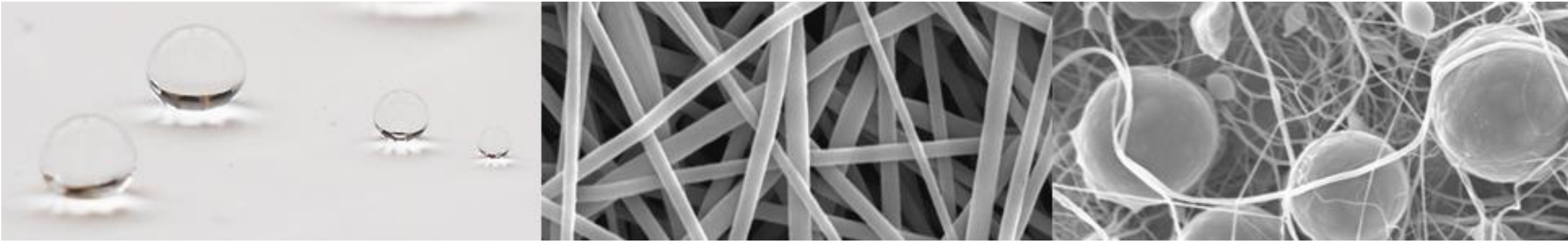

ERC TeleSeminar

Electrospun Fiber Membranes for Membrane Desalination

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Sep. 18, 2014

MIT & MI MIT and Masdar Institute Cooperative Program

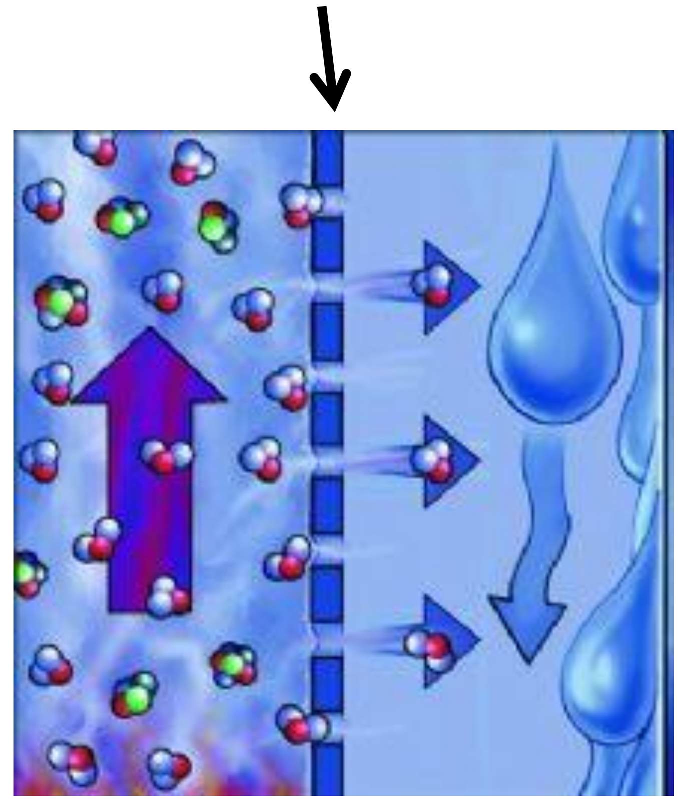
Massachusetts Institute of Technology

https://fguo.mit.edu/

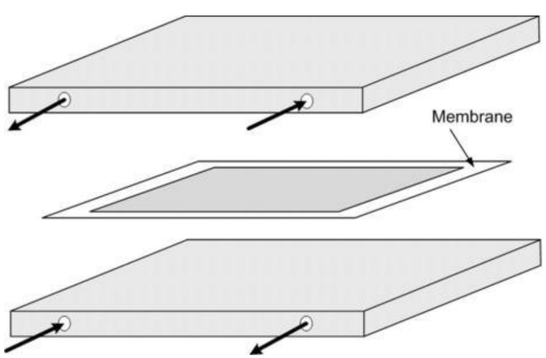
Membrane Distillation (MD)

- Lower operating temperatures than conventional distillation processes
- Low energy consumption (i.e., solar thermal energy or waste heat)
- Low operating pressure
- Simple membrane construction

Membrane barrier

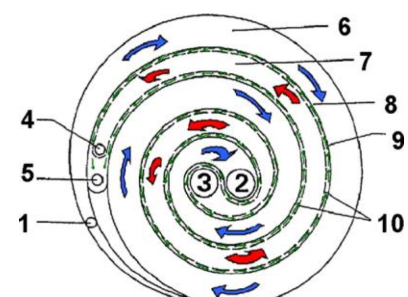


Flat module



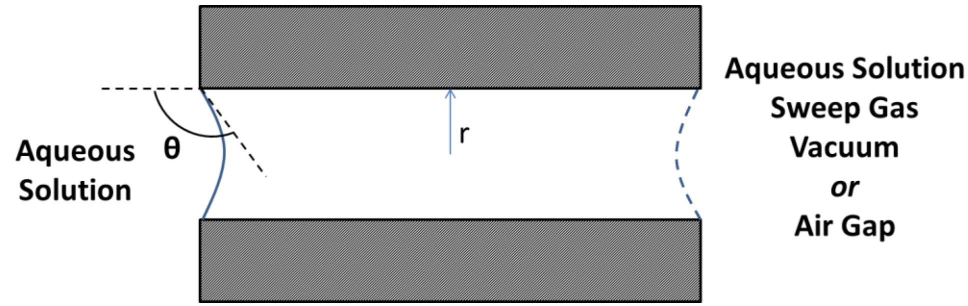
Pipe module

Spiral module



Membrane Distillation (MD)

Driving force: Vapor pressure difference across the membrane



Vapor-liquid interface in MD

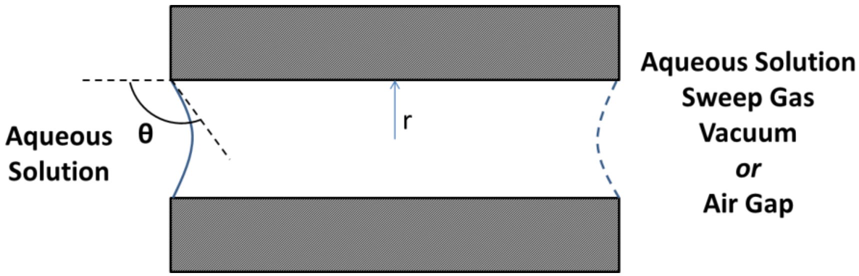
MD process should have the following characteristics:

- The membrane should be porous;
- The membrane should not be wetted by process liquids;
- Only vapor should be transported through the pores of the membrane;
- No capillary condensation should take place inside the pores of the membranes;

[Smolders, et al., *Desalination* **1989]**

MD Configurations

- Direct Contact Membrane Distillation (DCMD)

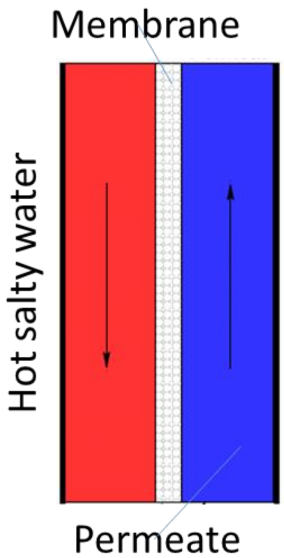


- Air Gap Membrane Distillation (AGMD)

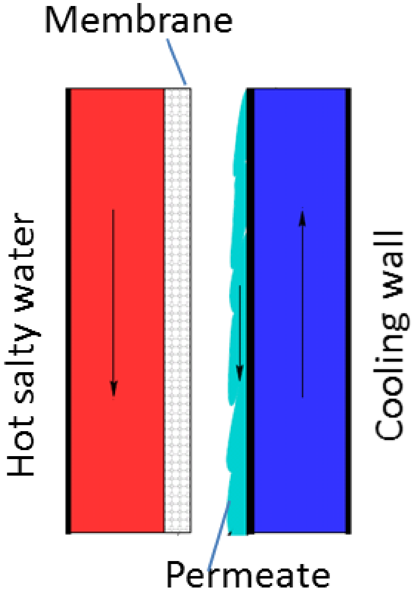
  -Vacuum Membrane Distillation (VMD)

  -Sweep Gas Membrane Distillation (SGMD)

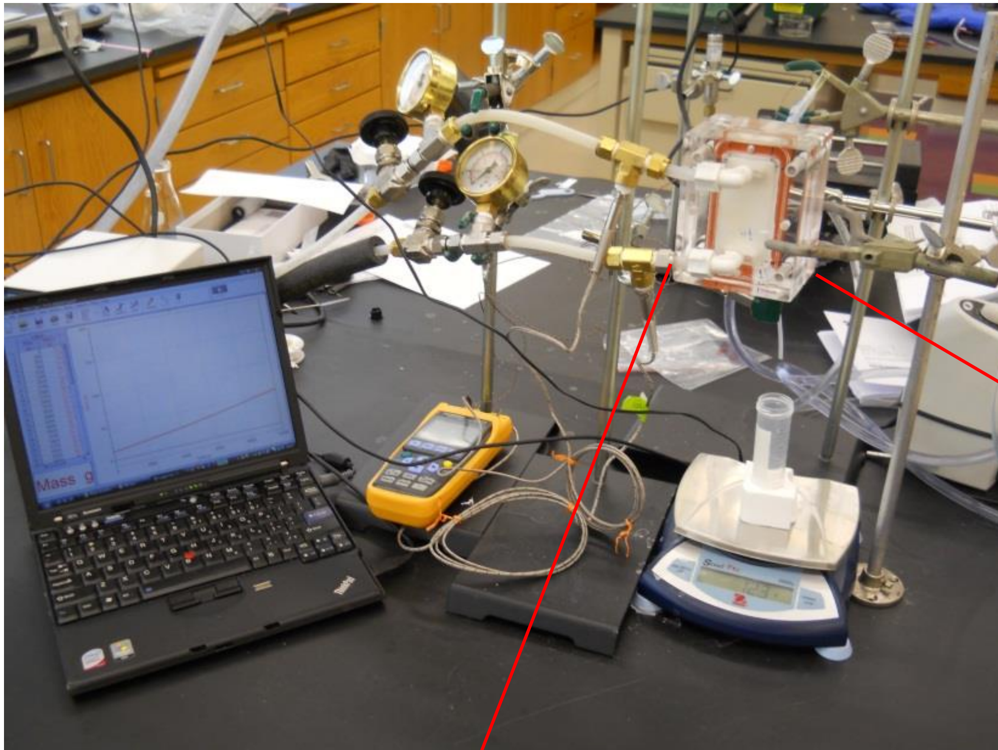
DCMD



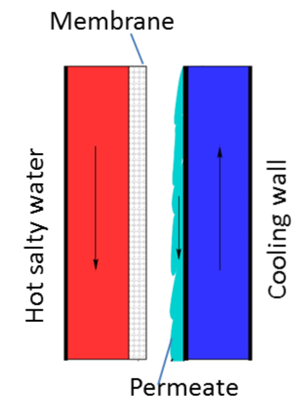
AGMD

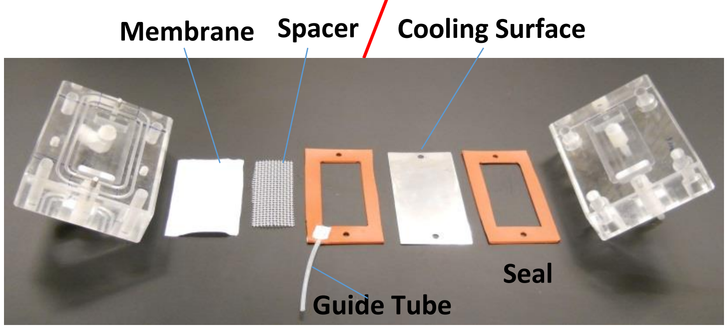


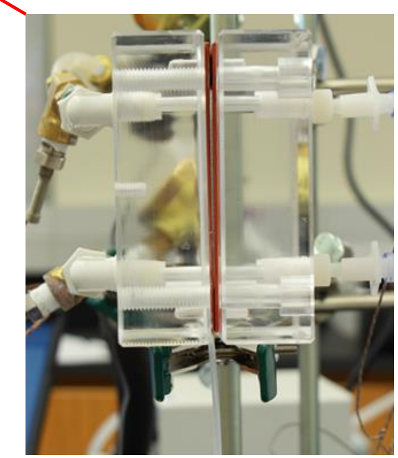
Membrane Distillation



Air Gap Membrane Distillation







Original salty water: ~ 21000 ppm (3.5 wt% NaCl)
DI water: 2-3 ppm
Tap water: ~64 ppm
Drinking water fountain: ~90 ppm

$$salt\ rejection\ rate = 1 - \frac{[Cl^-]_{perm}}{[Cl^-]_{feed}}$$

Membrane

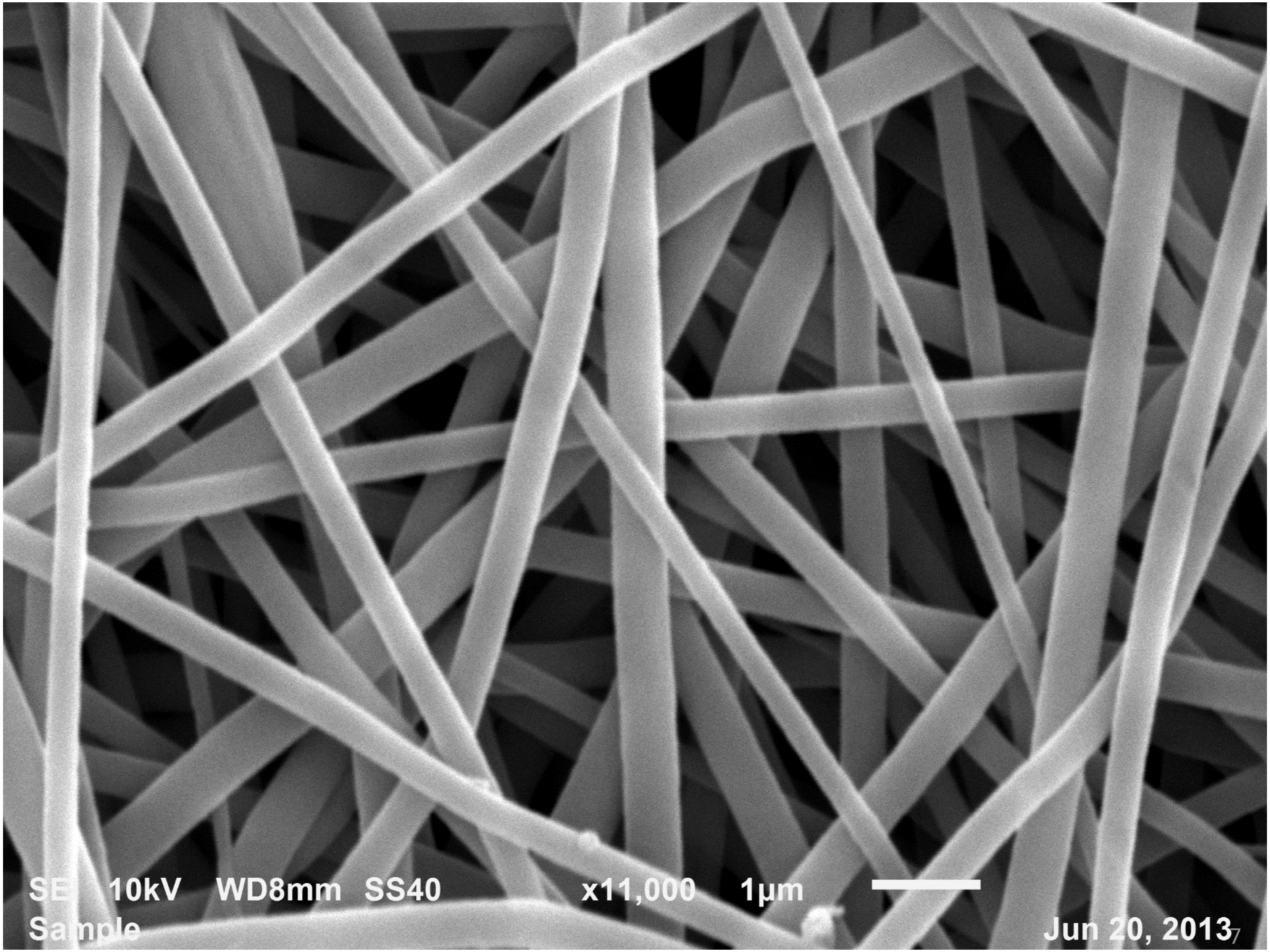
- *Hydrophobicity*
- *Porosity*
- *Pore size*

Membrane Distillation

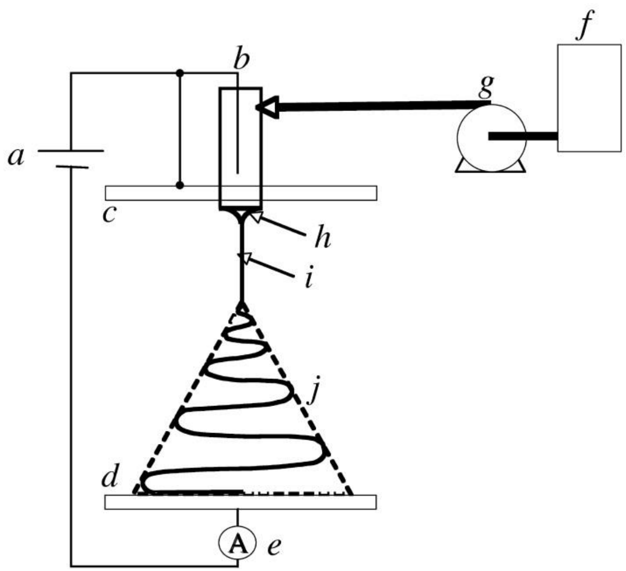
- *Permeate flux*
- *Salt rejection*
- *Stability*
- *Fouling*

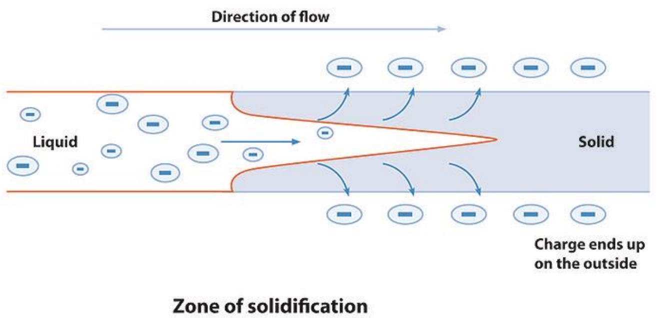
<u>Good Membranes</u>

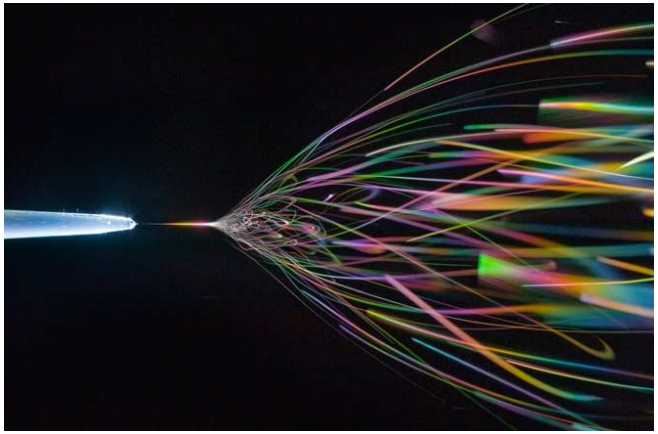
Fibrous membrane

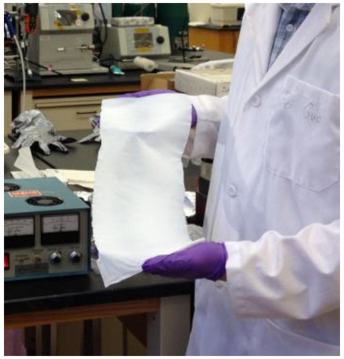


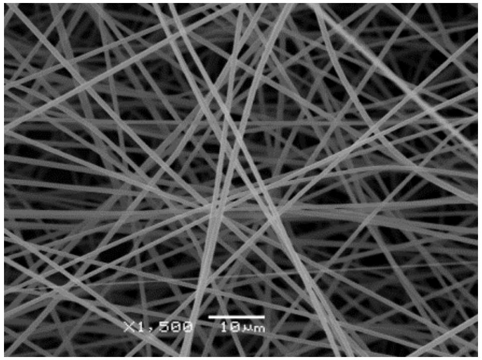
Electrospun Membrane Formation

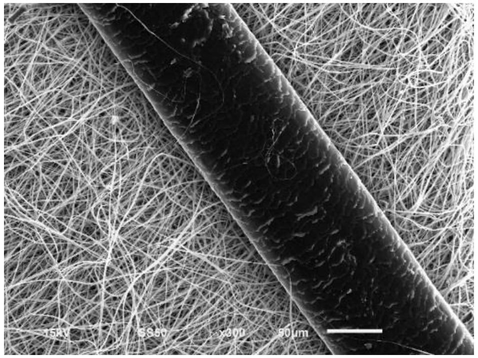








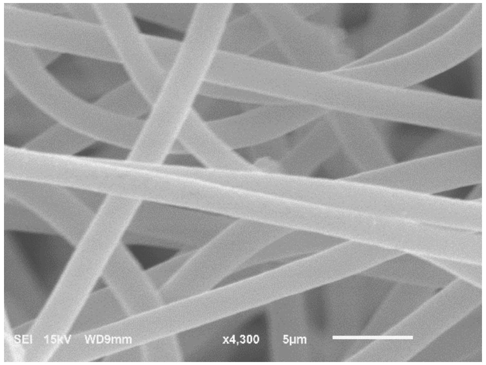




Hydrophobic polymers

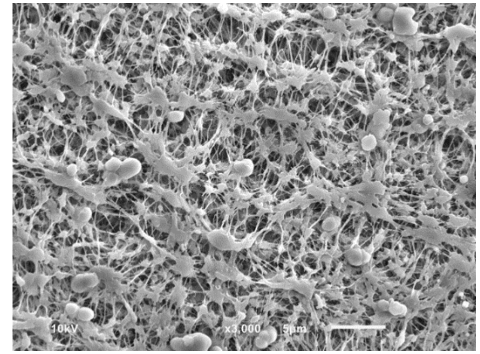
polytetrafluoroethylene (PTFE)
polypropylene (PP)
polyvinylidene fluoride (PVDF) ✓
...

Espun PVDF membranes



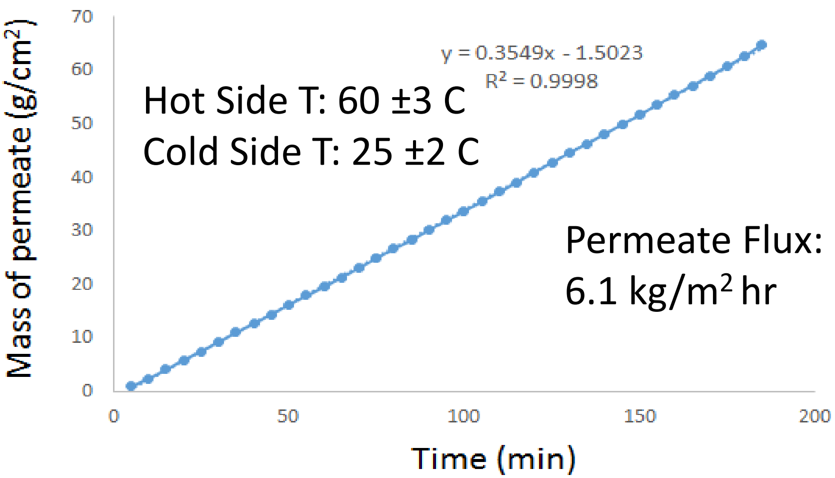
Fiber diameter: ~2 um
Membrane thickness: ~ 70 um
Fiber membrane CA: 105
Dense membrane CA: ~89

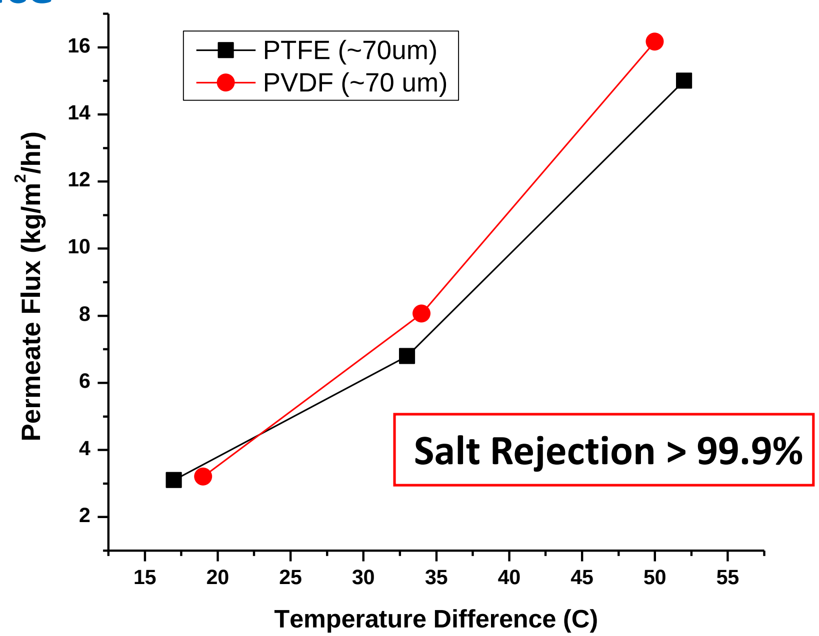
Commercial membrane PTFE (0.45 um)



Thickness: ~ 70 um
Contact Angle : 143

MD Performance

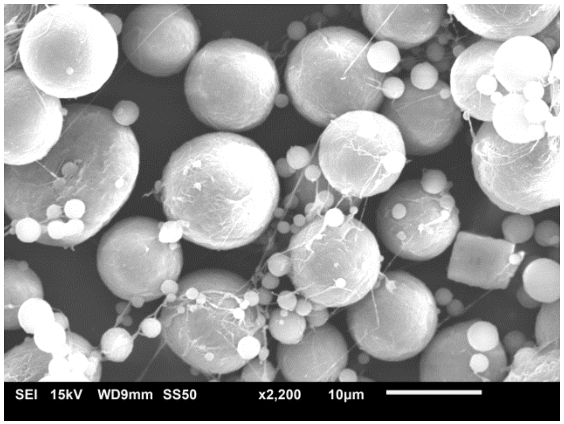




The permeate flux is very stable over time.

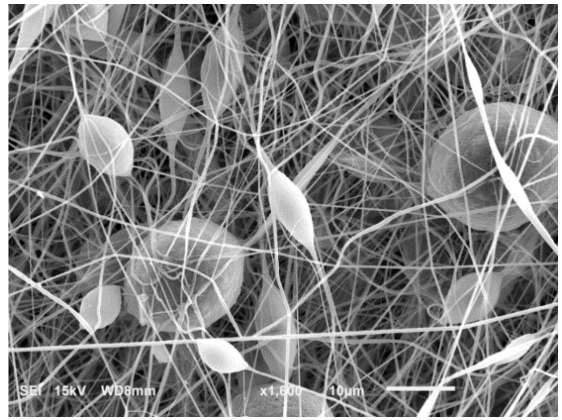
Espun PVDF membranes with various mophologies

Beads



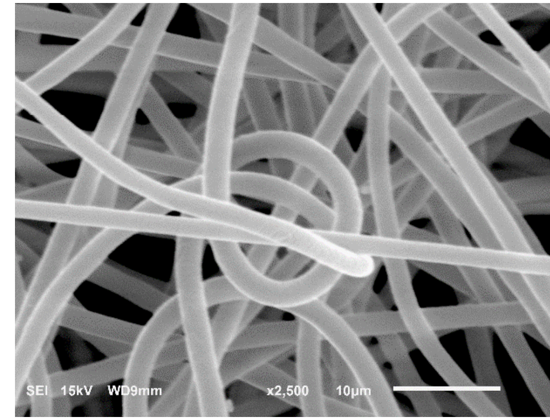
Solef 1010 (Mw 352 k)

Beaded Fibers (CA 141)

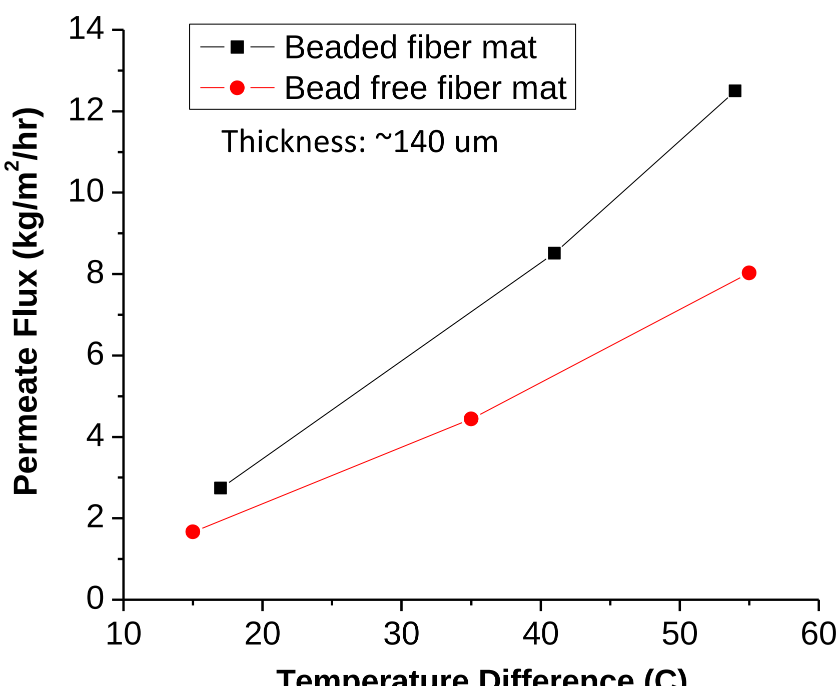


Solef 1012 (Mw 396 k)

Bead Free Fibers (CA 105)



Kynar 761 (Mw 444 k)

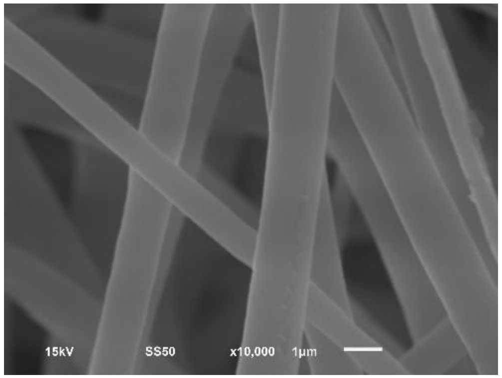


Salt Rejection > 99.9%

PVDF Fiber Membranes

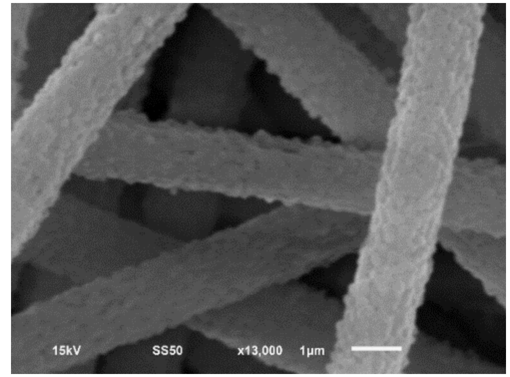
Thickness： 70 um

Smooth fibers



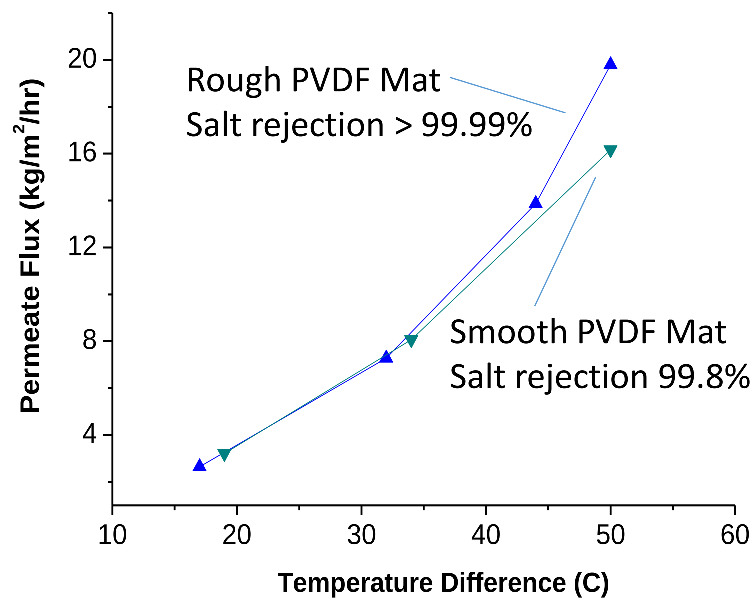
Electrospinning
RH: ~ 23%
CA: 105
Estimated Pore
Size (LEP): 5 um

Rough fibers



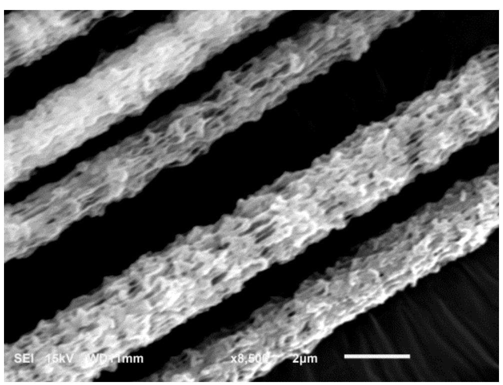
Electrospinning
RH: ~ 70 - 75%
CA: 127
Estimated Pore
Size (LEP): 5.6 um

MD performance

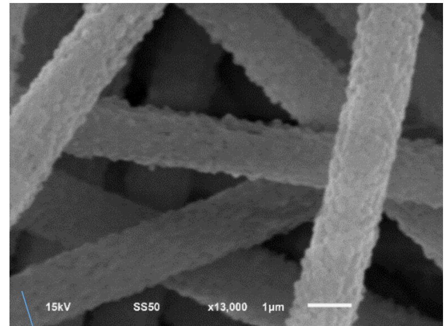


On going work…

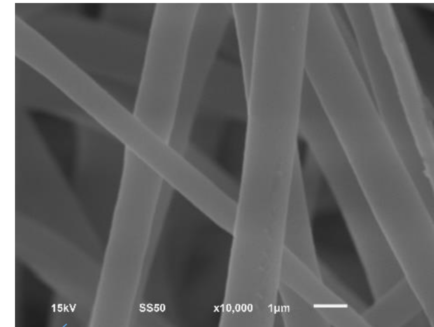
Porous fibers



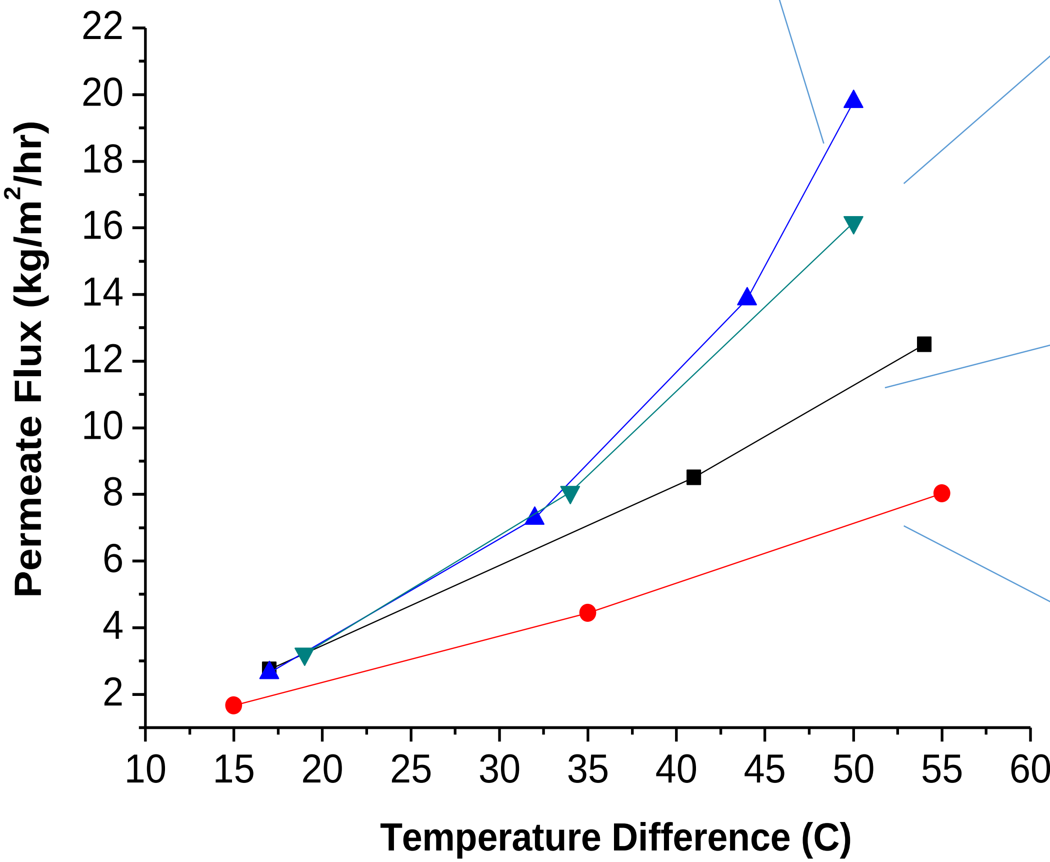
MD performance of PVDF fiber membranes with various morphologies

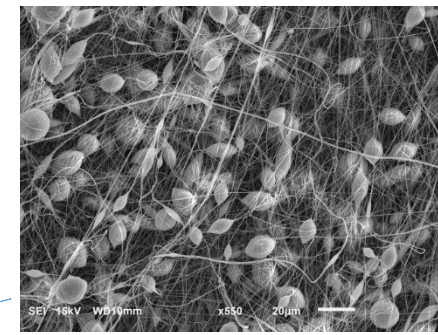


Thickness： 70 um

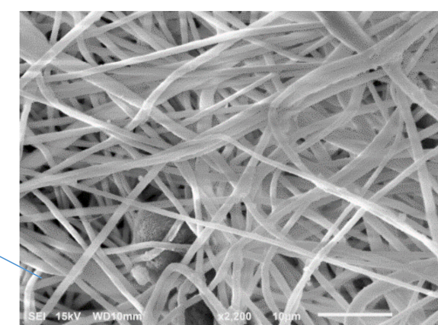


Thickness： 70 um





Solef 1012 (Mw 396 k)
Thickness: 140 um



Kynar 761 (Mw 444 k)
Thickness： 140 um

Fiber diameter vs. MD ?

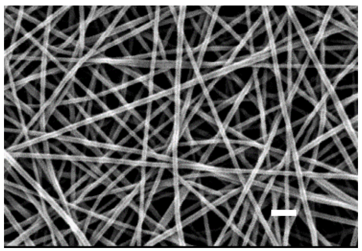
Hydrophilic polymers ?

Electrospun PA6(3)T Fiber Membranes

poly(trimethyl hexamethylene terephthalamide) (PA6(3)T)

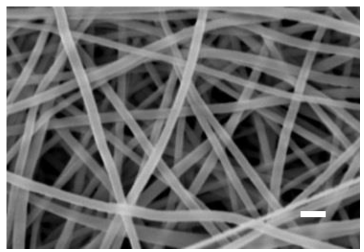
As spun

22 wt%



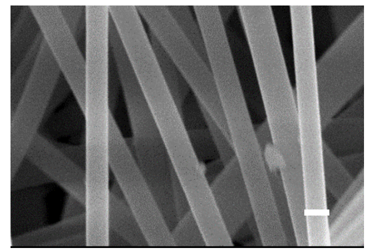
d≈0.17 um

28 wt %



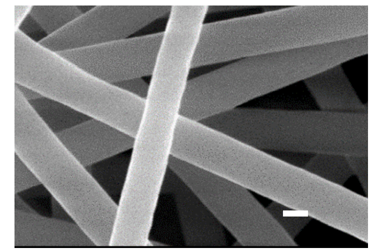
d≈ 0.32 um

30 wt %



d≈ 0.8 um

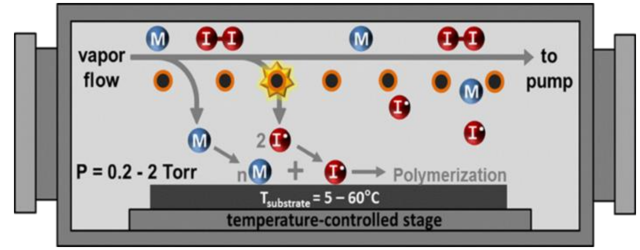
36 wt %



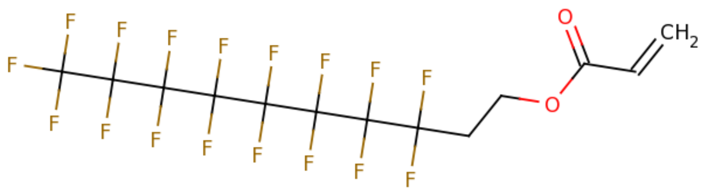
d≈ 1.6 um

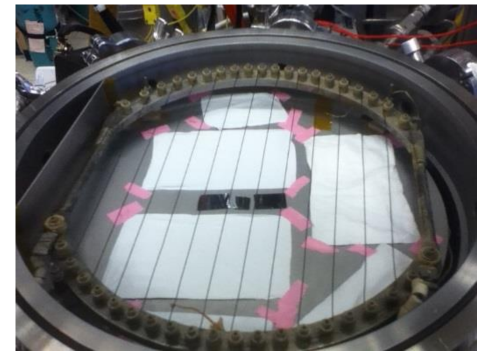
- **Uniform fibers**
- **Controllable wide range of average fiber diameters**
- **Hydrophilic ☹ → water bridging**

Initiated Chemical Vapor Deposition (iCVD) of PFDA Coating



- Monomer: (1H,1H,2H,2H-perfluorodecyl acrylate) (PFDA)
- Initiator: t-butyl peroxide

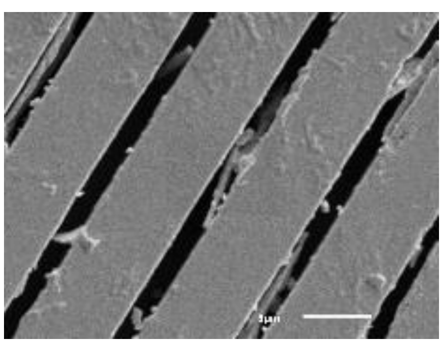


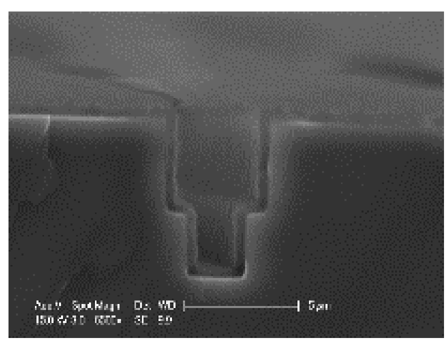


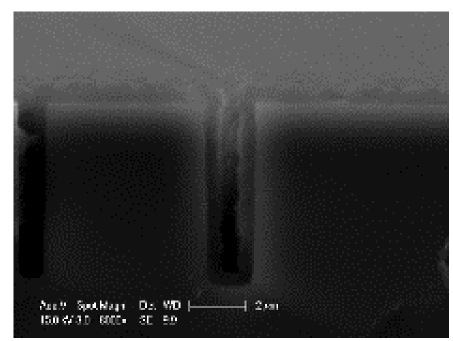
- 3D non-destructive coating
- Fluorinated pendant chains form crystalline structure, giving coating stable hydrophobicity

Amelia Servi
The Gleason Group, MIT

Tunable coating thickness and conformality.

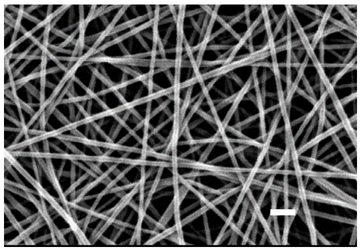




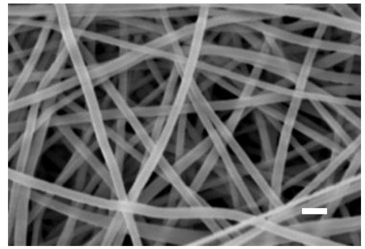


iCVD of PFDA Coating

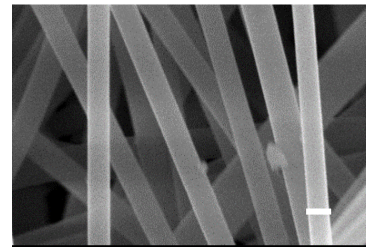
As spun



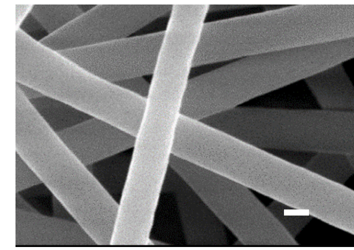
d≈0.17 um



d≈ 0.32 um

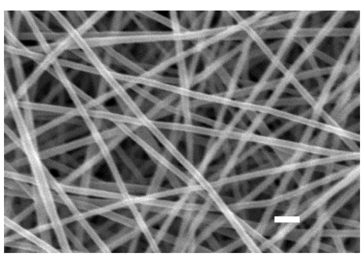


d≈ 0.8 um

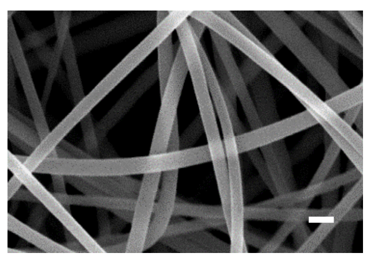


d≈ 1.6 um

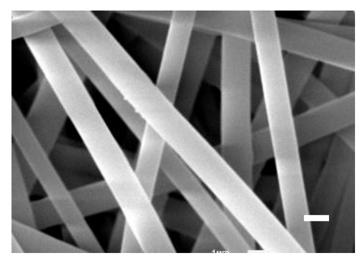
After iCVD of pPFDA treatment



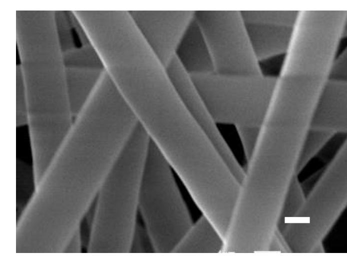
d≈ 0.25 um
CA:151



d≈ 0.43 um
CA:150



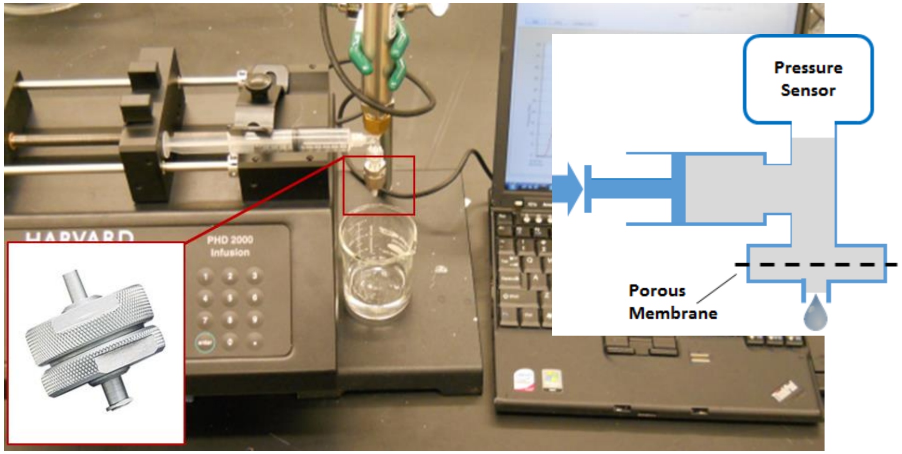
d≈ 1.1 um
CA:131



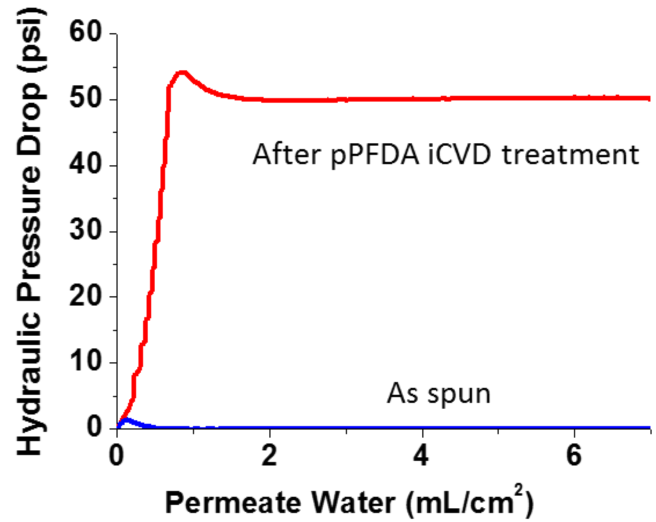
d≈ 1.8 um
CA:134

iCVD of PFDA coating thickness: ~ 0.2 um (on flat Si substrate)

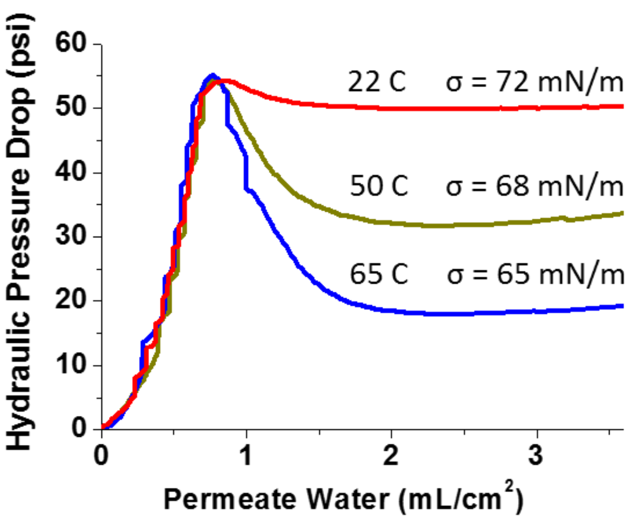
Liquid Entry Pressure



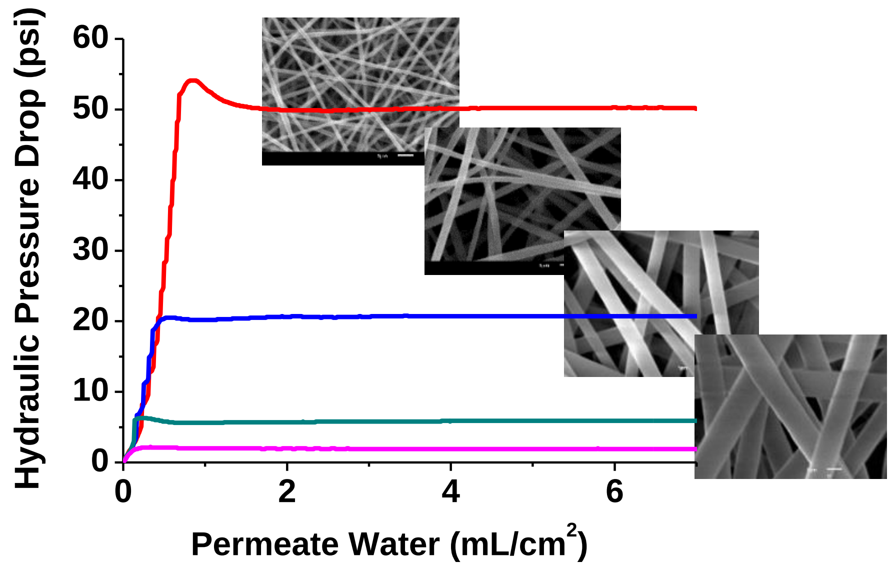
LEP vs. Hydrophobicity



LEP vs. Liquid surface tension (temperature dependent)

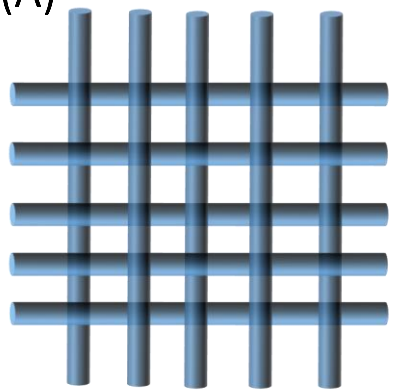


LEP vs. Fiber diameter



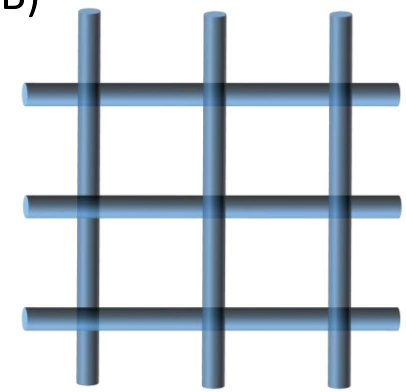
Pore Size Estimation

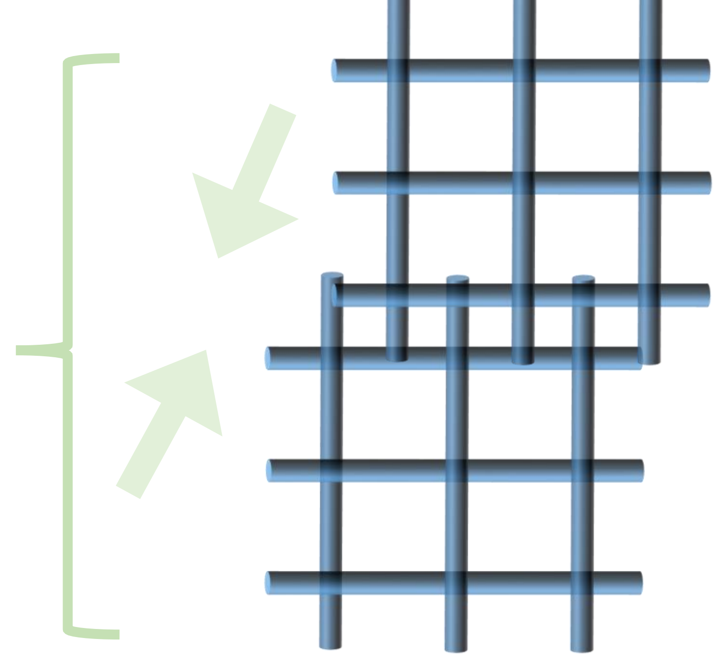
(A)



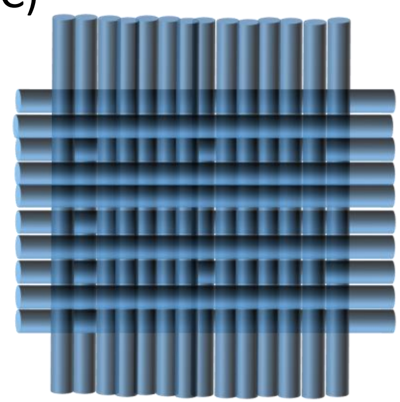
vs.

(B)

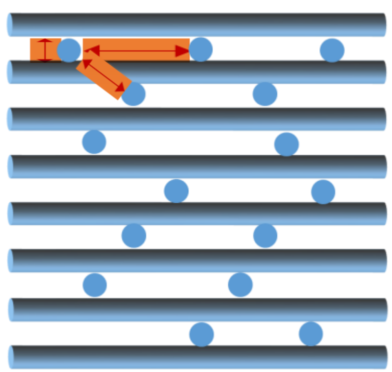


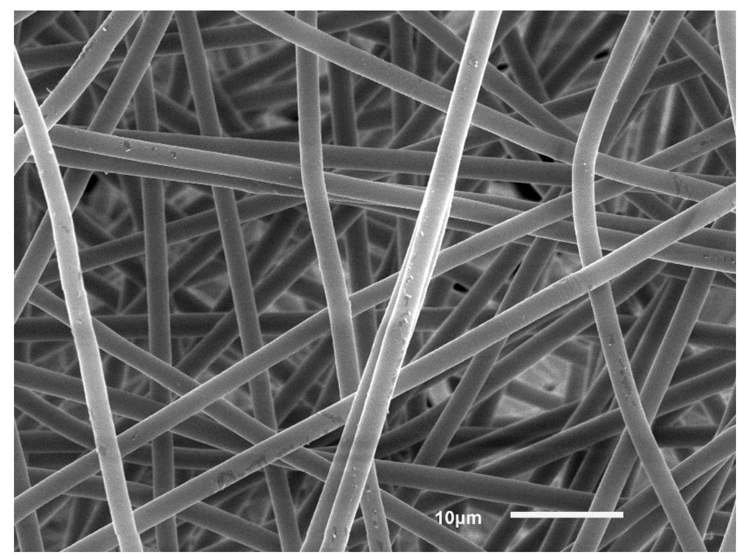


(C)



(D)

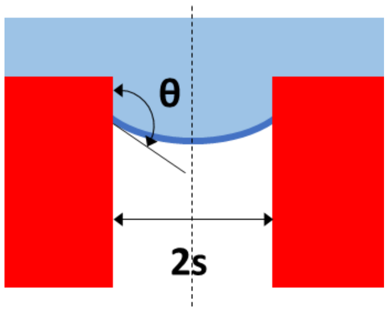




Fiber diameter → Pore size

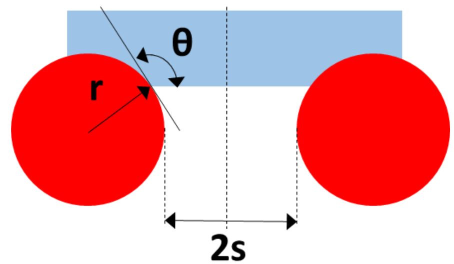
Pore Size Estimation

Hydrophobic cylindrical pore
[Laplace-Young, 1806]



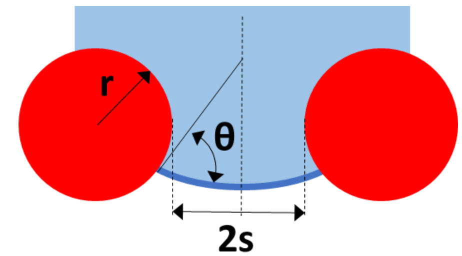
$$P = -2\gamma\ \cos\theta / s$$

Parallel fibers
[Rijke, 1970]

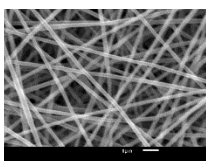


$$P = \frac{\gamma}{r}\left[\cos\theta + \sqrt{\left(\frac{r+s}{r}\right)^2 - \sin^2\theta}\,\right]^{-1}$$

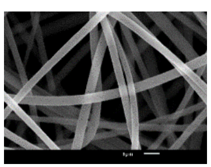
Equilibrium contact angle< 90°
[Tuteja, et al., 2008]



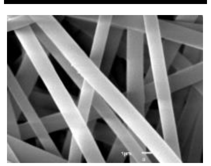
$$P = 2\gamma\,(1 - \cos\theta)(r/s)/s$$



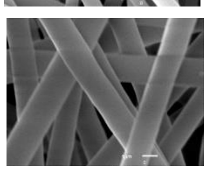
r=0.25 um
CA: 151



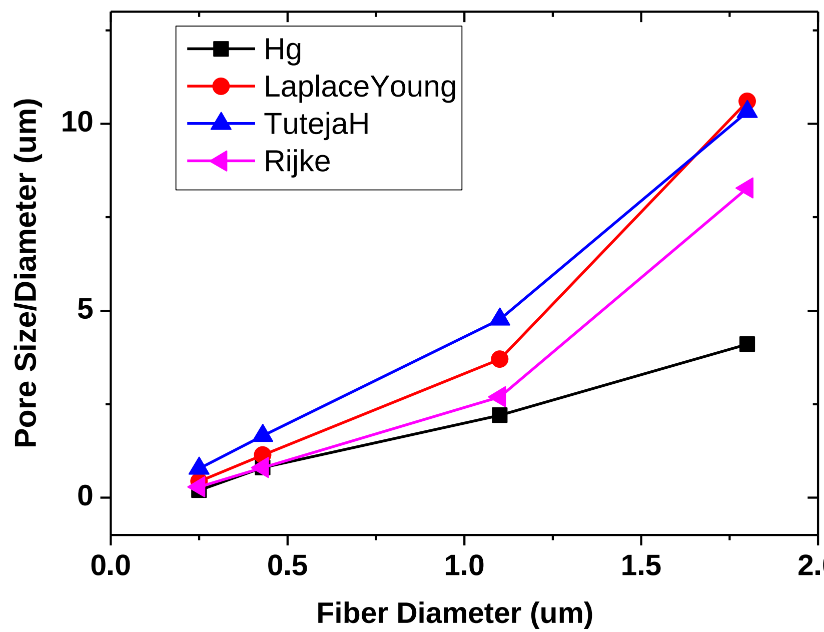
r=0.43 um
CA: 150



r= 1.1 um
CA: 131

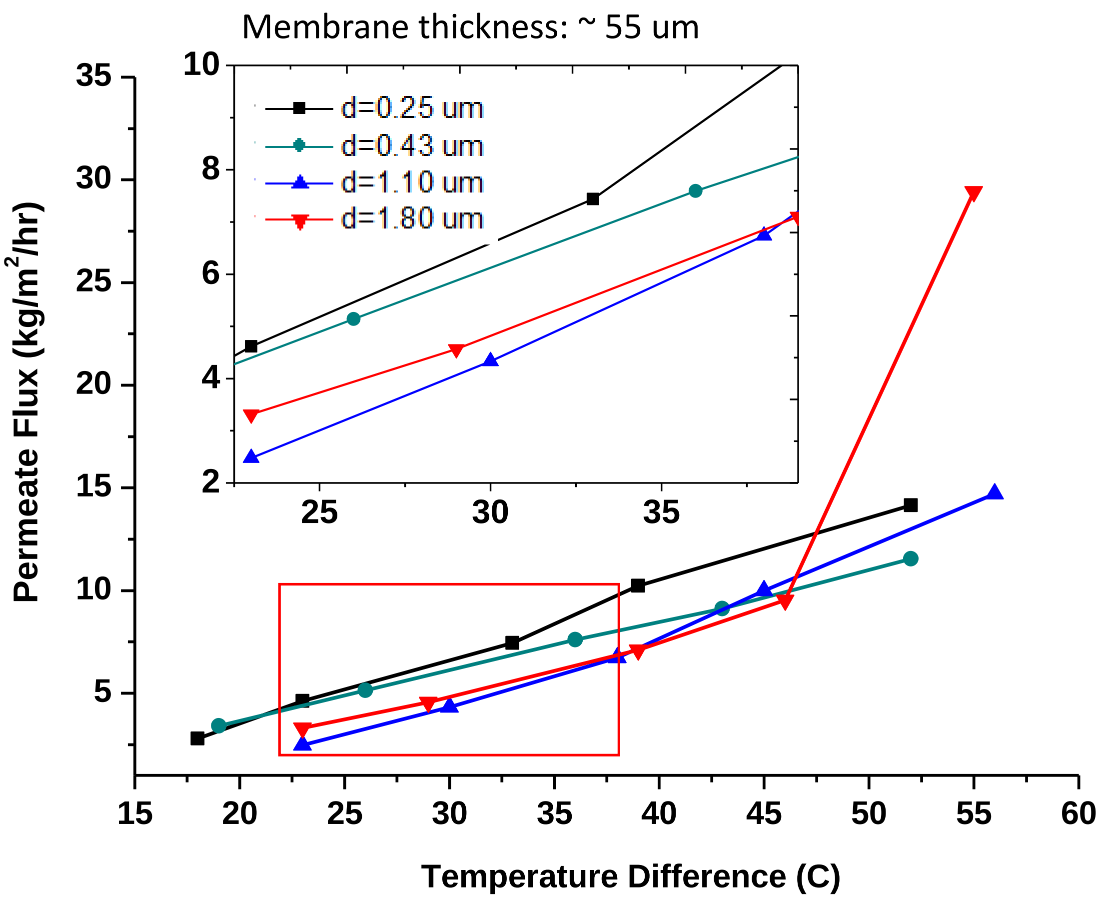


r=1.8 um
CA: 134



(Equilibrium CA of a iCVD treated flat Si substrate is 124 degrees)

MD Performance



d (um)	ΔT (C)	[Cl⁻] (ppm)	Salt rejection
0.25	18	2.6	0.9998
	23	3.9	0.9998
	33	2	0.9999
	39	1.1	0.9999
	52	1.1	0.9999
0.43	19	3.3	0.9998
	26	1.5	0.9999
	36	0.9	0.9999
	43	1.3	0.9999
	52	1.1	0.9999
1.1	22	1.7	0.9999
	29	1.7	0.9999
	37	1	0.9999
	45	1.4	0.9999
	55	332	0.9842
1.8	22	1.2	0.9999
	28	1.1	0.9999
	38	1.2	0.9999
	45	4.4	0.9998
	54	12238	0.4172

Small fibers are preferred for MD

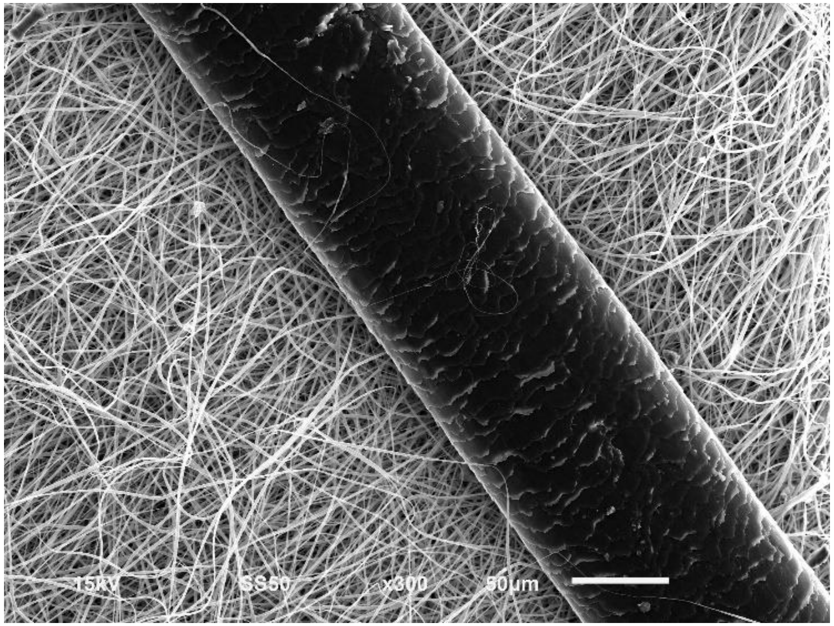
- *higher permeate flux*
- *higher salt rejection ratio*

Original salty water: ~ 21000 ppm (3.5 wt% NaCl)

Salt concentration limits in drinking water: 1000 ppm

Summary

- Espun membranes are good candidates for membrane distillation application.
- Fiber morphologies → MD performance
- Hydrophilic membranes→ iCVD →MD
- Fiber diameter → pore size
- Membranes with small fiber diameters are preferred for the MD application

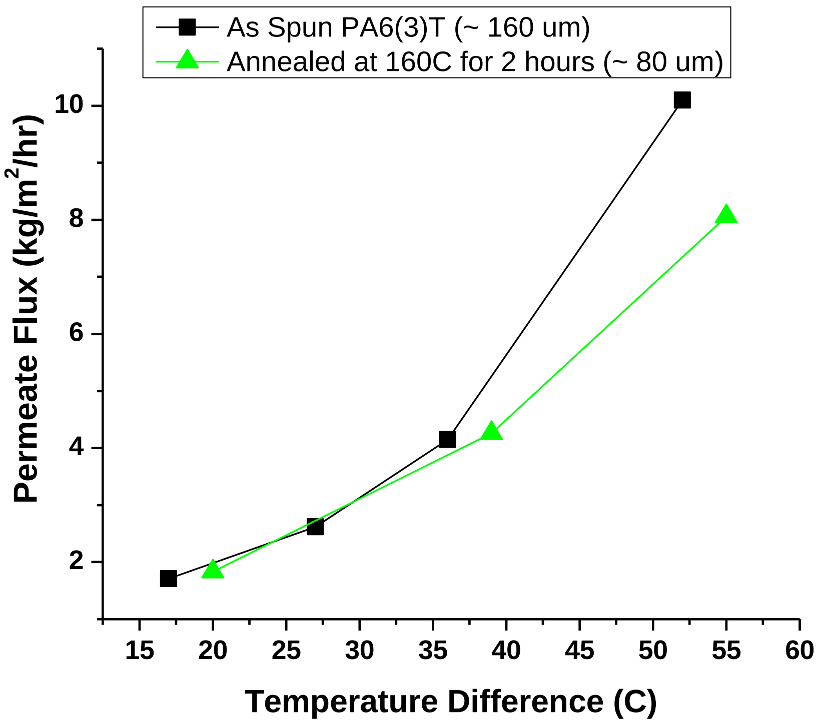


Thank you!

Backup

<u>After treatment_thermal annealing</u>

Espun PA6(3)T



Pulling
150 C_2 hours

Fusing
160 C_2 hours