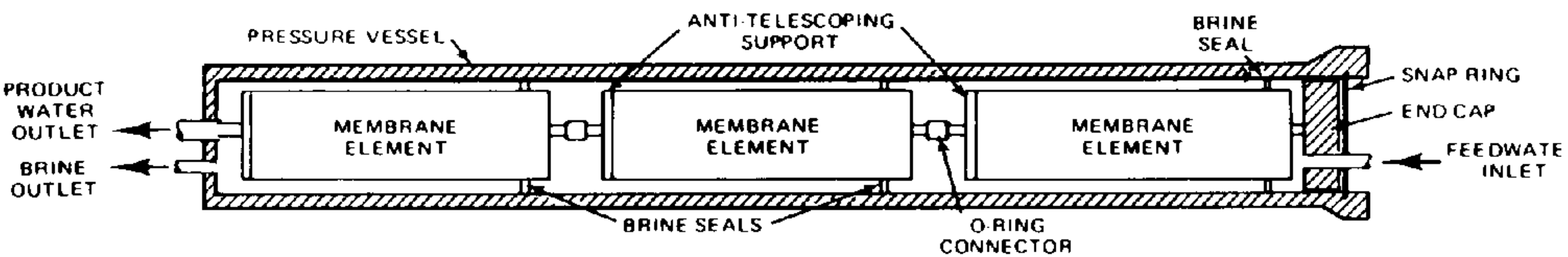


http://www.h2odistributors.com/global/productpics/misc/diagram_ro-membrane-cutout_l.gif



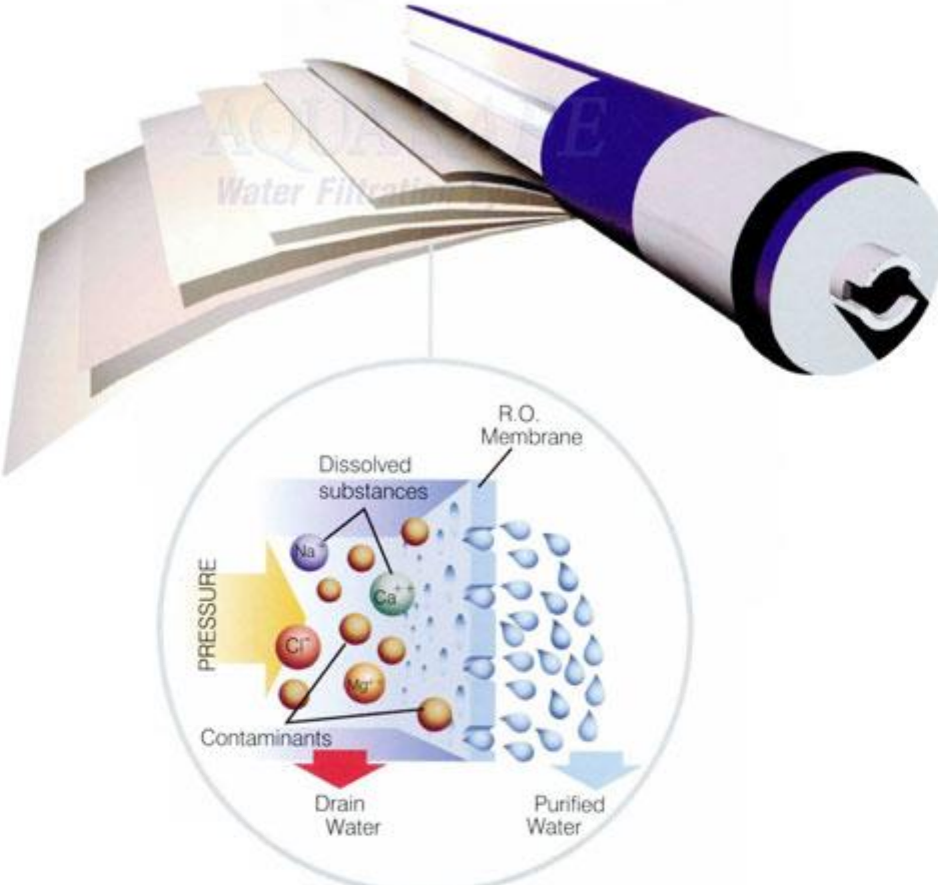


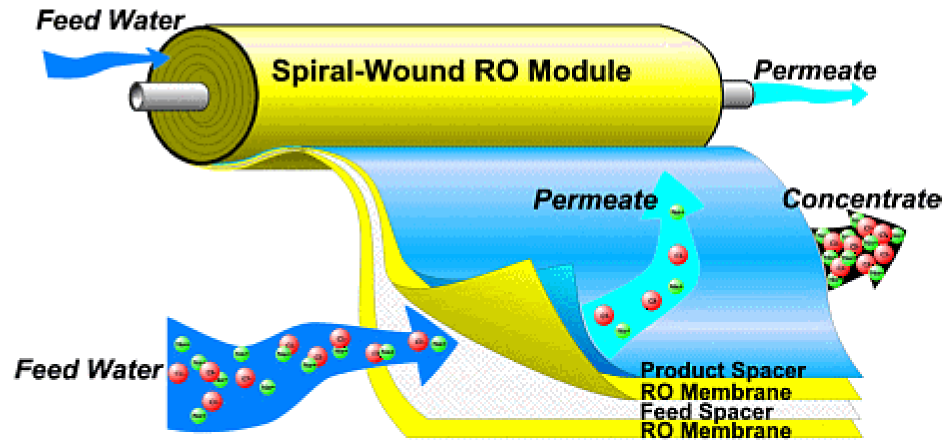
CUTAWAY VIEW OF A SPIRAL MEMBRANE ELEMENT



CROSS SECTION OF PRESSURE VESSEL WITH 3 MEMBRANE ELEMENT

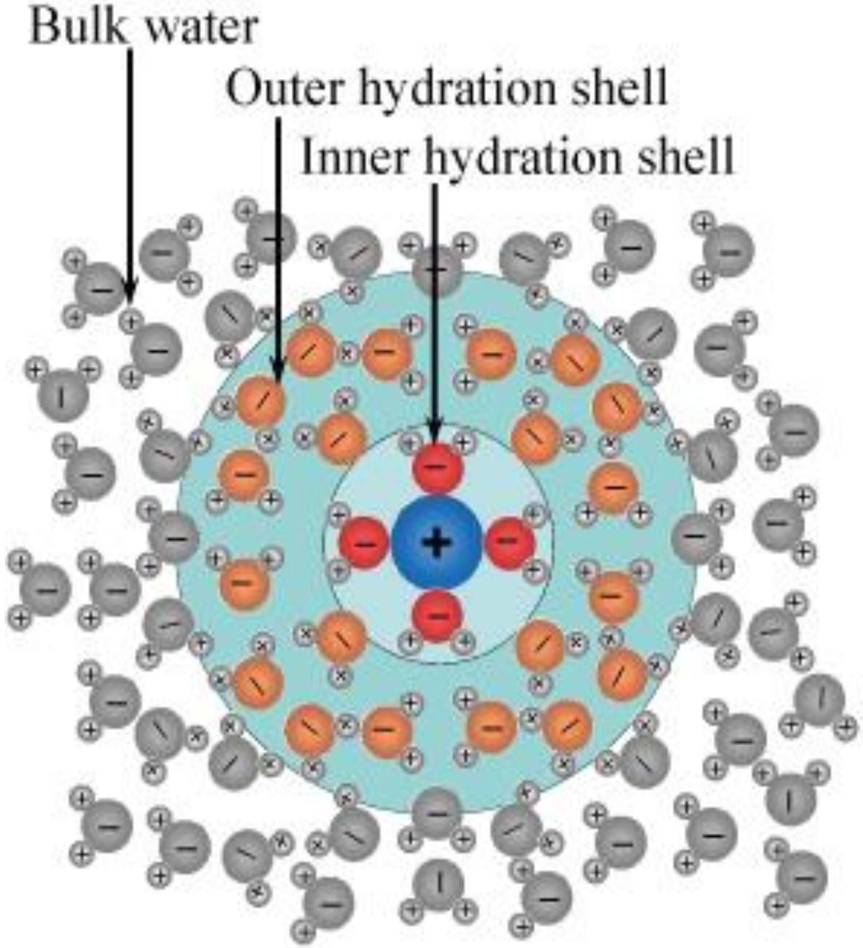
http://www.nzdl.org/gsdl/collect/hdl/index/assoc/HASH01b9/4e80bbba.dir/80858e2o.gif
http://i00.i.aliimg.com/photo/v0/122652432/Sea_Water_RO_Membrane.jpg





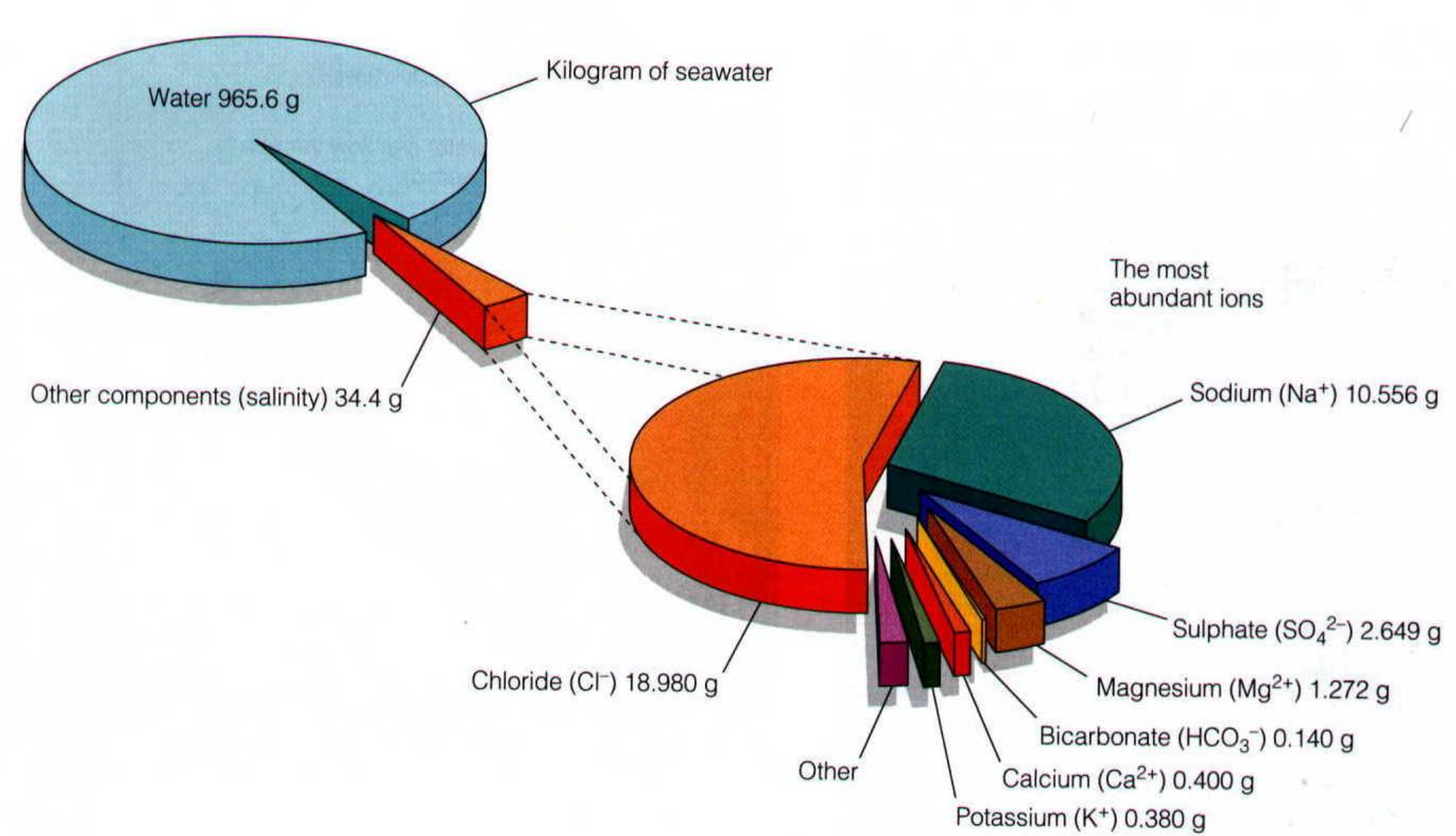
http://sswaterlifetechnology.com/images/url.gif
http://www.aquasafe.com.au/skin/frontend/default/aquasafe/images/website-images/RO-Process.jpg

Hydration



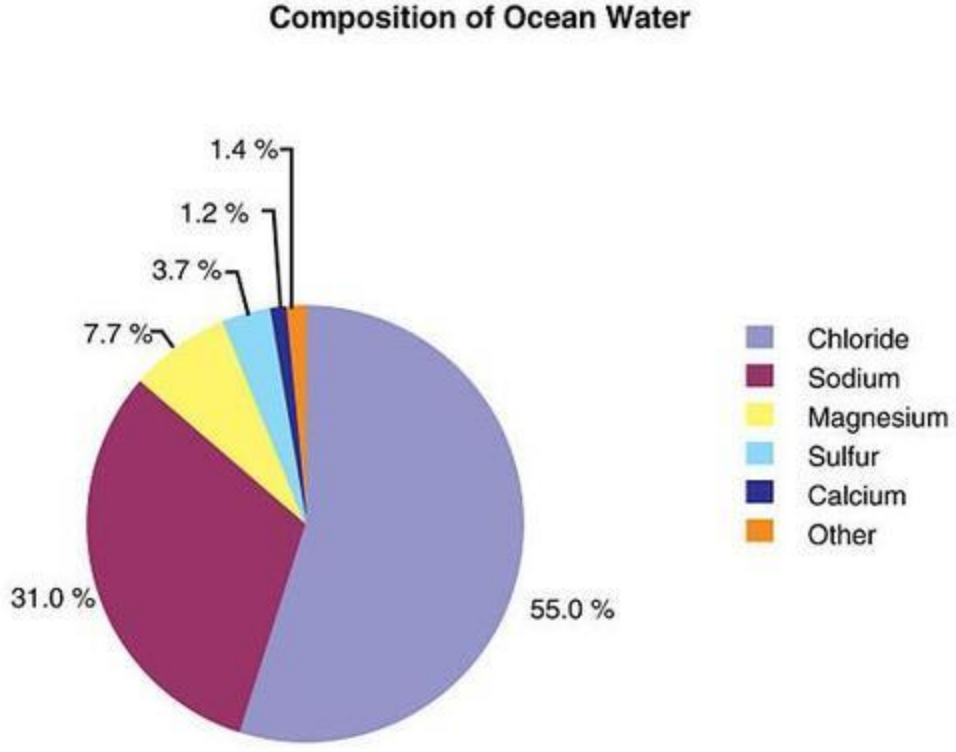
http://www.itst.ucsb.edu/~vinhnguyen/Salt_solutions/Hydration-shell-IONS.png

Seawater composition



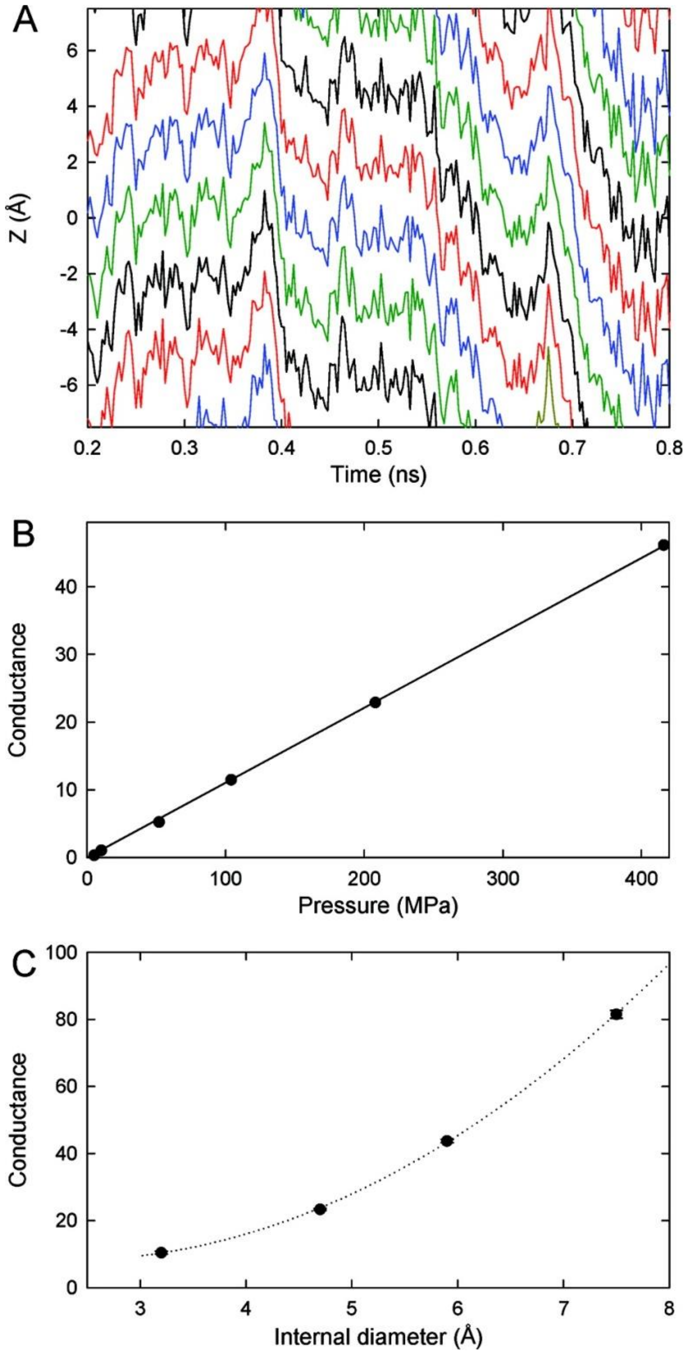
http://earth.usc.edu/classes/geol150/stott/variability/images/oceandeep/salt.jpg

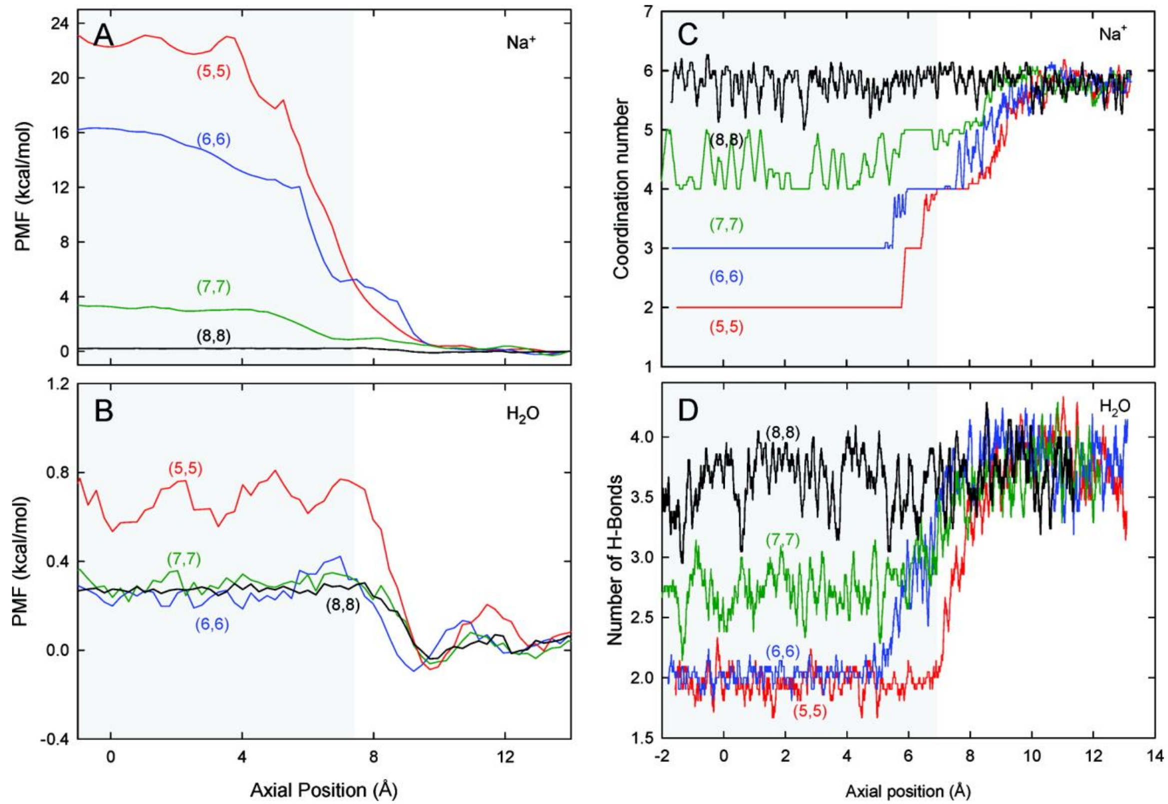
Ocean (Sea water) composition



http://dr282zn36sxxg.cloudfront.net/datastreams/f-d3Aab061723f4ee0ef2d4bba86ec1bfad110f08dc999e29cfe9c2997ef3%2BIMAGE_THUMB_POSTCARD%2BIMAGE_THUMB_POSTCARD.1

Extra Data – Corry





Potential of mean force and coordination numbers for ion and water permeation into a CNT membrane. The PMF is shown for pulling an ion (A) and water (B) into each of the (5,5), (6,6), (7,7), and (8,8) nanotubes. The ion or water is moved from the bulk solution (z = 14) into the center of the pore (z = 0) in each case. The coordination number of Na+ (C) and the number of hydrogen bonds formed with the water molecule (D) are indicated. The location of the nanotube is indicated by the gray background.

Water conductance through nanotubes. (A) Motions of the individual water molecules are plotted over a short section of the molecular dynamics simulation conducted with a hydrostatic pressure difference of 208 MPa across the (6,6) nanotube membrane. The conductance of the membrane (in water molecules per tube per ns) is plotted against (B) th applied hydrostatic pressure and (C) the internal diameter of the nanotube

Corry, B. The Journal of Physical Chemistry B 2008, 112, 1427–1434; PMID: 18163610