SAND2016-1486C

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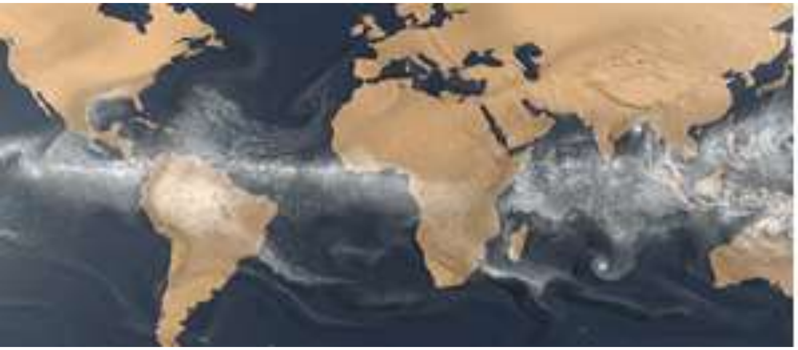

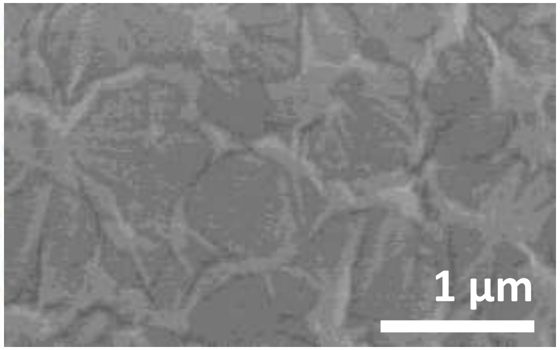

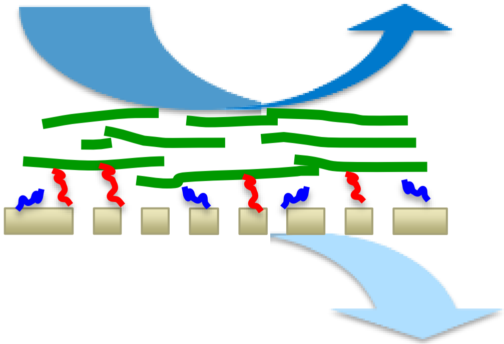

GO desalination membranes

Laura Biedermann, lbieder@sandia.gov

Susan Altman, Michael Hibbs, Mike Hightower, Curt Mowry, Trey Pinon, Craig Stewart and Kevin Zavadil

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Outline

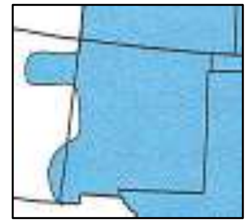
Sandia's interest in desalination membranes

U.S.ARMY NET ZERO

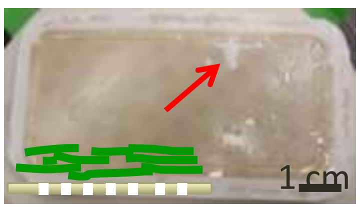
DOE NE, EPRI

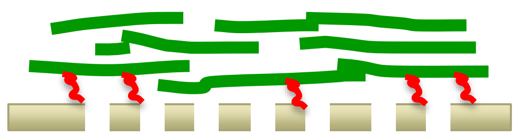
Produced water

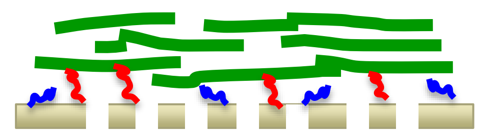
NM brackish aquifers



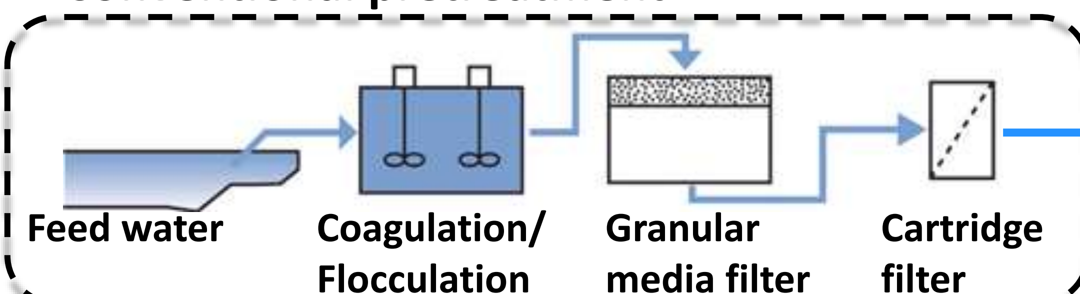
Design and performance of GO/polymer composite membranes





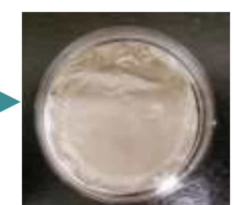


Conventional pretreatment



GO/polymer

Anti-scalants?
Softening?
Chlorination?



Chemically robust desalination membranes are required for complex water streams

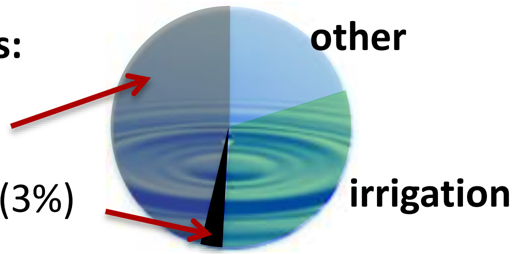
Evaporation pond for produced water

US Army: 3000 gallon water bladder in Pakistan

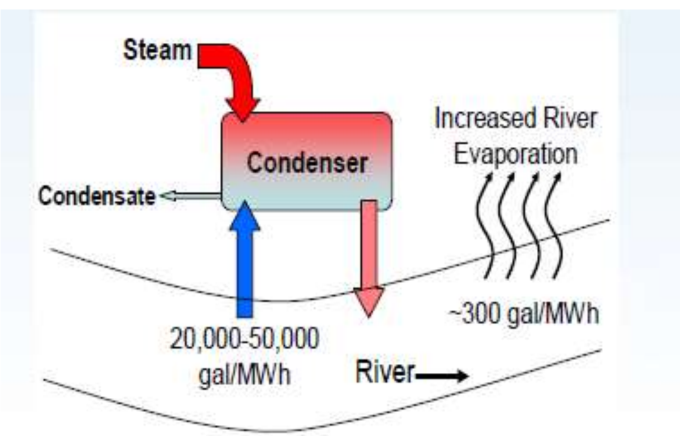
Desalination of brackish water would increase resiliency of wet-cooled power plants

US freshwater withdraws:

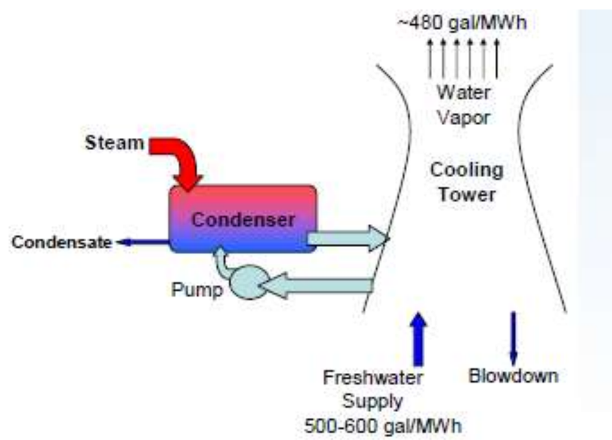
Thermal power plants:
- Water returned to the environment
- Evaporated water (3%)



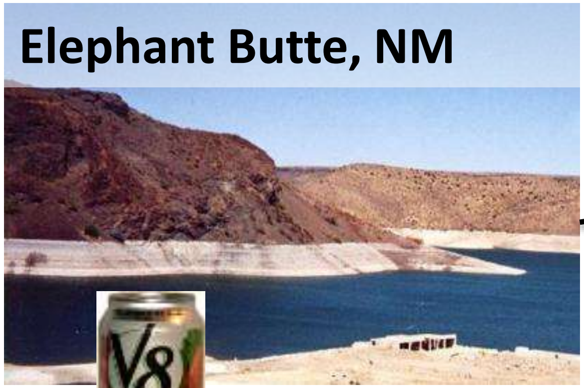
Once-through Cooling
Impact: 20,000 – 50,000 gal/MWh



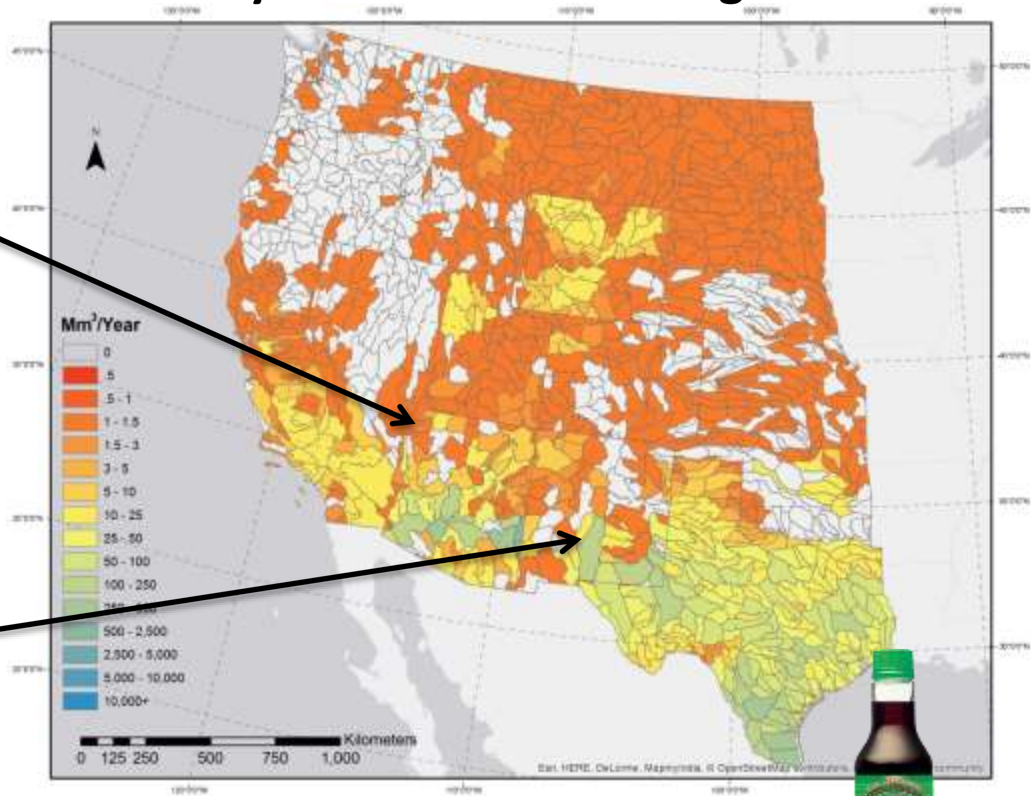
Closed-Loop (Evaporative) Cooling
Impact: 500-600 gal/MWh



Brackish water is abundant in the US



Availability of shallow brackish groundwater



brackish | **sea water**

1000—10000 ppm | **35,000 ppm**

Ideal properties of nanoscale-enabled desalination membranes

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Physical properties

- Pore diameter < 1 nm
- High pore density
- Chlorine-tolerant
- Resistant to biofouling and sulfate scaling
- Bottom-up manufacturability

	Desired Performance	Reverse Osmosis
Salt rejection	> 95 %	99.0 % (min)
Permeance	> 10 LMH/bar	2.9 LMH/bar
Energy use	< 0.1 W/L	
Chlorine tolerance	5 ppm	< 0.1 ppm

DOW FILMTEC BW30-400 membrane used for RO comparisons, msdssearch.dow.com

Graphene and graphene-oxide are related robust nanosheet materials

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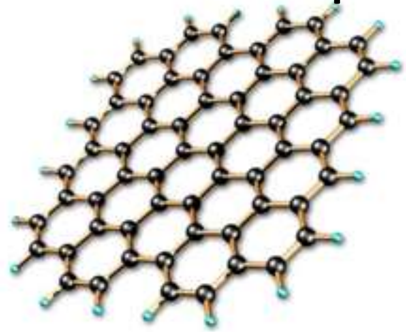
Natural graphite

Mechanical exfoliation

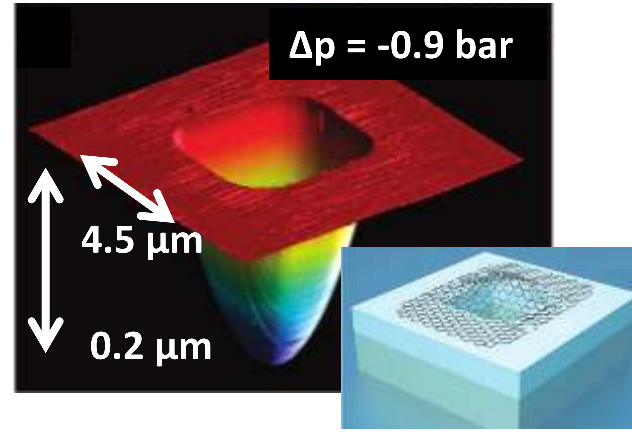
Chemical oxidation

Graphene

Hexagonal carbon network forms the basal plane

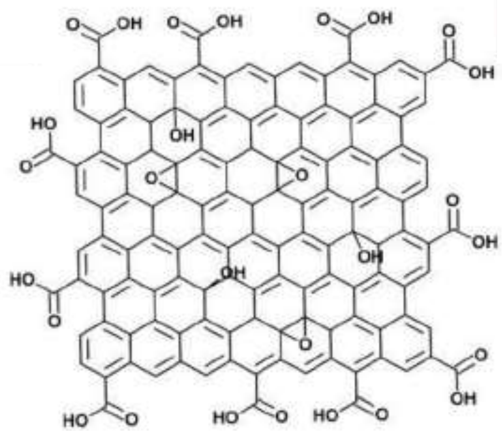


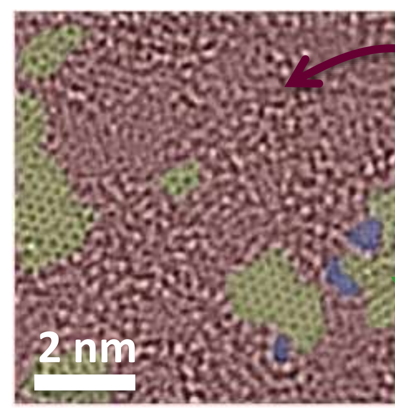
A pristine graphene membrane is impervious to gasses



Graphene Oxide (GO)

oxygen functional groups decorate the basal plane



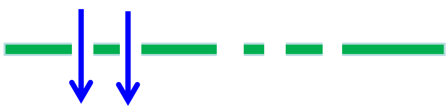


oxidized domains

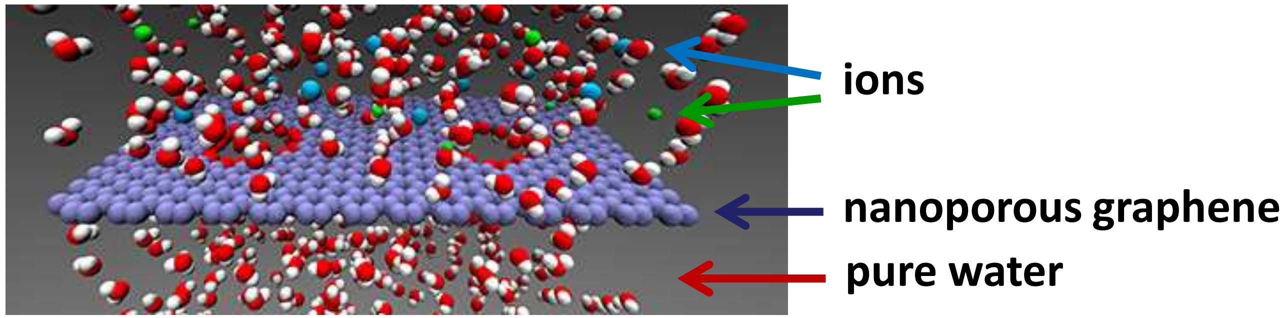
graphitic domains

Two proposed structures for graphene-based desalination membranes

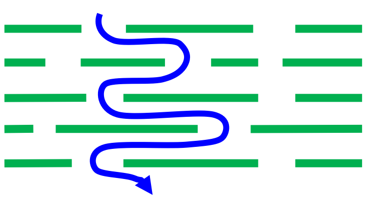
Permeation through nanoporous monolayer graphene



[1]



Permeation around GO sheets in laminar GO membranes



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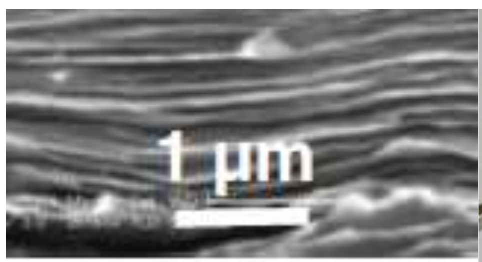
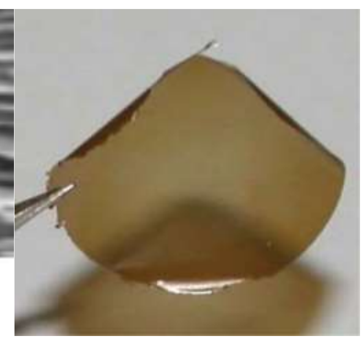
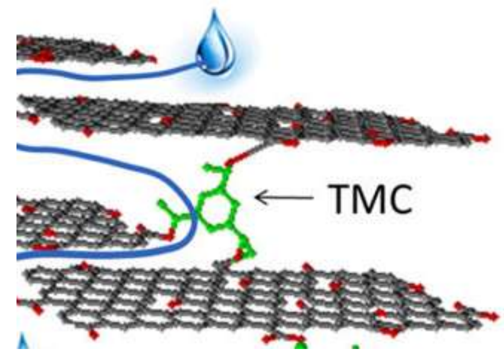




[3]

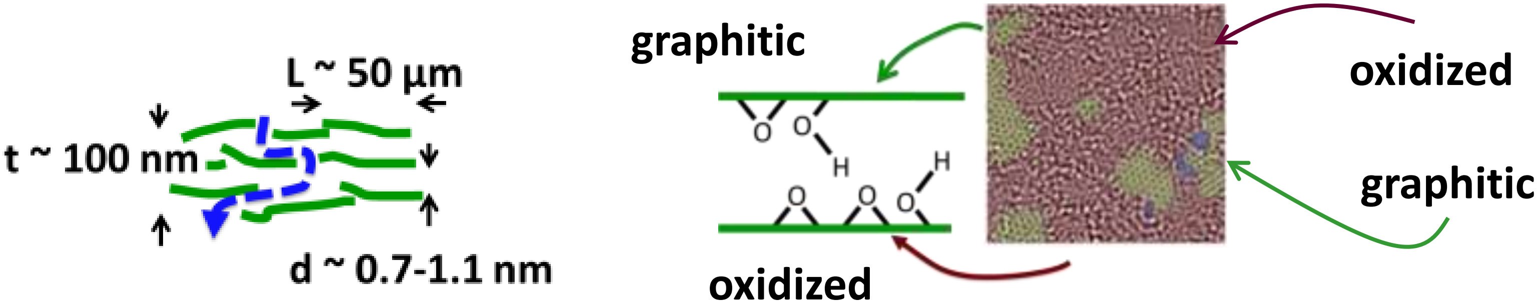


Theory and experiment suggest that nanosheet-based desalination membranes will have 10x-100x flux of current technologies, revolutionizing low-energy water production and recycling.

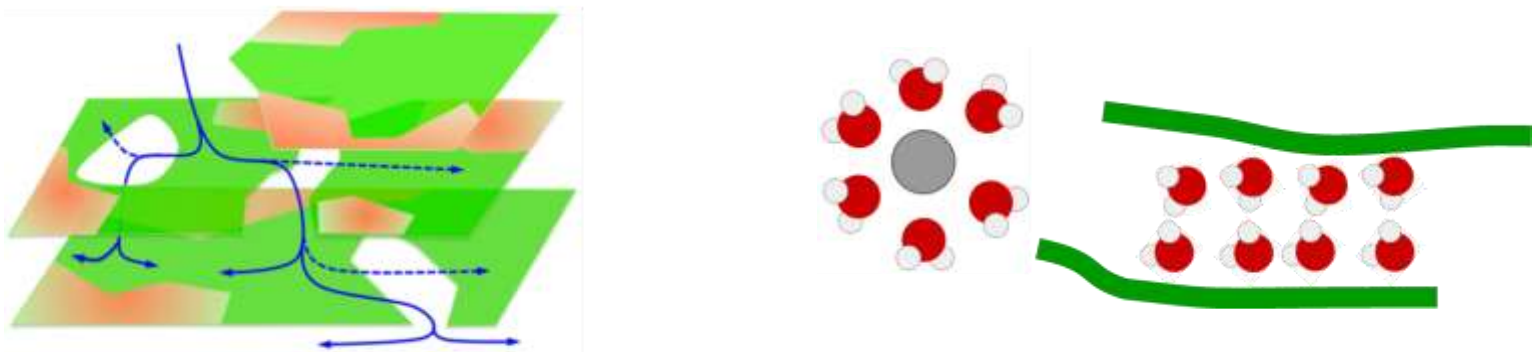
[1] Lockheed Martin Perforene membrane, [2] R. Nair *et al.*, *Science* 335 (2012), [3] M. Hu and B. Mi, *Environ. Sci & Tech.* 47 (2013)

Nanoscale graphene oxide (GO) structure enables low energy desalination

Thin-slit permeation pathway defined by oxygen moiety "nanopillars"



Intrinsic nanoscale properties of laminar GO drive water permeation and are optimum for desalination



→ **Low-energy flow: Water flux is driven by strong interactions with the GO sheets, not by external pumps.**

Vacuum-filtration directed assembly of GO on polymer membrane supports

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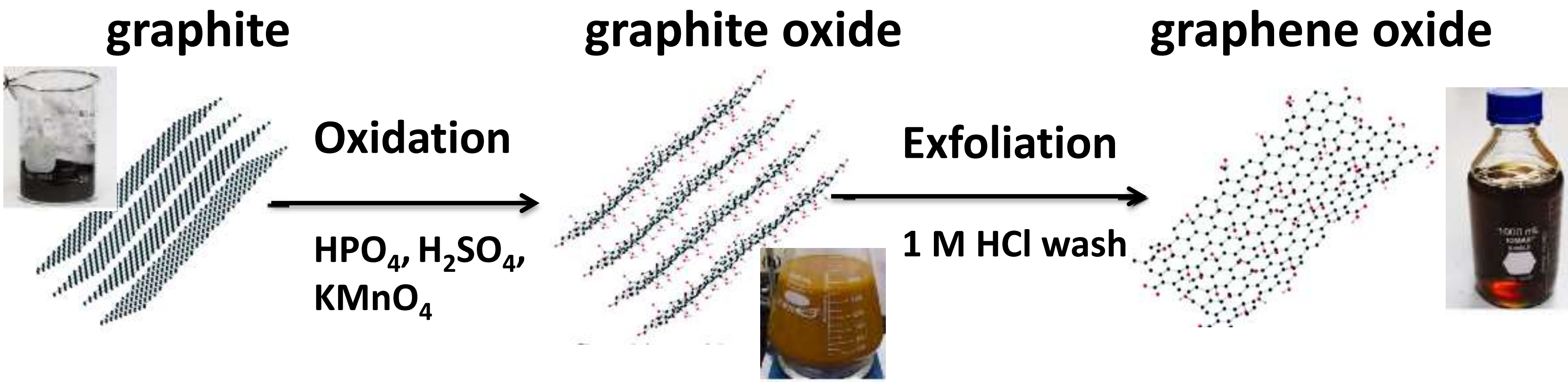
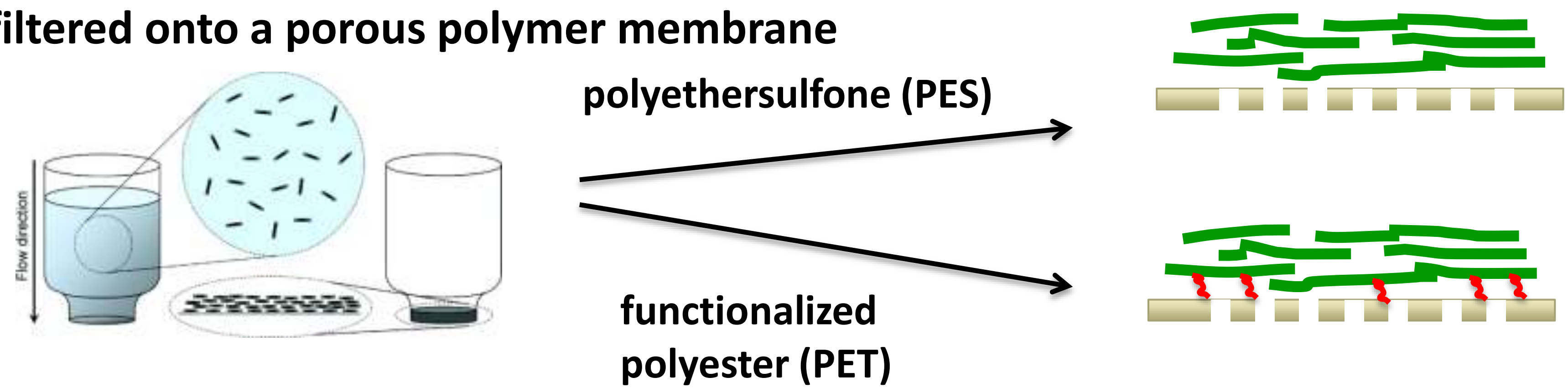
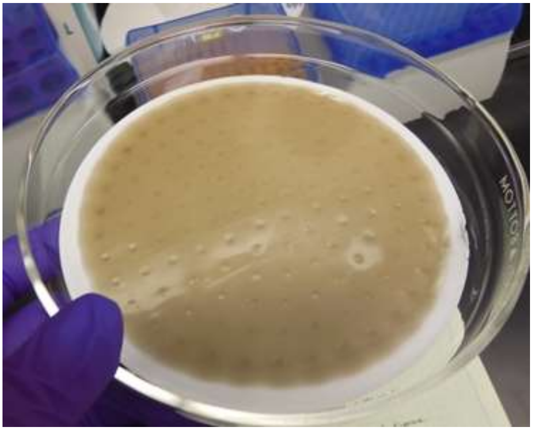


Material cost: \$0.10/m^2 for a 100-monolayer GO membrane

GO sheets are re-dispersed in a dilute filtration suspension and vacuum-filtered onto a porous polymer membrane



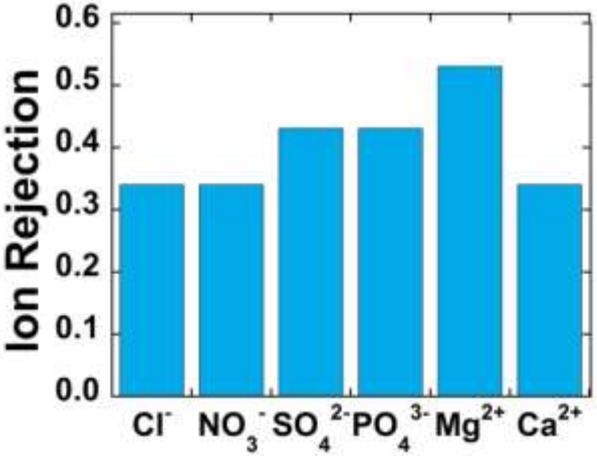
GO/PES membrane: Moderate ion rejection following 60-100 ppm bleach exposure



~100 GO monolayers on a polyethersulfone (PES) membrane, 124-mm diameter

Dead-end filtration (post-bleach)

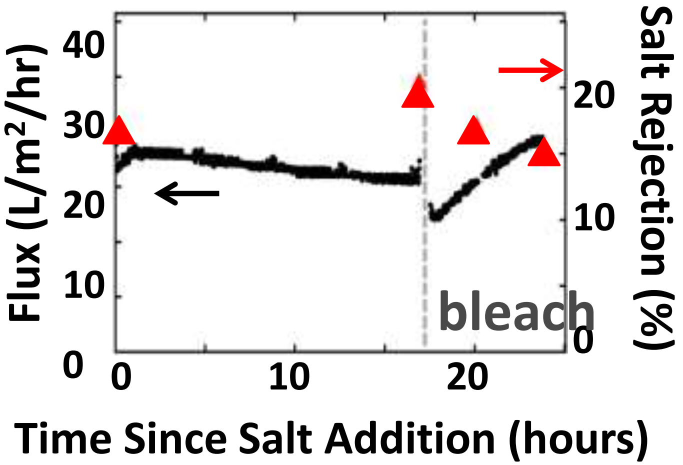
Flux ~10 L m^{-2} h^{-1} at 1 bar



Following 100 ppm, 30 min bleach

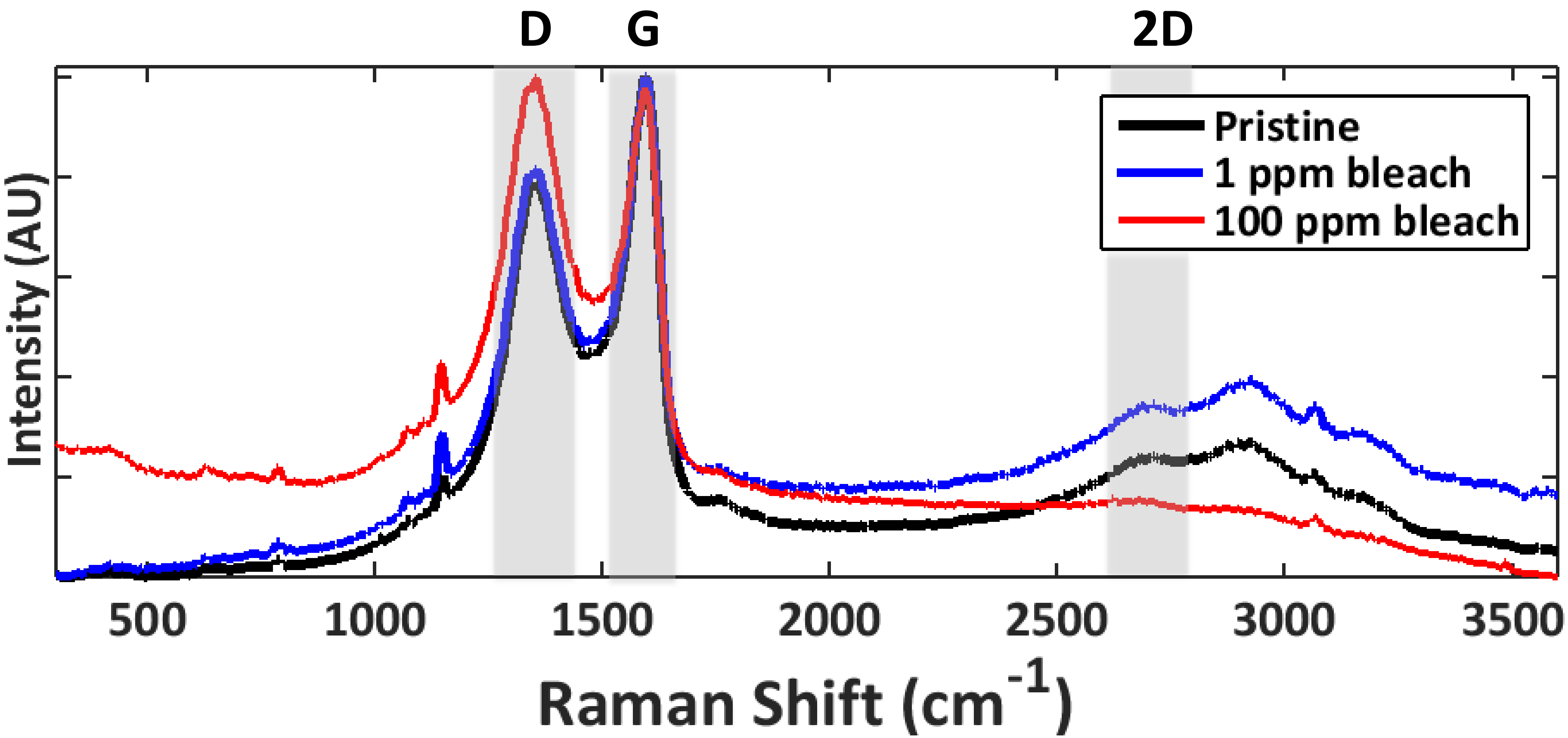
Cross-flow filtration

Flux ~25 L m^{-2} h^{-1} at 14 bar



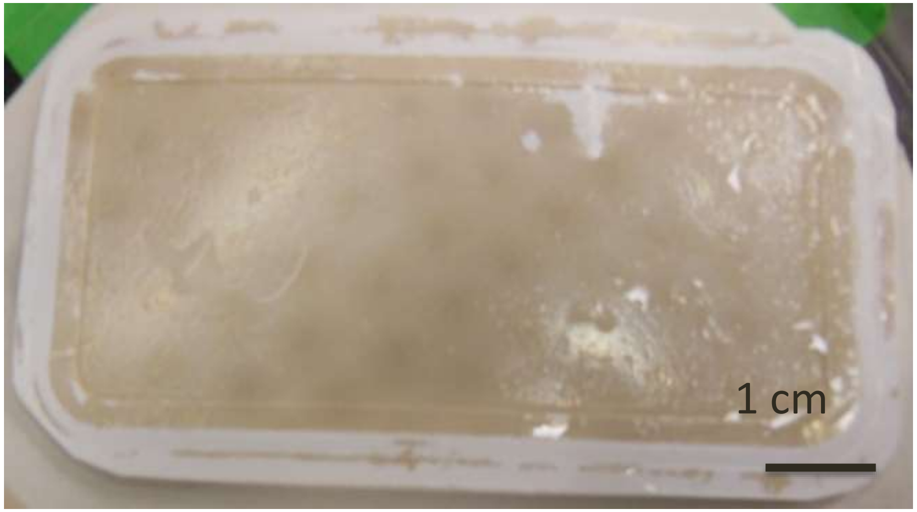
1200 ppm $MgSO_4$; 60 ppm bleach

GO structure is robust to 1-ppm, **one month** free chlorine exposure

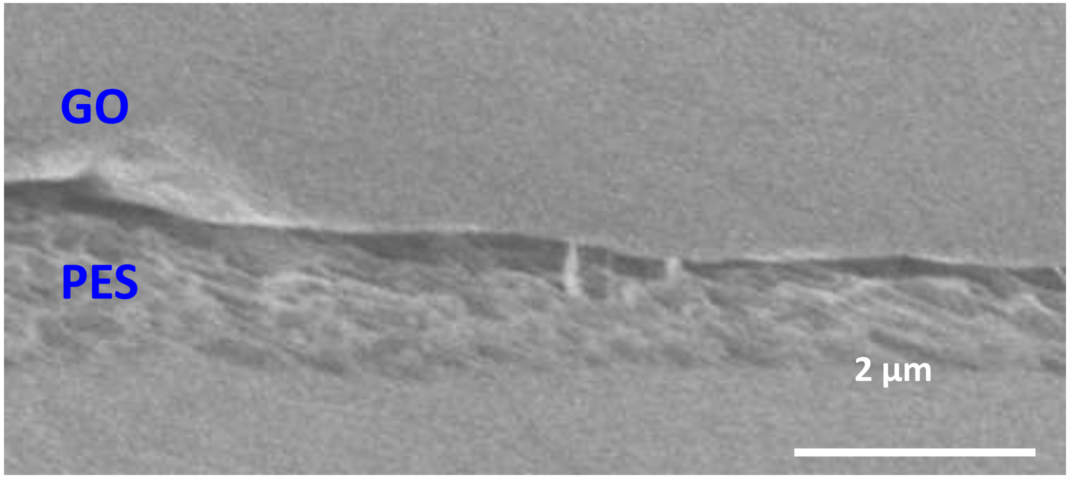


Low-levels of chlorination (~1—5 ppm) will minimize biofouling in greywater recycling

GO/PES: Delamination during cross-flow permeation limits ion rejection



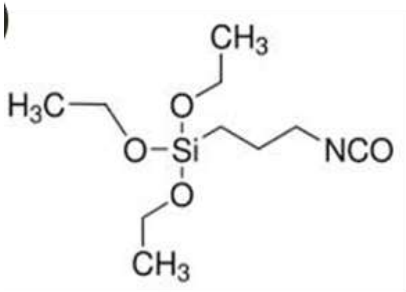
Delamination following 1 ½ -day permeation test at 14 bar and 8-hour exposure to 60-ppm bleach.

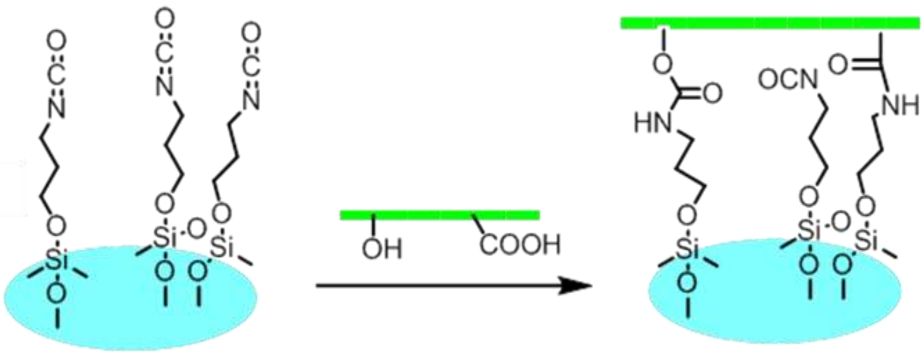


Representative delamination at the GO/PES interface.

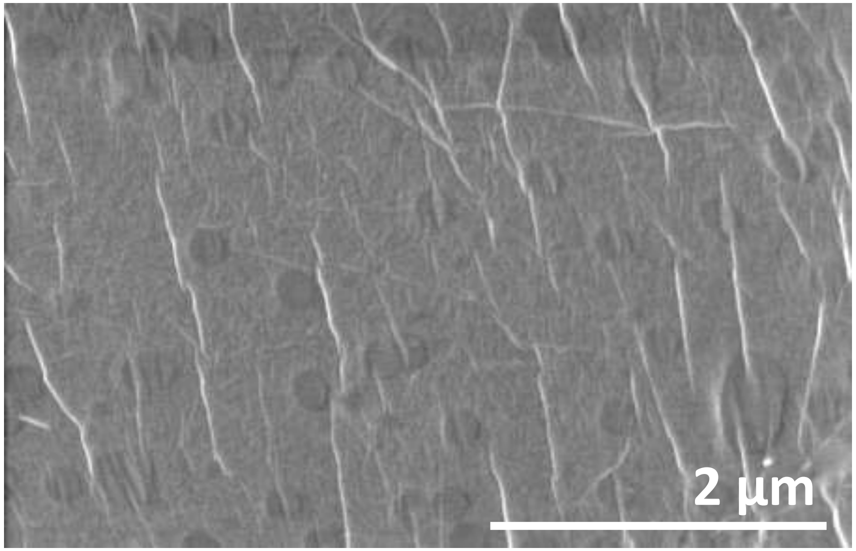
Will covalently binding GO to PES prevent delamination of the laminar GO?

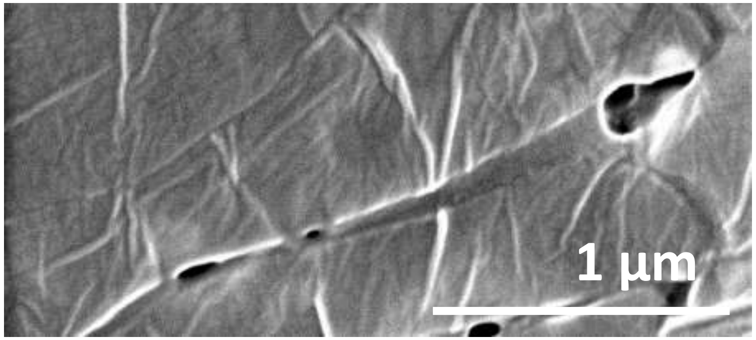
Covalent linking isocyanate agents prevent delamination of the laminar GO





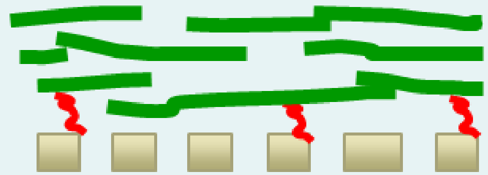
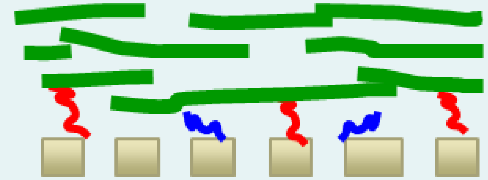
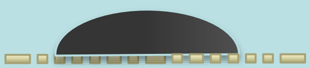
GO/Isocyanate/PET, following permeation tests





Effective isocyanate binding,
even over fractured polyester (PET)

Hydrophilic polymeric membrane interfaces required for high flux GO membranes

	Isocyanate only	Isocyanate and spacer
Functional groups		
Contact angle 	**45º** 	**40º** 
Permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	0.5	2.1
Power needed (W/L)	0.3	0.2
Sulfate ion rejection	80 %	90 %

We are currently developing scalable GO/polymer membranes

Scale-up to spiral-wound membrane elements requires robust polymer supports and covalent linker molecules stable in aqueous environments

Demonstrated

- GO/dimethylformamide solution filtered over polyester membranes
- 0.1 kWh/m^3 energy intensity for 2000 ppm $MgSO_4$

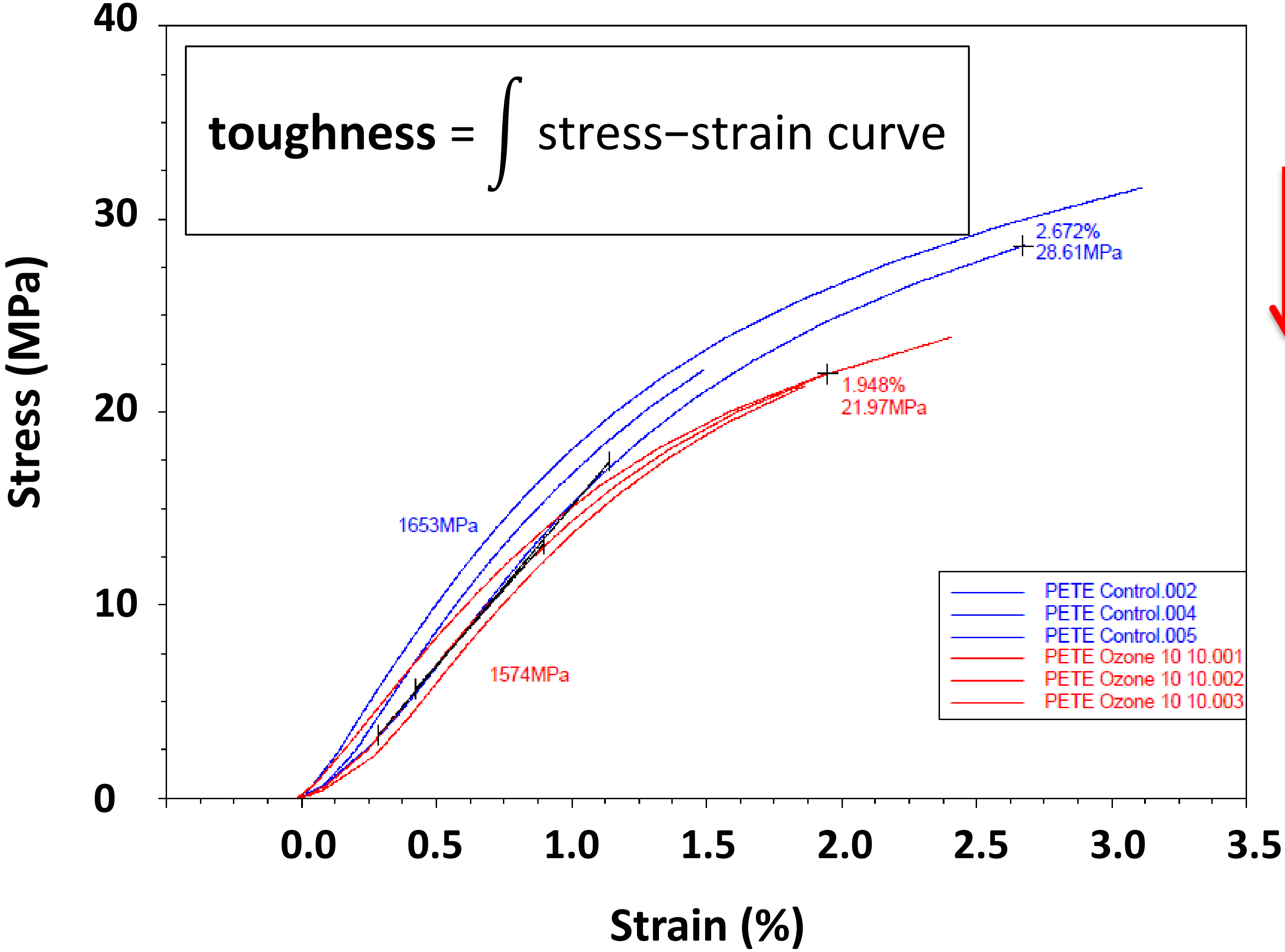
Current work

- Aqueous GO solution filtered over polyethersulfone membranes
- What is the optimum covalent linker chemistry?

Goal

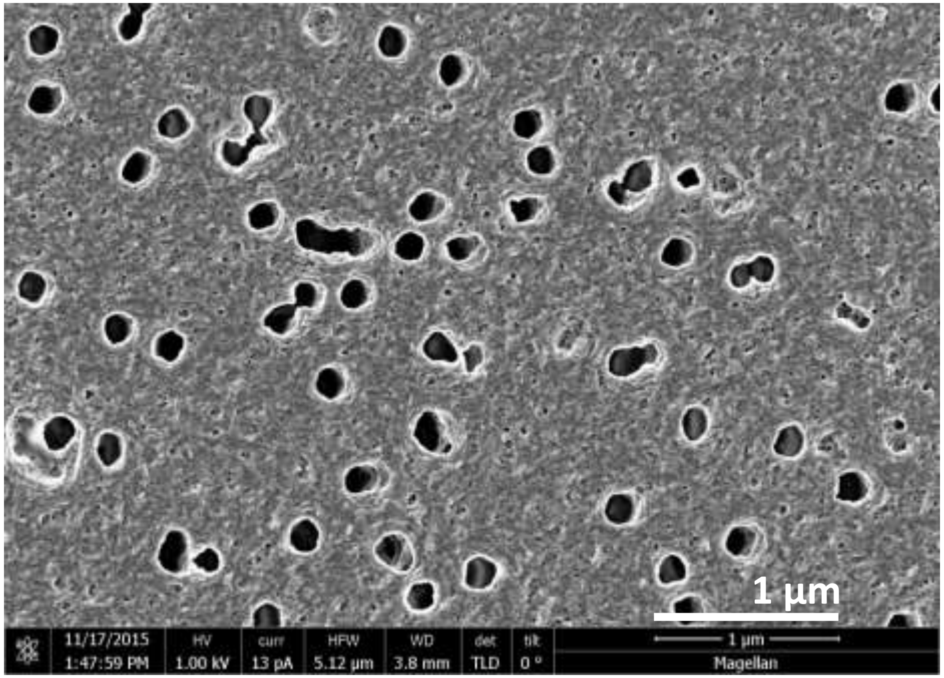
- Transition to roll-to-roll processing
- What operating conditions will maximum GO/polymer lifetime?

Stress-strain measurements show polyester membranes are brittle



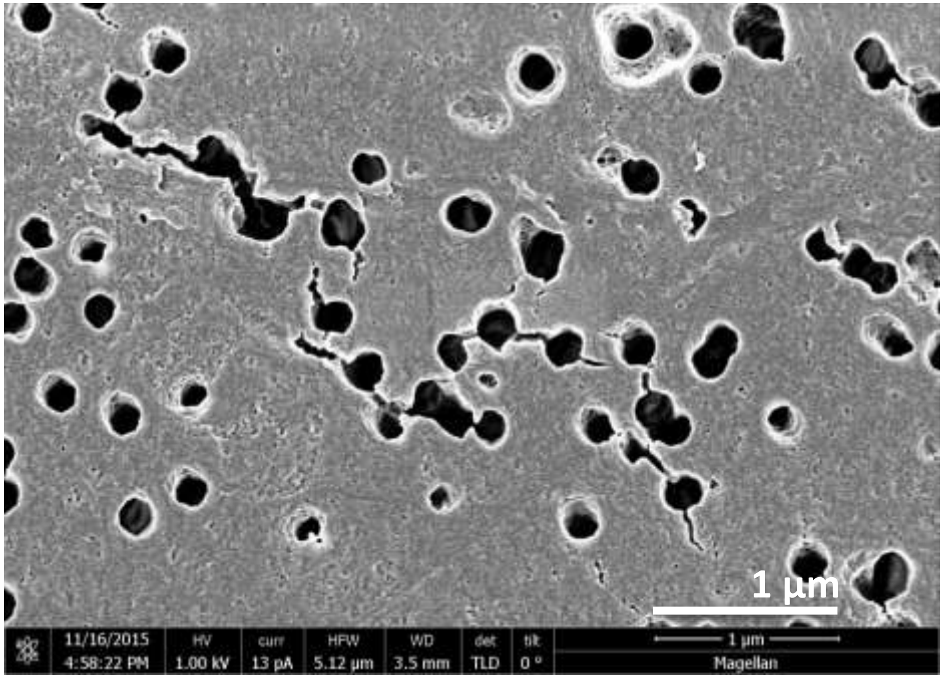
UV/ozone decreased toughness to 28 x 10^4 J/m^3

SEMs show cracks connecting pores of UV-ozone treated PETE membranes

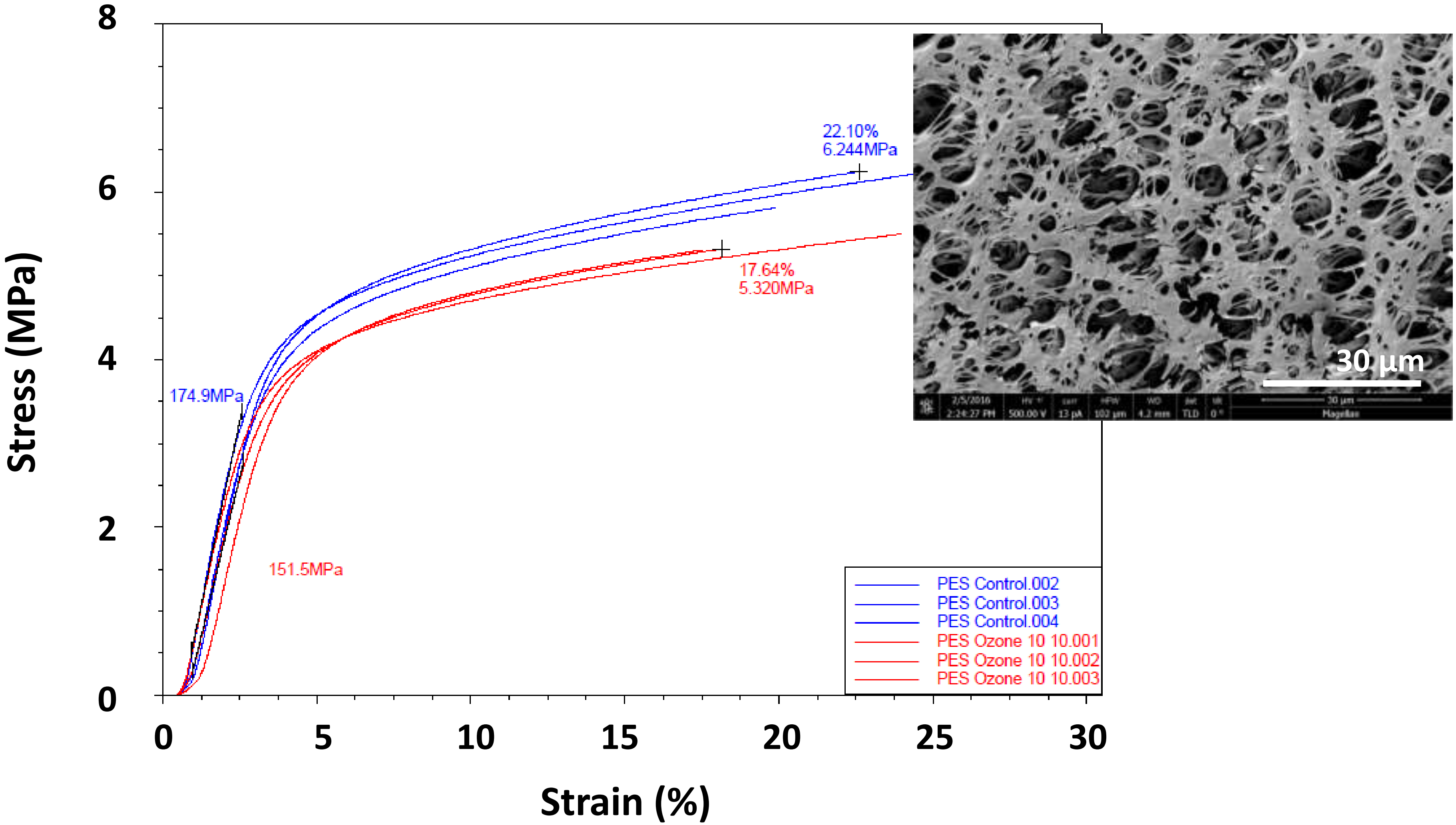


← **Pristine PETE**

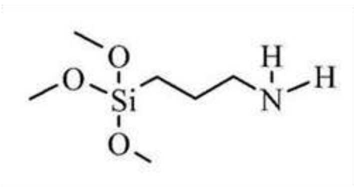
Following 10-min UV-ozone exposure →

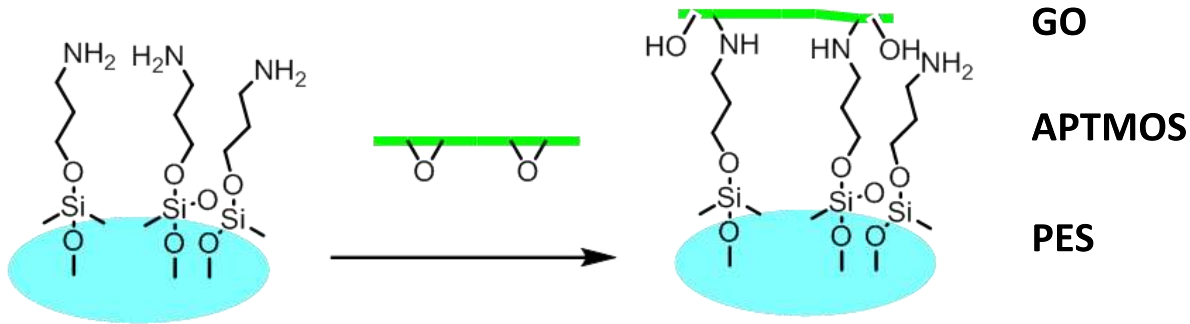


Polyethersulfone membranes can withstand strains ~20 % before fracture

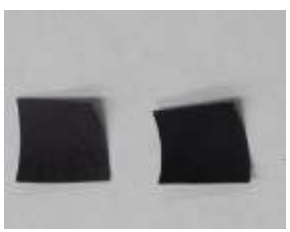


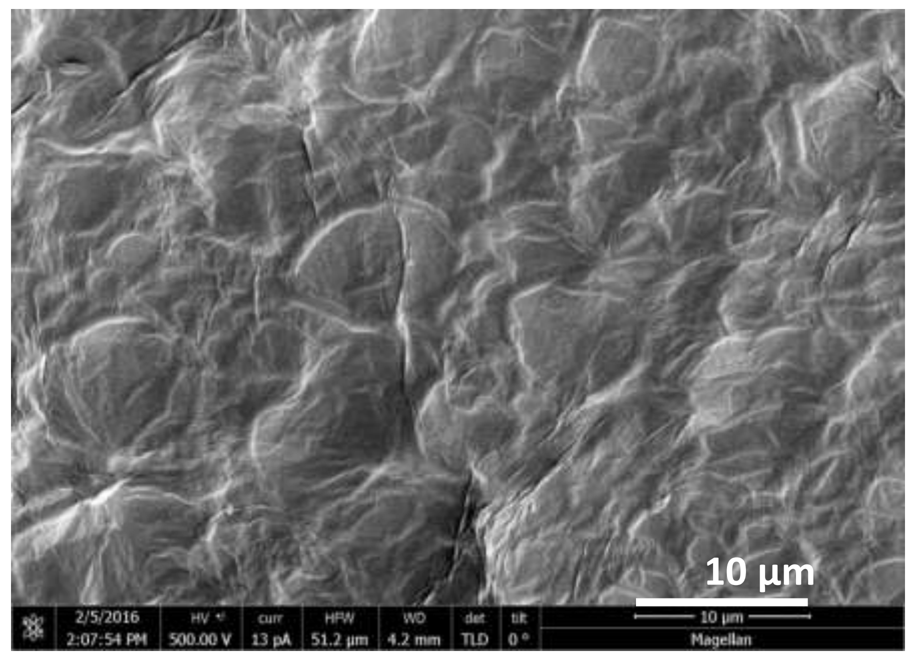
Covalent linking amine molecules allow for aqueous GO membrane assembly



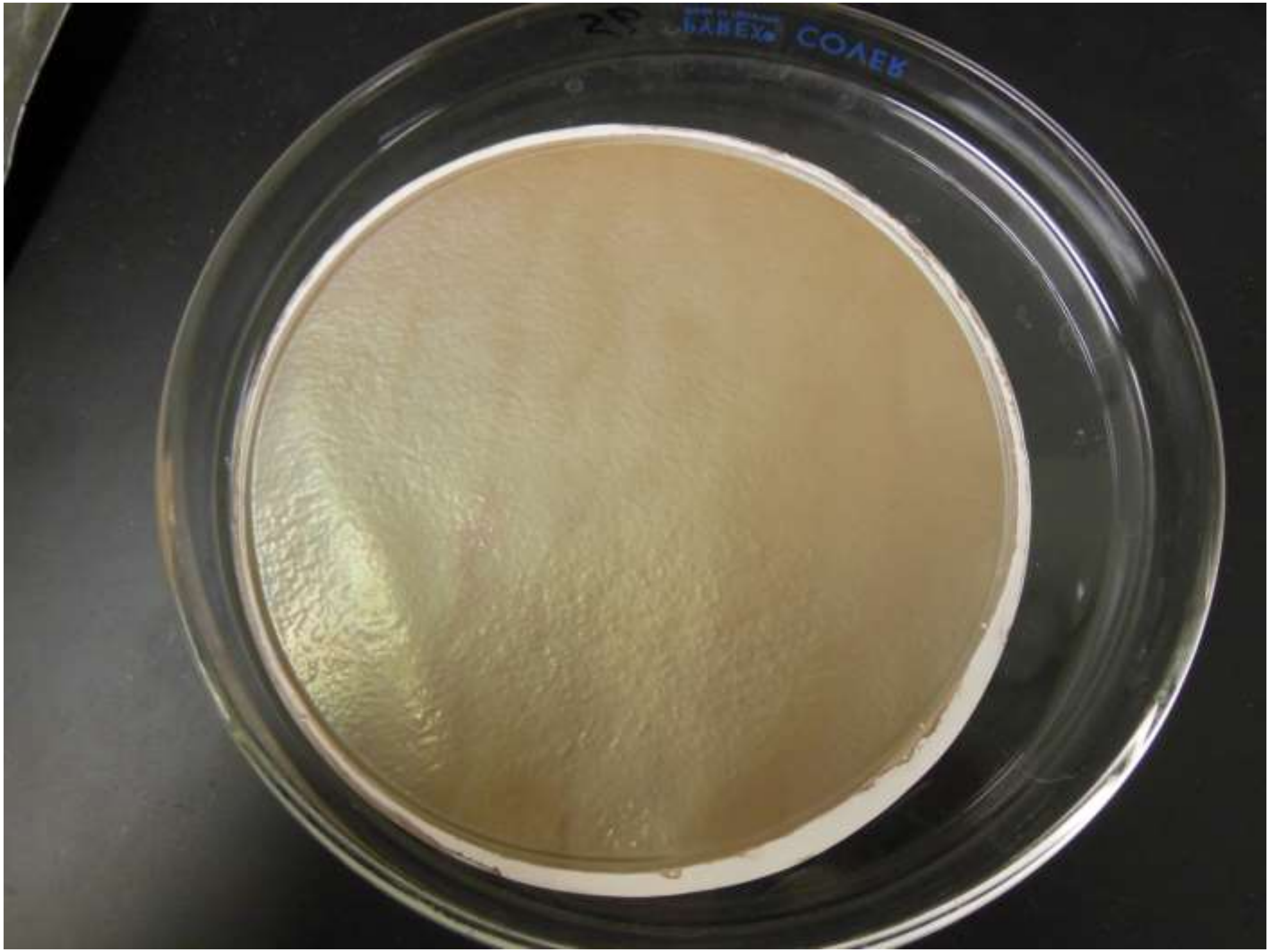


Optical stain turns dark purple in presence of an amine



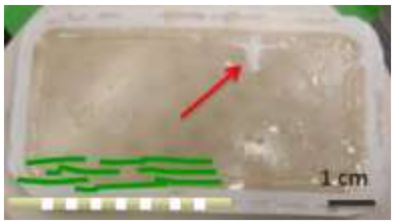


Coming soon: Flux and rejection of GO/APTMOS/PES membranes



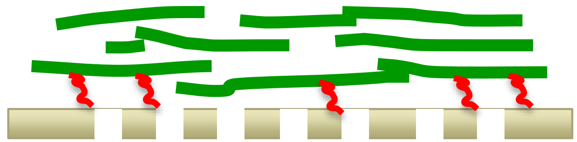
Conclusions

No cross-linker molecules



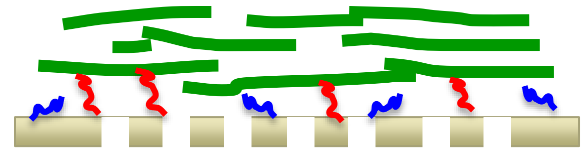
1.8 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 15-20 %

Slightly hydrophilic



0.5 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 80 %

More hydrophilic



2.1 L m^{-2} h^{-1} bar^{-1}
Sulfate ion rejection: 90 %

- **Covalent linking of the laminar GO to the polymer support is required for stability in cross-flow permeation**
- **Increasing the hydrophilicity of the GO/polymer interface improves flux**
- **GO sheets are tolerant to 1 ppm chlorine**
- **PES membranes and amine-based covalent linkers may allow for roll-to-roll processing of GO/polymer membranes**

Acknowledgements

Current research team: Michael Hibbs, Mike Hightower, Curt Mowry, Trey Pinon, Craig Stewart and Kevin Zavadil

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Los Alamos National Laboratory
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