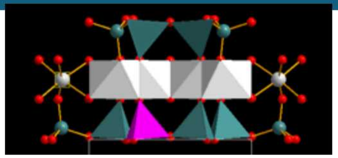
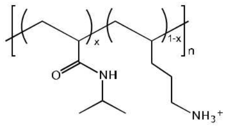
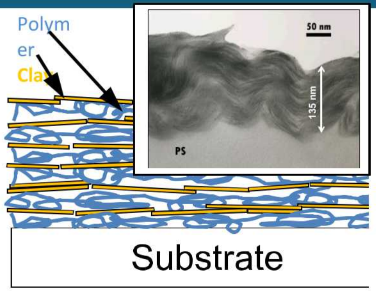
SAND2019-13694C

The Ion Seeps Tonight:
Assessing Ionic Transport in Multilayered Nanocomposites







Amanda Peretti
Stephen Percival
Leo Small
Martha Gross
Eric Schindelholz
Michael Melia
Susan Rempe
Derek Nelson
Sara Russo

PRESENTED BY

Erik D. Spoerke

Composites at Lake Louise 2019 (CALL2019)
November 10-14 | Lake Louise, Alberta, Canada

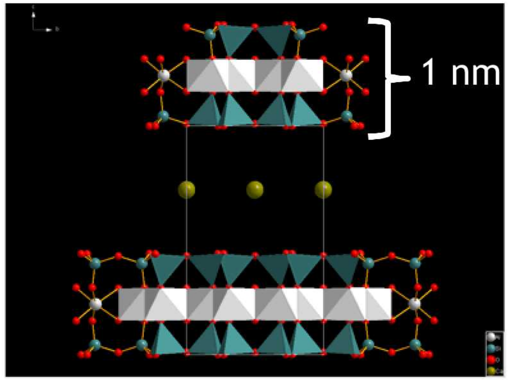
This work at Sandia National Laboratories is supported by Sandia's Laboratory Directed Research and Development Program and Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

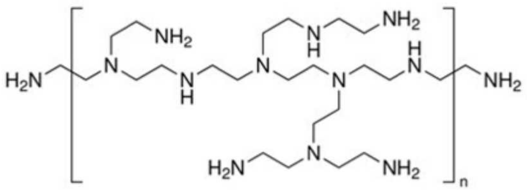
SAND No.: SAND

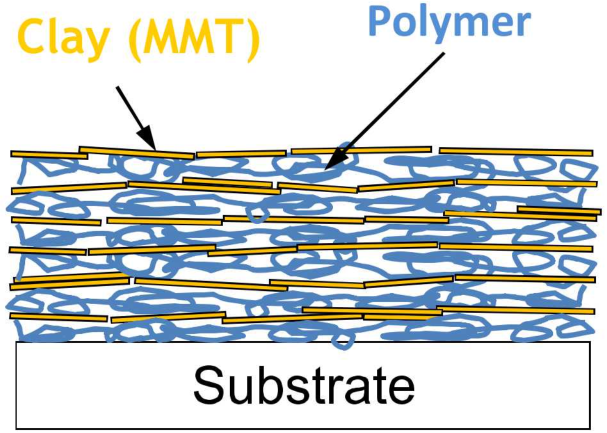
Layered Functional Materials

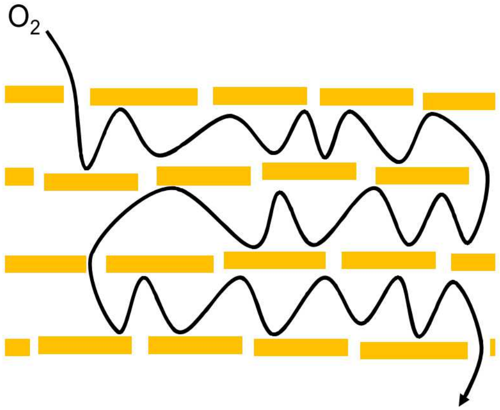
Montmorillonite (MMT)



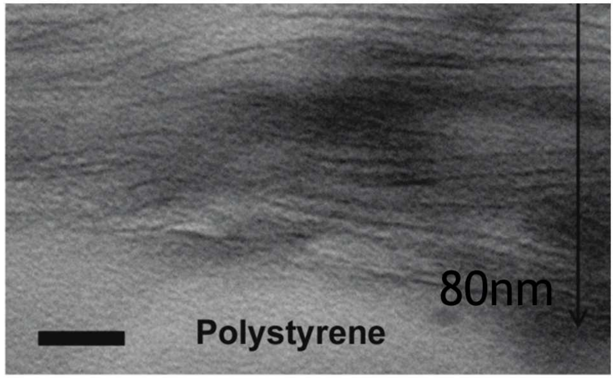
Polyethyleneimine (PEI)





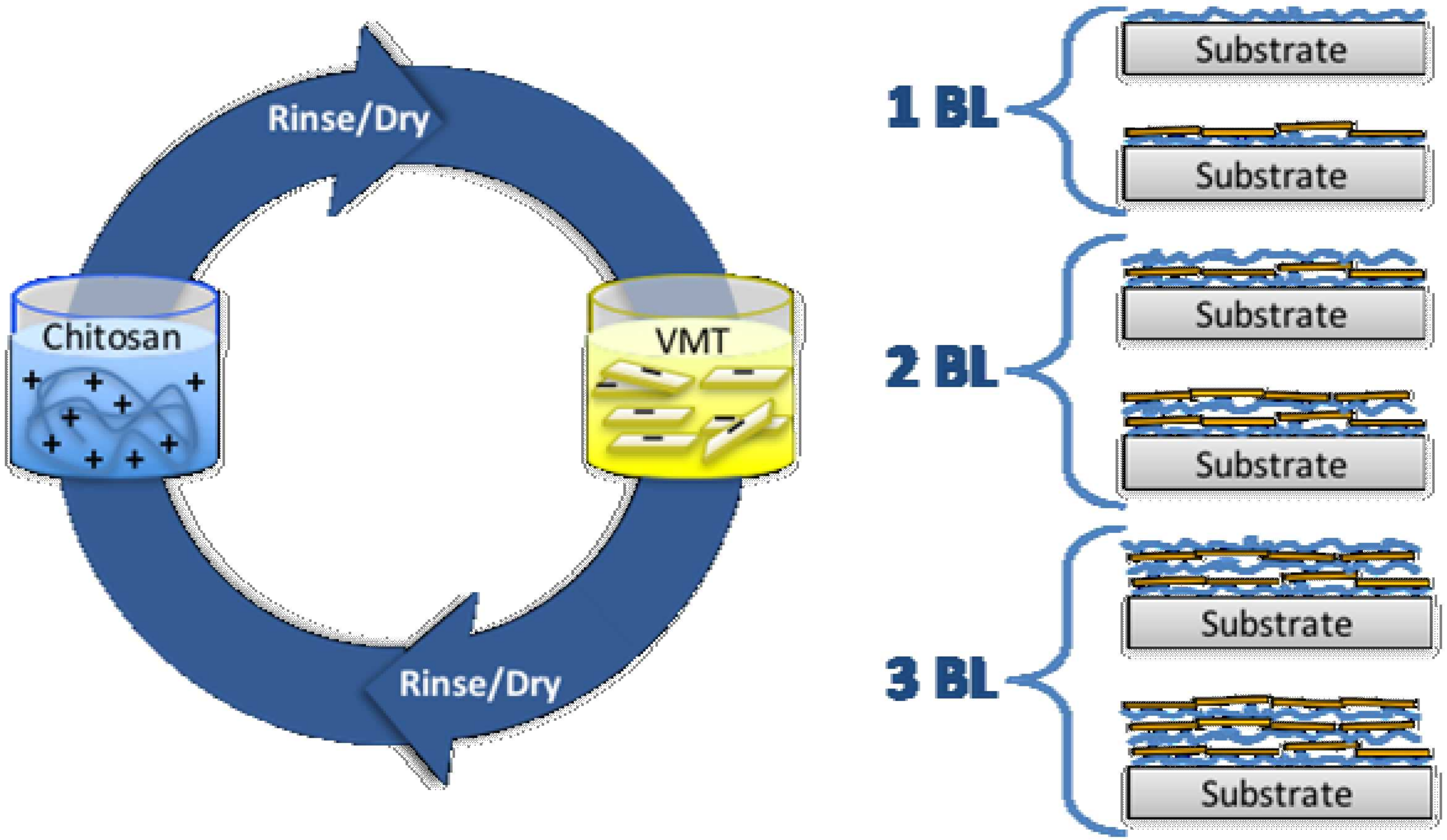


Highly organized layers of exfoliated clay and functional polymers make unique barrier thin films.



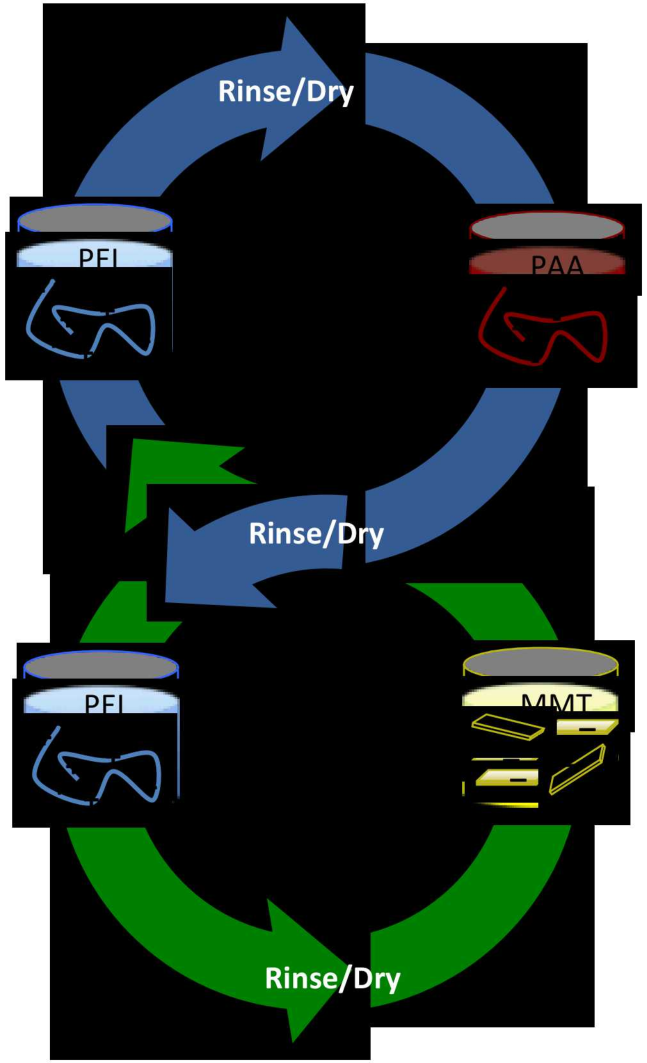
Nano Lett. **2010,** *10,* 4970--4974

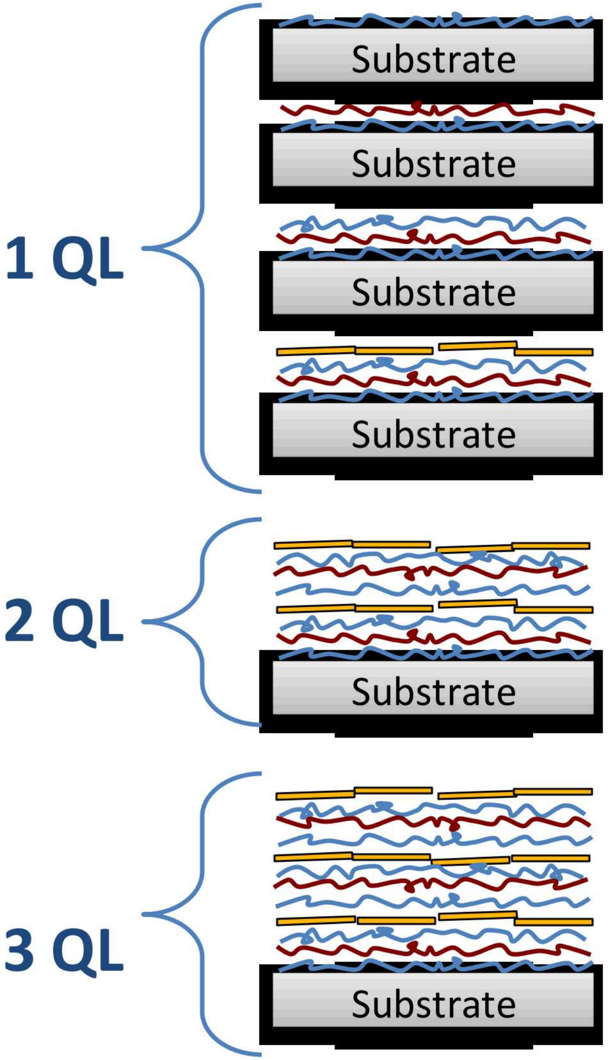
Layer-by-Layer Assembly of Composite Films



Using layer-by-layer (LBL) assembly, functional composites films can be produced on macroscopic scales.

Quadlayer Assembly

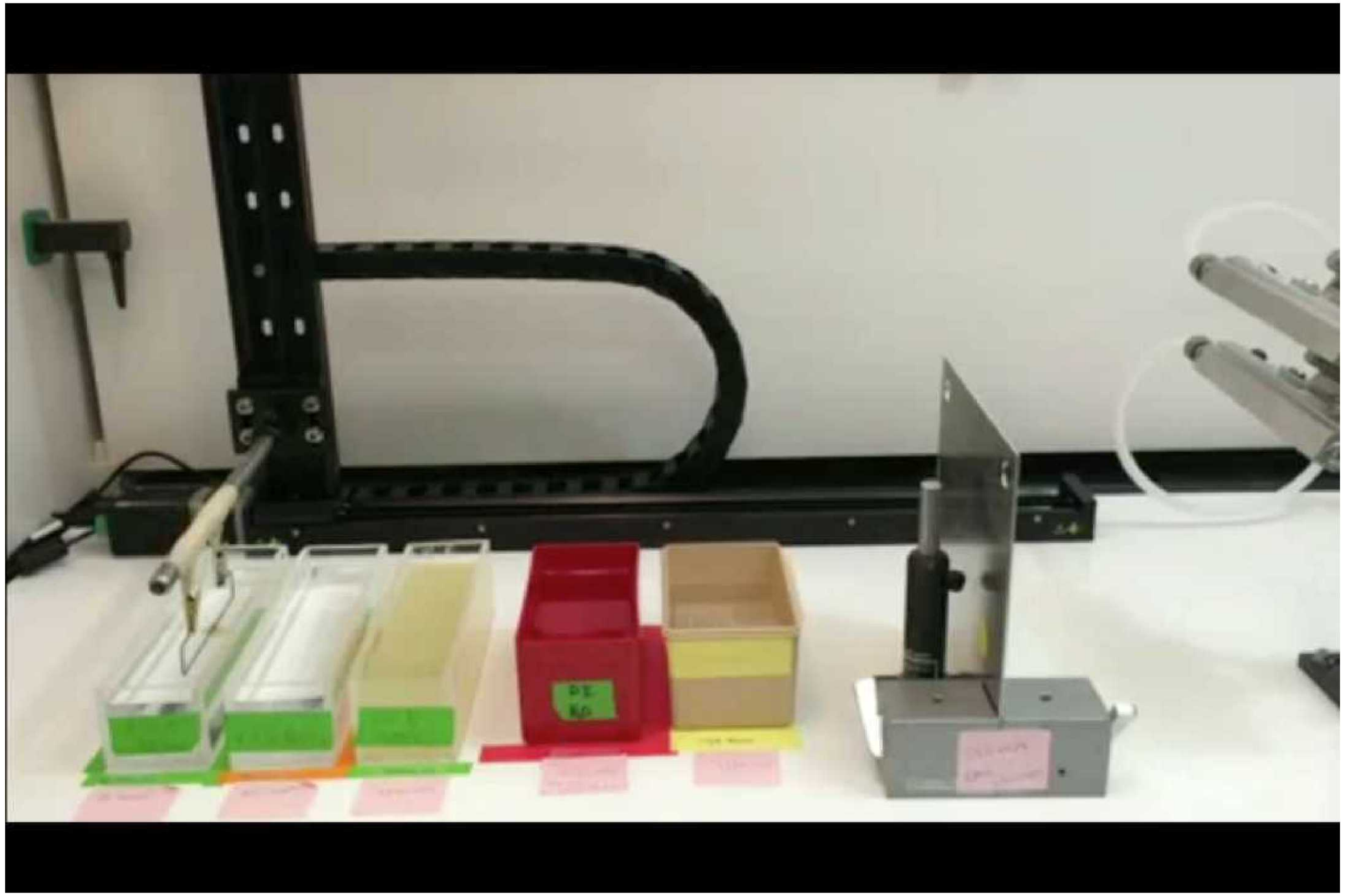




QuadLayer assemblies involve not only polymer-clay interactions, but polymer-polymer interactions.

These secondary polymer interactions significantly affect PCN properties!

Robot Automation of Multilayered Thin Film Growth

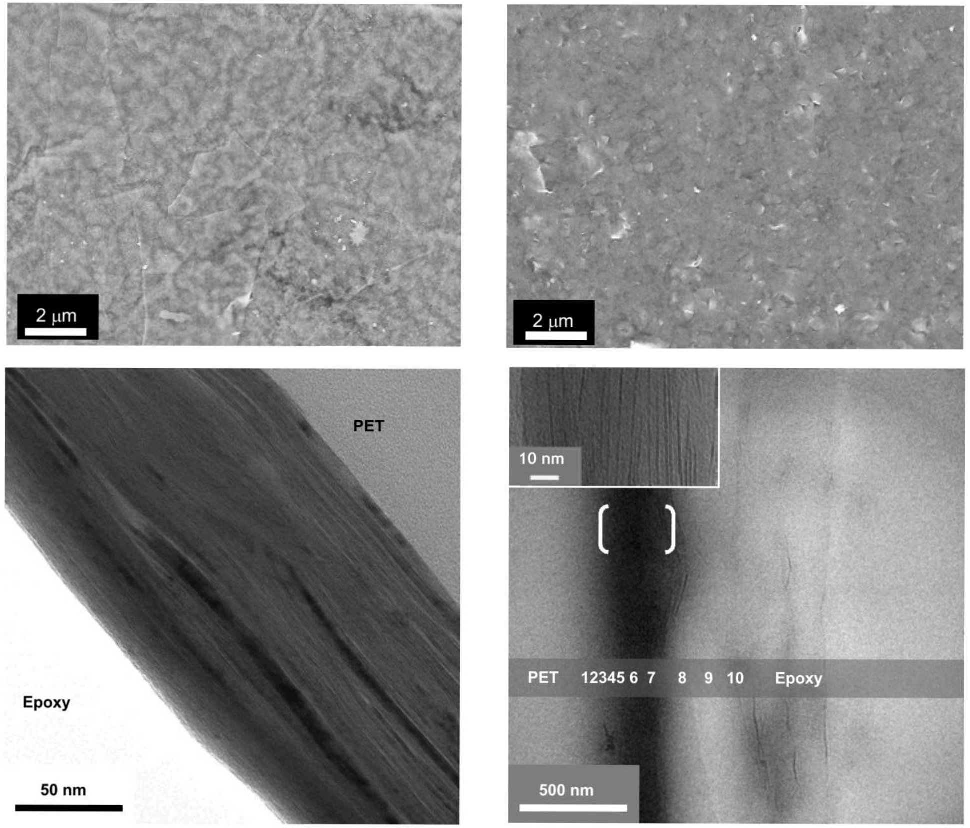


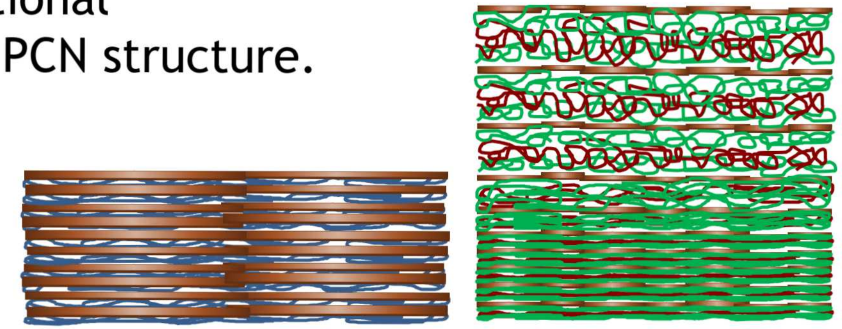
Characterizing PCN Structure

Scanning Electron Microscopy (above) and X-sectional Transmission Electron Microscopy (below) shows PCN structure.

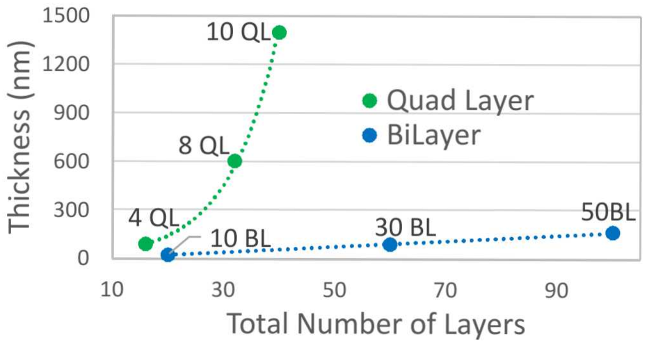
Chitosan/Vermiculite BL

PEI/PAA/PEI/MMT QL

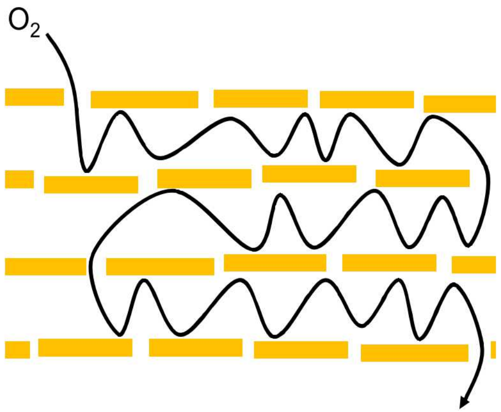


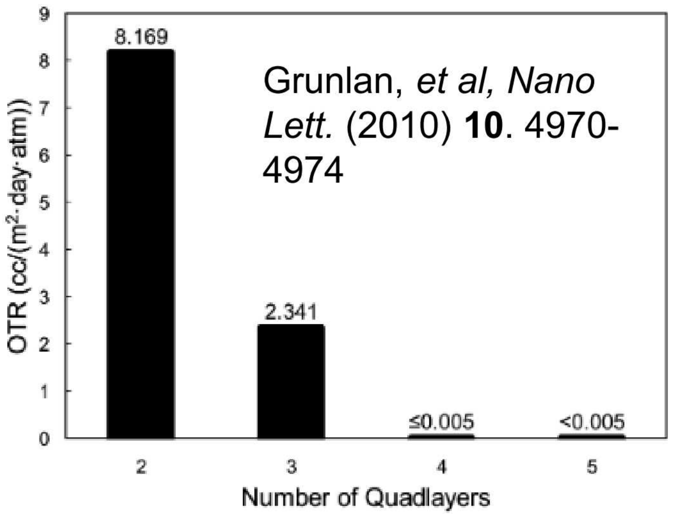


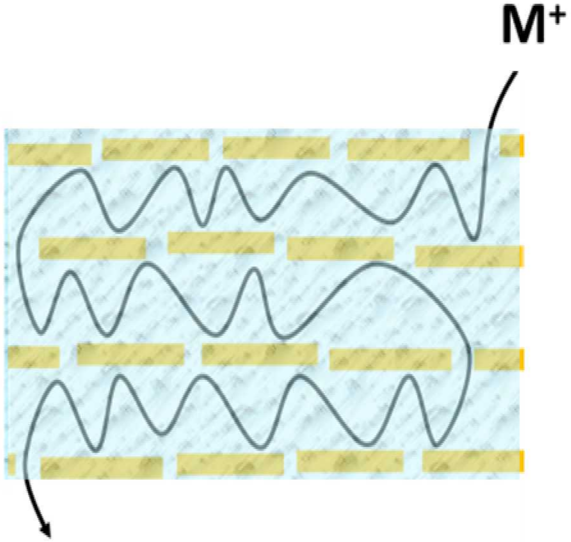
Although bilayers grow ”linearly” quadlayers grow in an “extra-linear” fashion, forming thick polymer layers near the top of the films.



Using PCN Films as Molecular Barriers







Gas barrier properties

EVA*: O_2 (90% RH): ~2000-10,000 cc/m^2/day
H_2O (RT): ~7 g/m^2 day

PCN thin films: 0.093 cc/m^2/day (100% RH)
H_2O (RT): ~0.65 g/m^2 day

*EVA Data based on reports from Dow Chemical (1998), Dupont (2001), and NREL (2008).

Cost: Commercial Montmorillonite (~$0.50/kg)
Commercial Polyethyleneimine ($1-10/kg)

50¢ of clay will cover ~2 soccer fields, 40 layers thick!

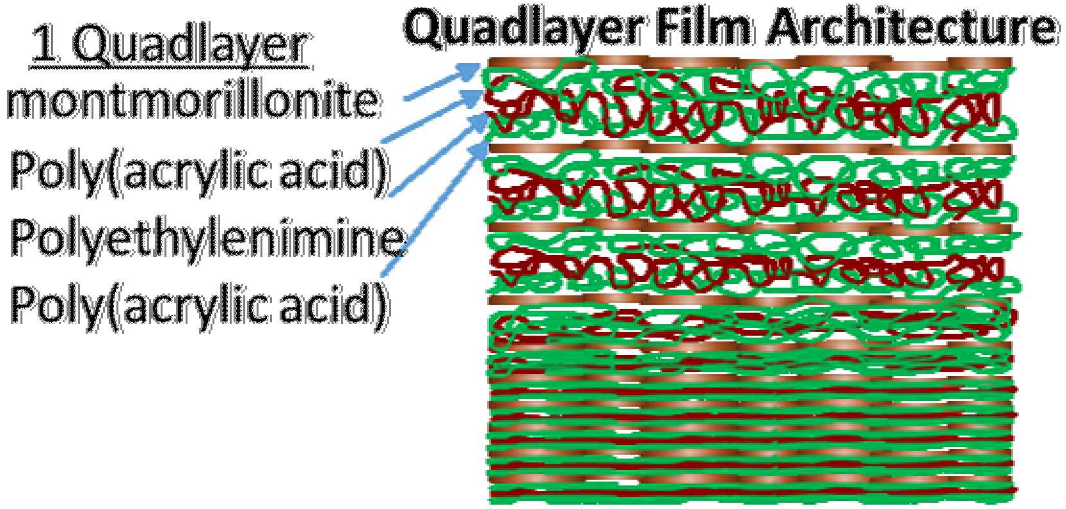
Atmospheric Corrosion Testing

Film preparation:

- Clean/Polish Cu coupons
- Deposit Quadlayer PCNs: 2, 6, 10QL and 10QL (no clay) with robot

Exposure Testing:

- Samples placed in a sulfidizing environment
    - 10 ppb H_2S gas
    - 70% RH at
    - 30°C
    - Up to 800 hours
- Corrosion Assessment
    - Samples visually inspected (quantification in progress)
    - Samples weighed (high resolution balance) to determine copper sulfide formation



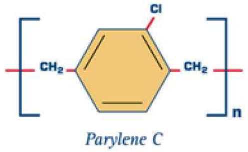
QL film architecture grown by alternating polyelectrolyte charges and montmorillonite clay.

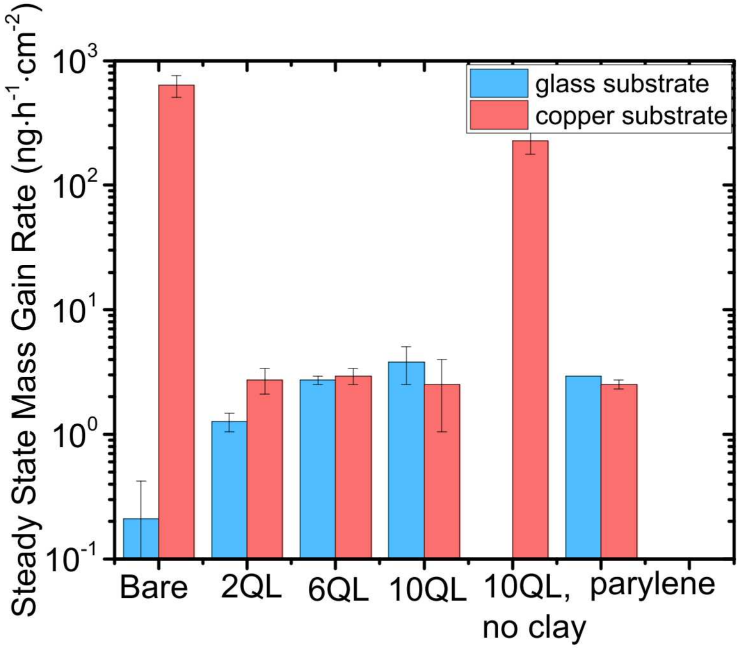
PCNs Form Effective Atmospheric Corrosion Barriers

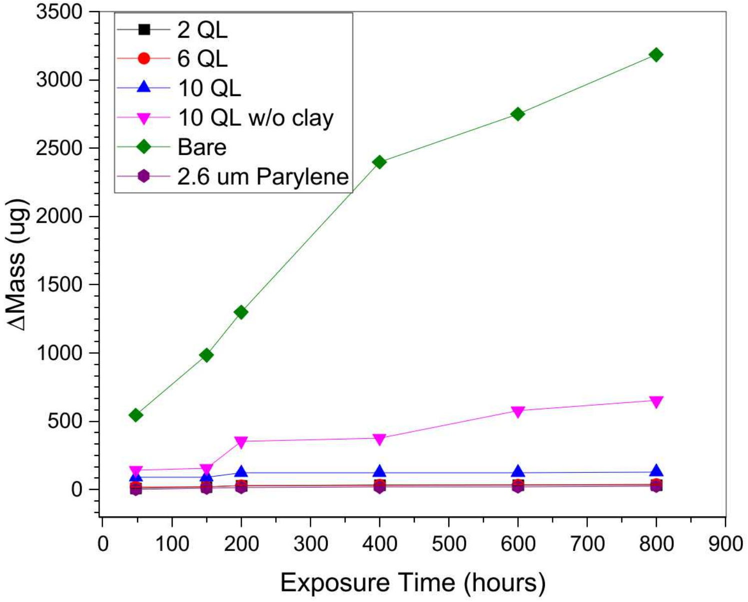
Copper coupons were coated with quadlayer PCNs and exposed to an aggressive H_2S-based corrosive atmosphere. Visual analysis and quantitative mass gain (from CuS_x) formation PCN coatings are as effective or *more effective than thicker parylene* coatings.

Incorporation of clay in the coating is vital to film integrity and performance.

Copper coupon appearance after 800 hours exposure to corrosive H_2S environment.





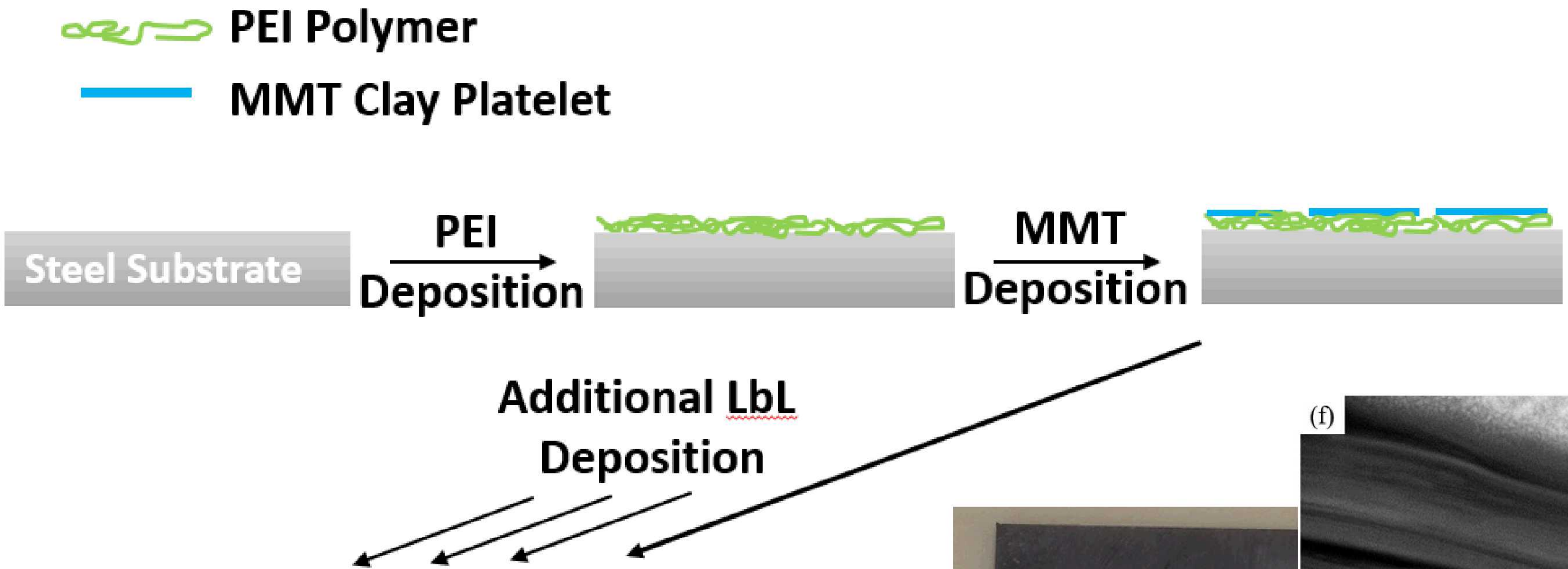


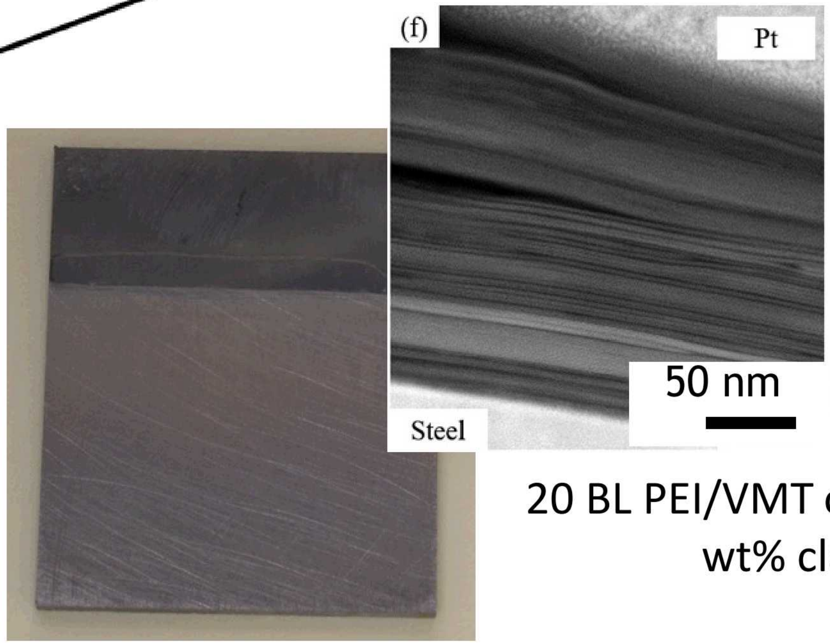
Schindelholz and Spoerke, et al. (2018) *ACS Appl. Mater. & Interfaces*. **10** (26) 21799-21803.

What About Immersion Corrosion?

http://www.lovethesepics.com/2012/09/48-eerily-intriguing-shipwrecks/

Consider Corrosion of Steel in Saline

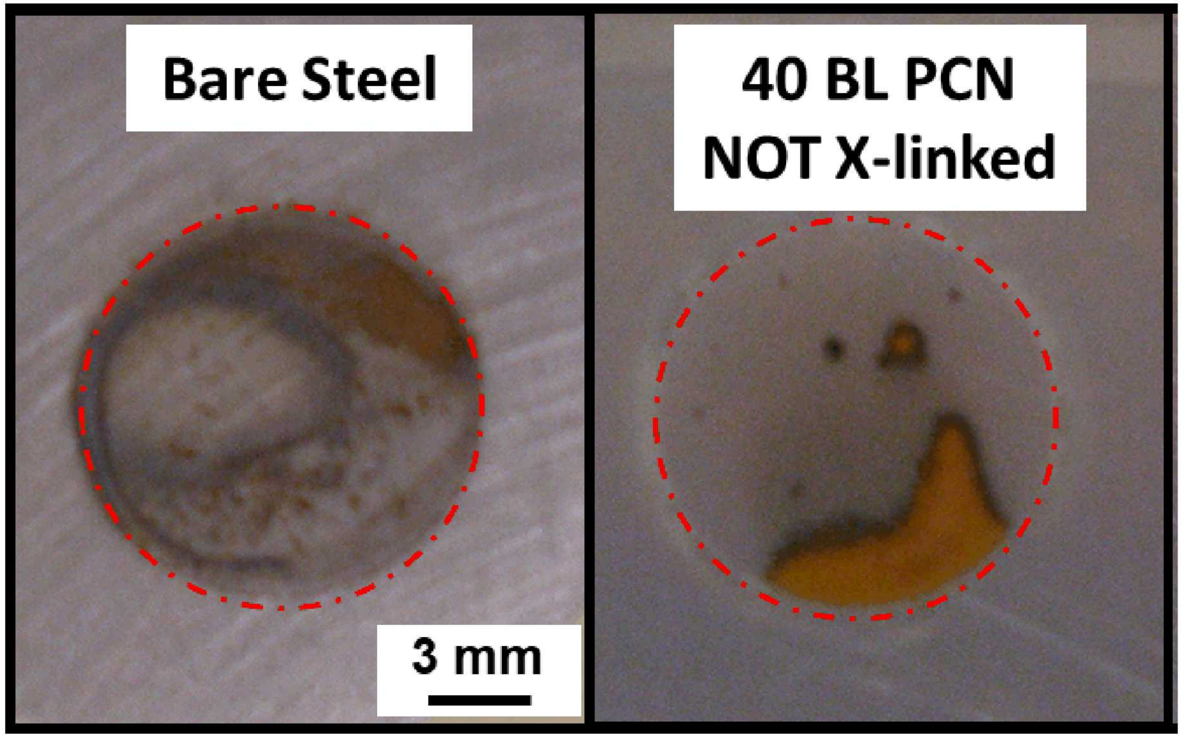




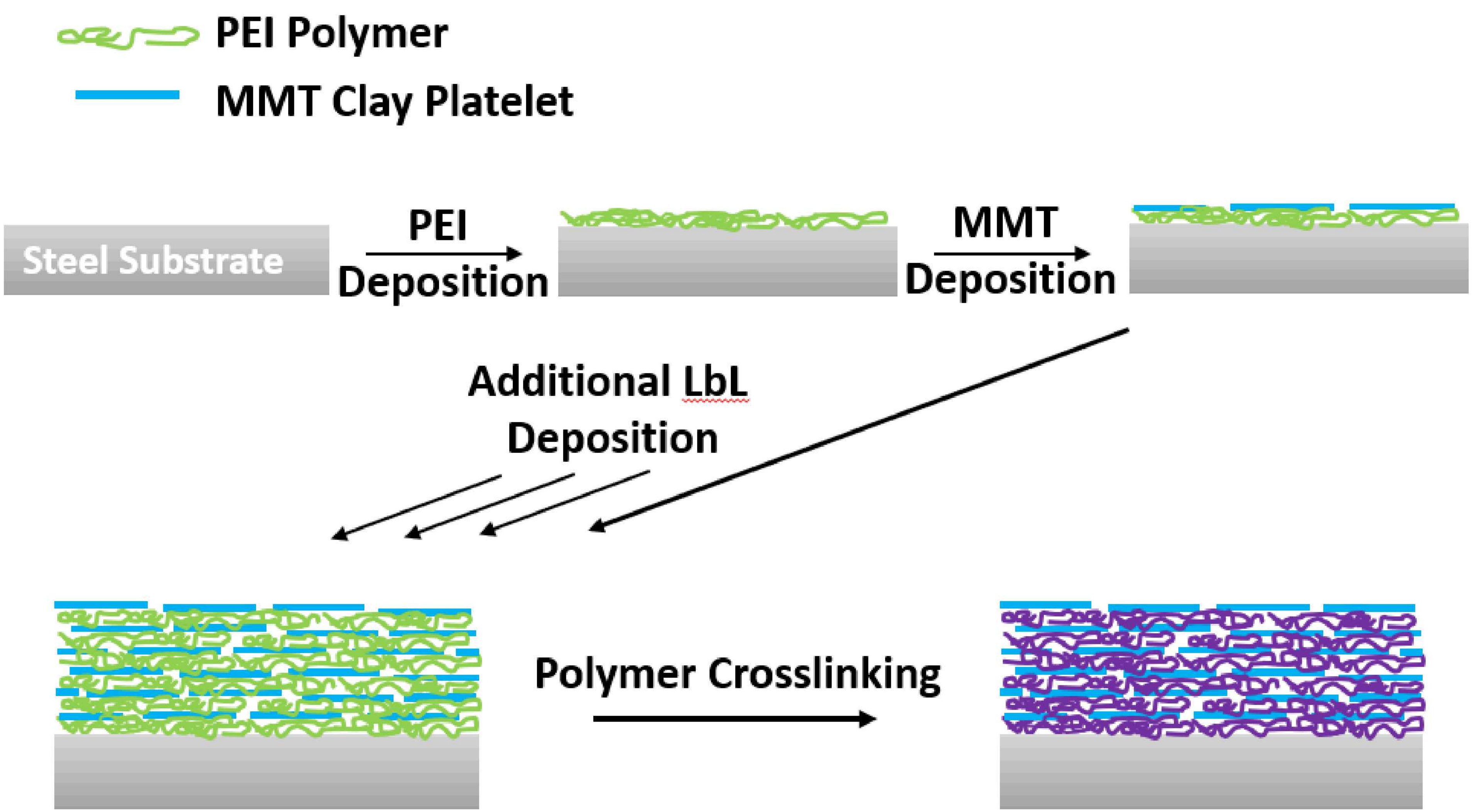
20 BL PEI/VMT on steel, 96 wt% clay

Percival, Spoerke, Melia, Schindelholz, et al., In Review.

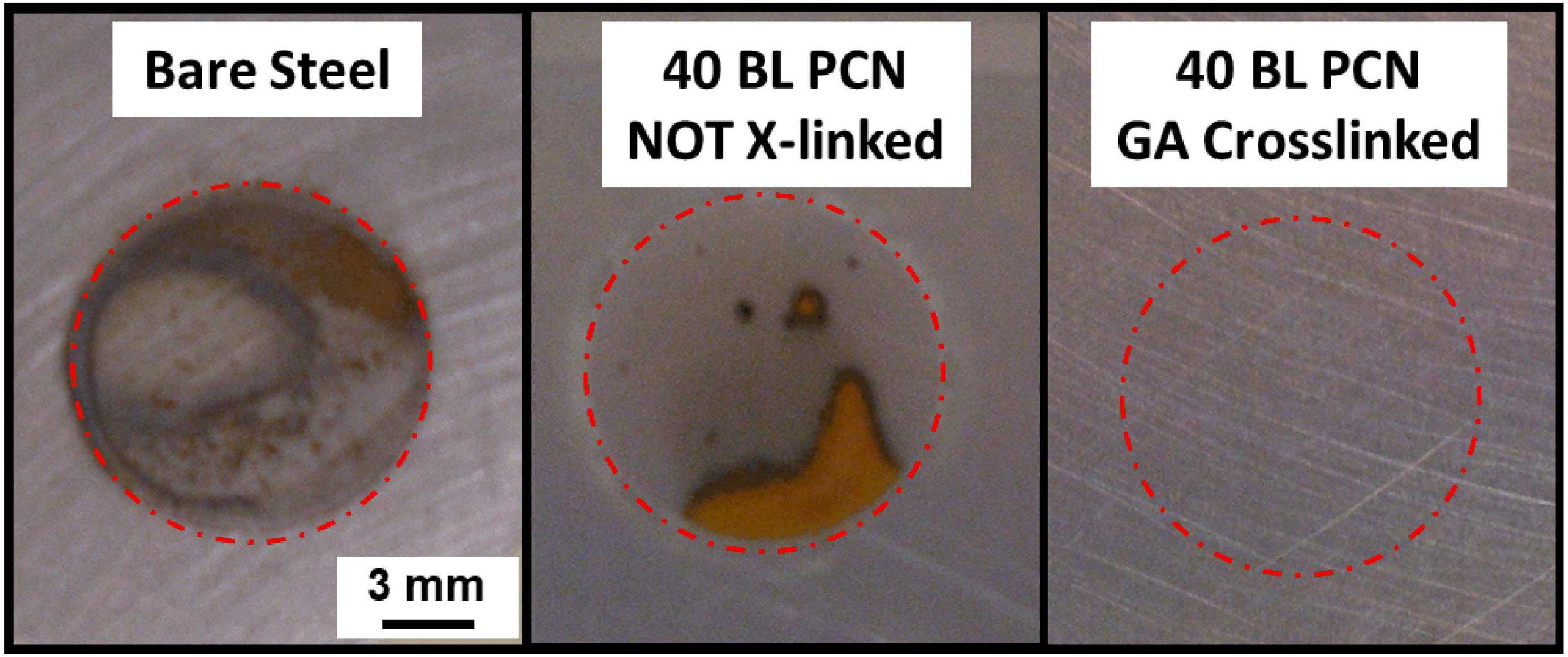
Corrosion Inhibition?



Crosslinking the Polymeric Component of PCN Barrier

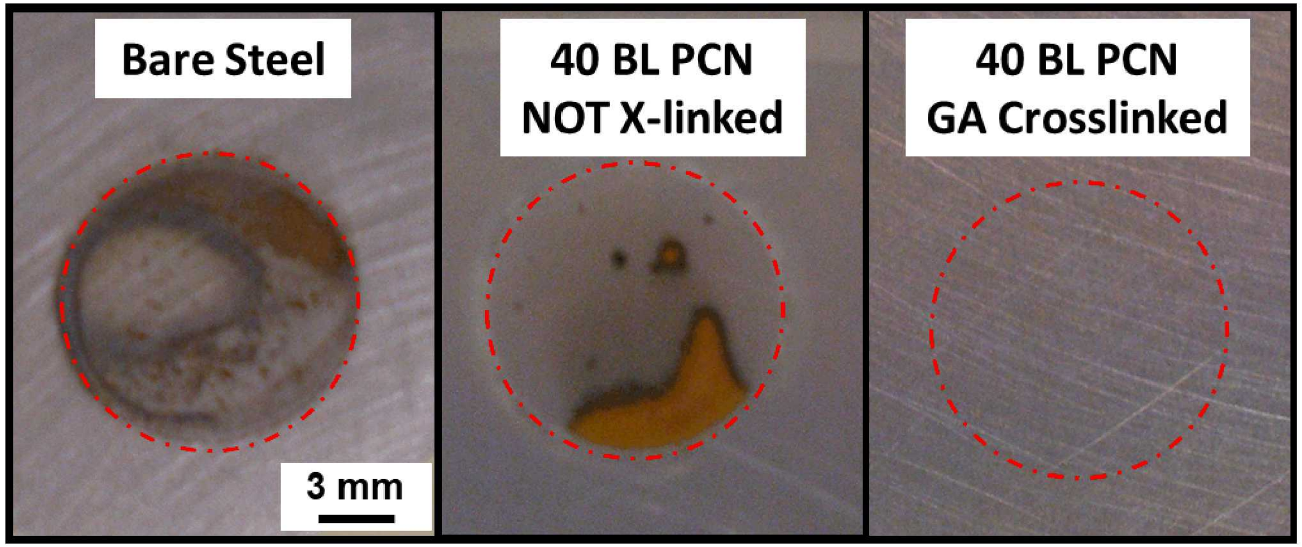


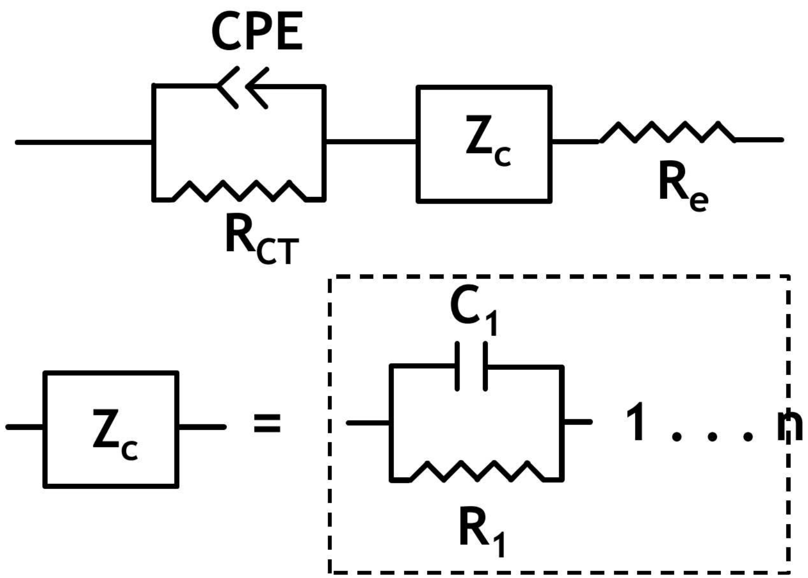
Corrosion Inhibition!

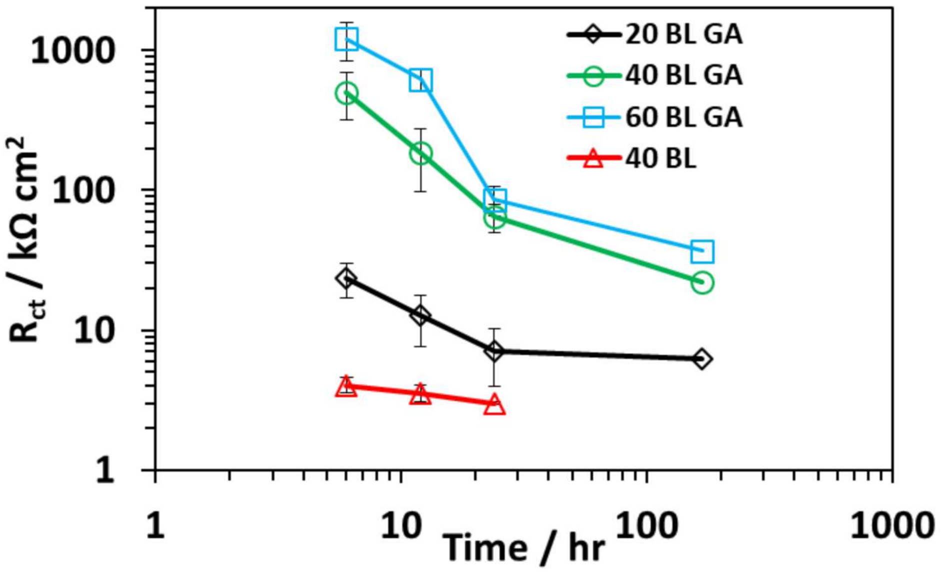


Percival and Spoerke, et al., In Review.

Corrosion Inhibition!

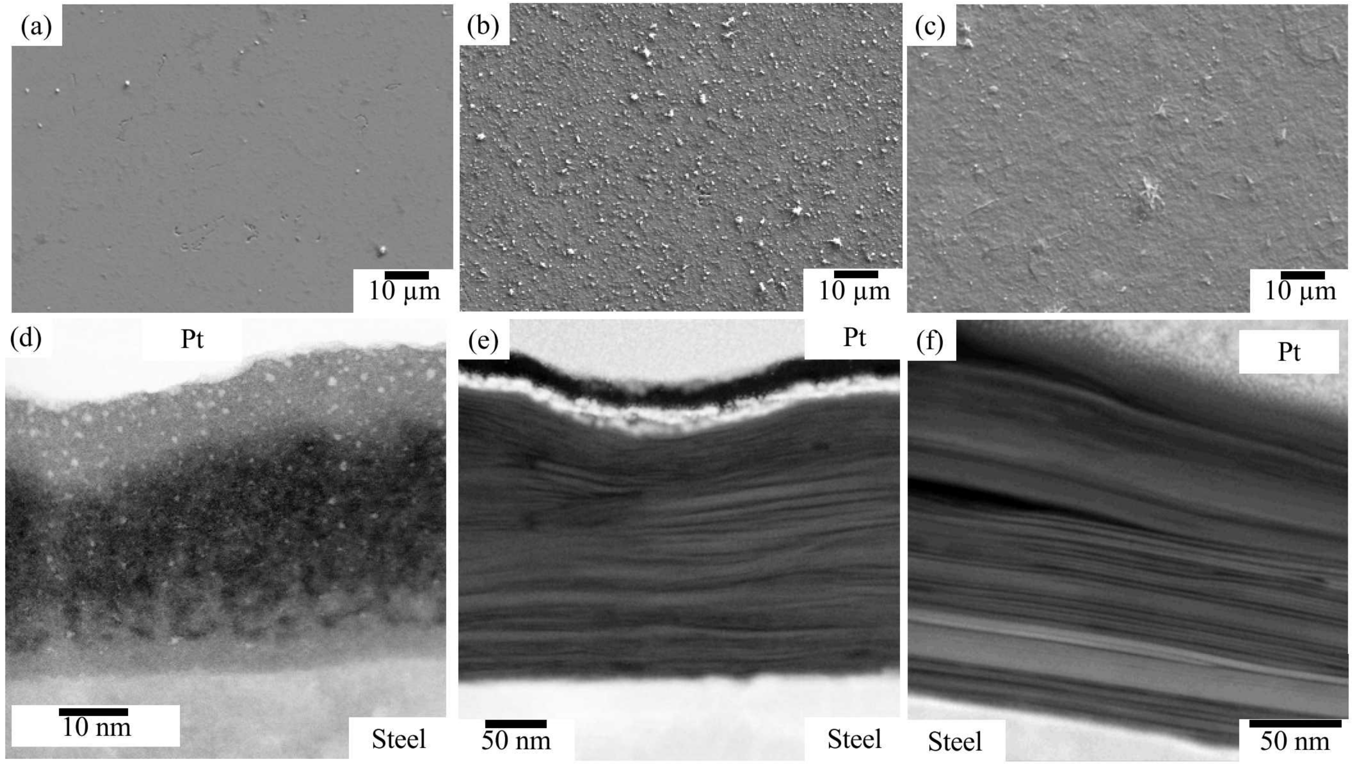




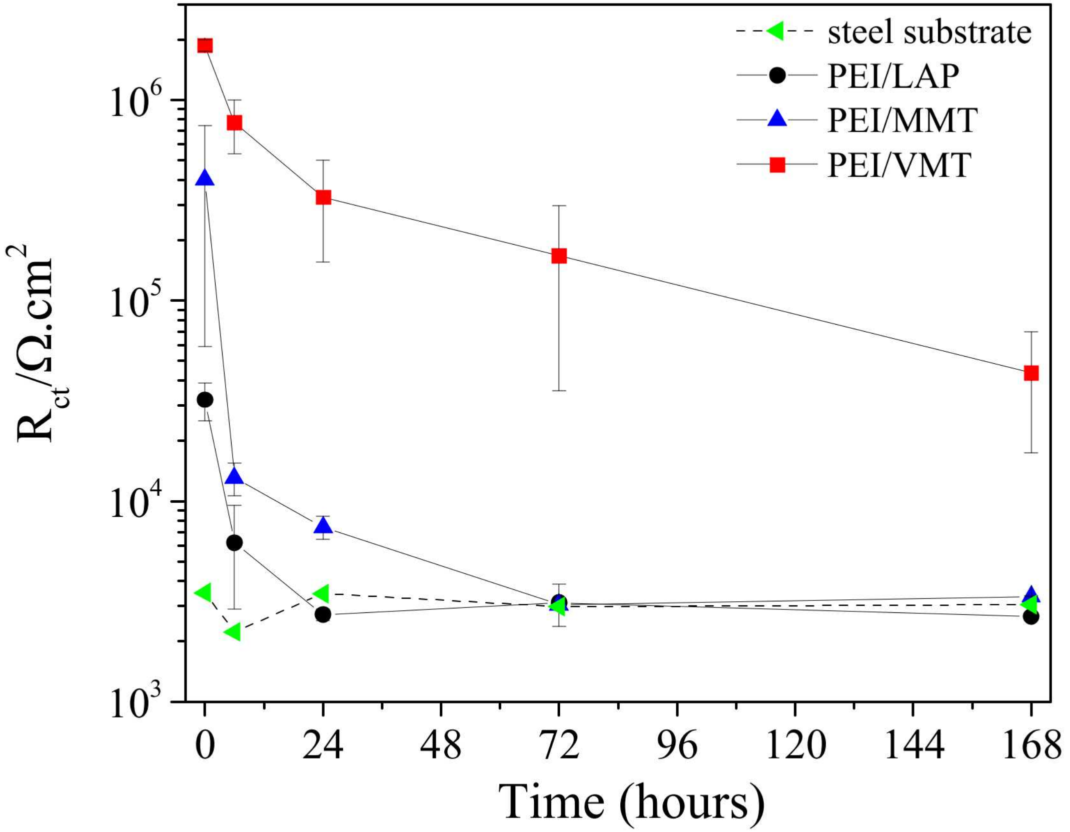


Percival and Spoerke, et al., In Review.

Modifying Performance with Clay Aspect Ratio



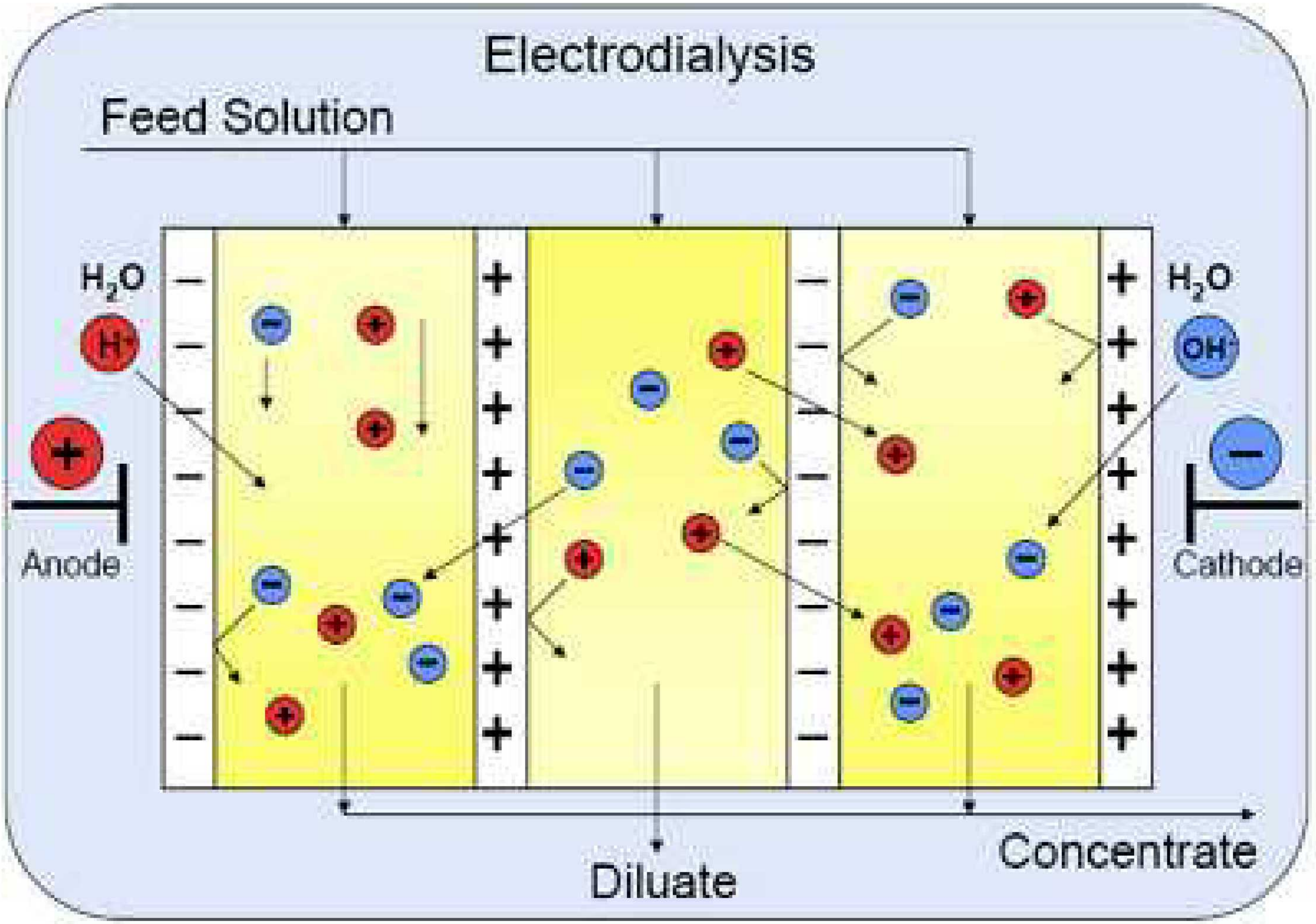
Upper row are secondary electron images of the surface for as-deposited 20 BL (a) PEI/LAP, (b) PEI/MMT, and (c) PEI/VMT. Bottom row are MAADF STEM images of the same films in cross-section, showing the layered structures for (d) PEI/LAP, (e) PEI/MMT, and (f) PEI/VMT. The light grey bands in the cross-sections, especially apparent in (e) and (f), are the clay layers, while the associated dark bands are the polymer.



Charge transfer resistance, R_{ct}, as a function of immersion time in 0.6 M NaCl for coated and uncoated steel plates. The error bars represent min and max values of R_{ct} for each time of immersion.

Consider Electrodialysis

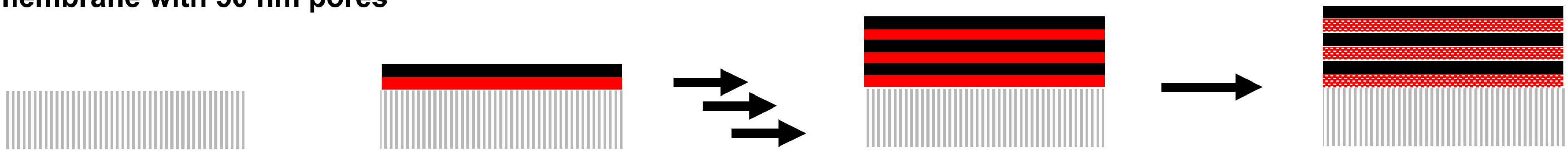
- ***Electrodialysis is an industrial-scale technique used to purify water where a DC electric field drives dissolved ions across ion-selective membranes to create a purified water stream.***
- ***Key membrane properties include: <u>ionic conductivity,</u> <u>ionic selectivity</u> and <u>materials cost.</u>***



www.fumatech.com/EN/Membrane-processes/Process%2Bdescription/Electrodialysis/index.html

Layer-by-Layer Deposition of Polyelectrolytes for Ion Separation

Ion-tracked polycarbonate (PC) membrane with 50 nm pores

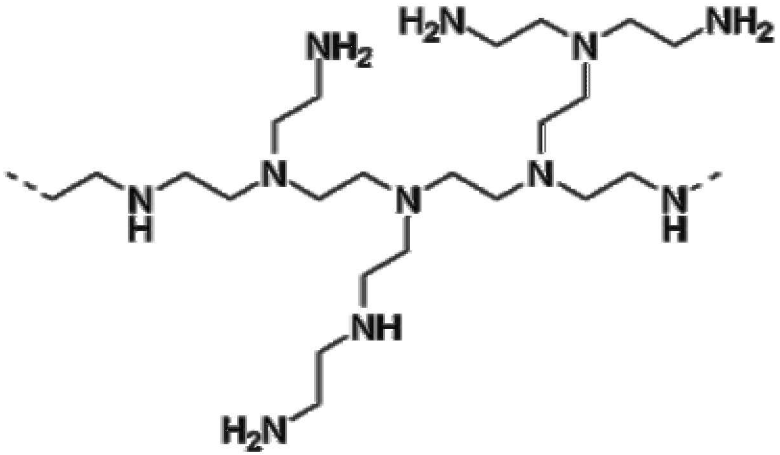


Dip coat PEI then PAA

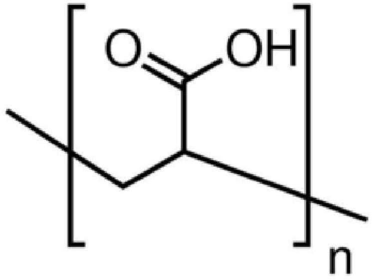
1 bilayer (BL)

Additional LbL Assembly

Crosslink films with Glutaraldehyde (GA)



PEI

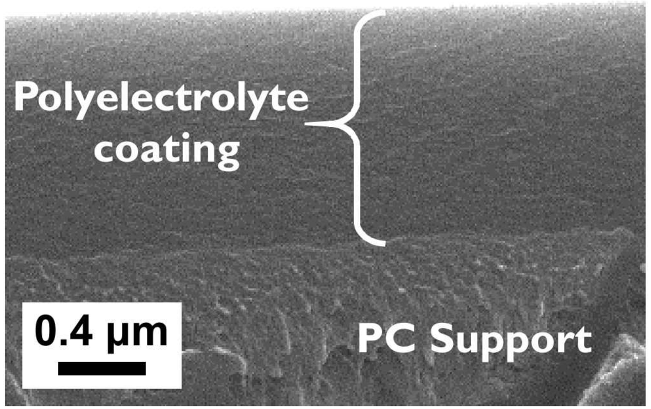


PAA

Percival, S.J., et al. *RSC Advances, (*2018), ***8**,* 32992-32999.

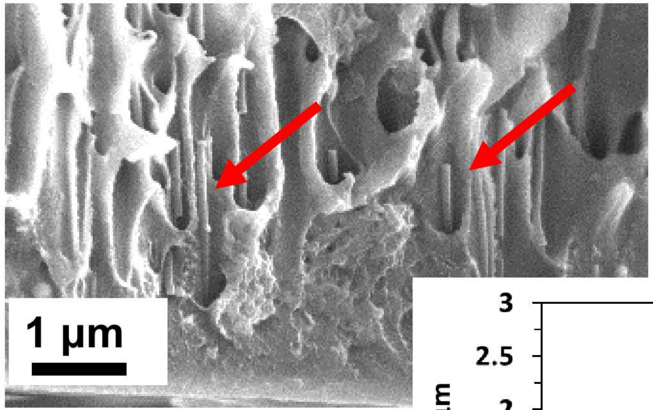
Visualizing Multilayered Polyelectrolytes

5 BL GA Crosslinked

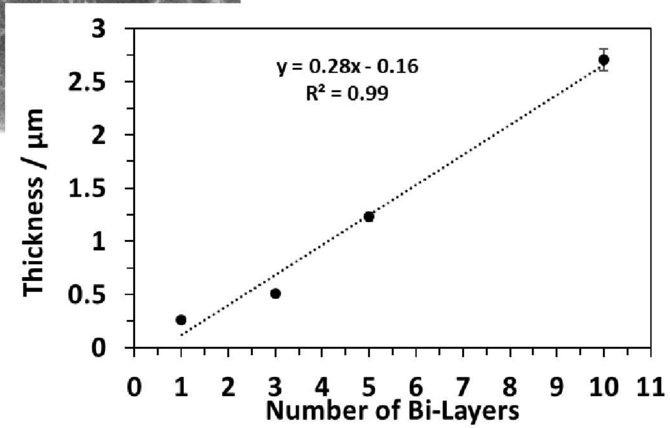


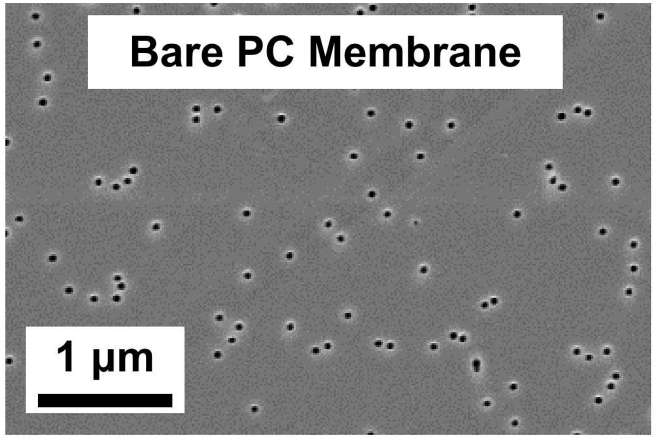
SEM micrographs reveal poor coverage on films either not crosslinked or 1 BL thick. Uniform film morphology on crosslinked 3, 5 and 10 BLs.

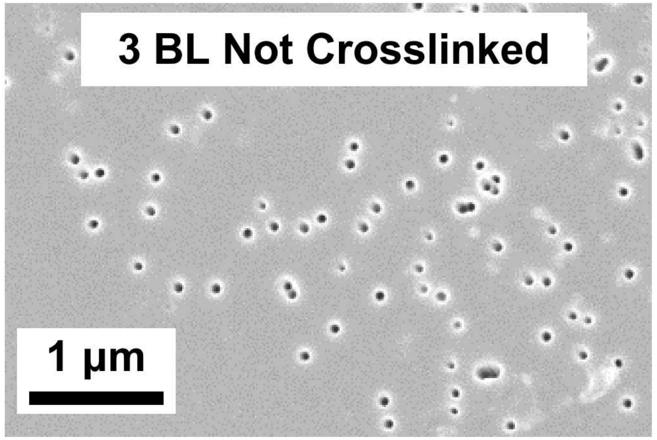
Cross sectional SEM images used to show polyelectrolyte thickness increases with number of applied bilayers.

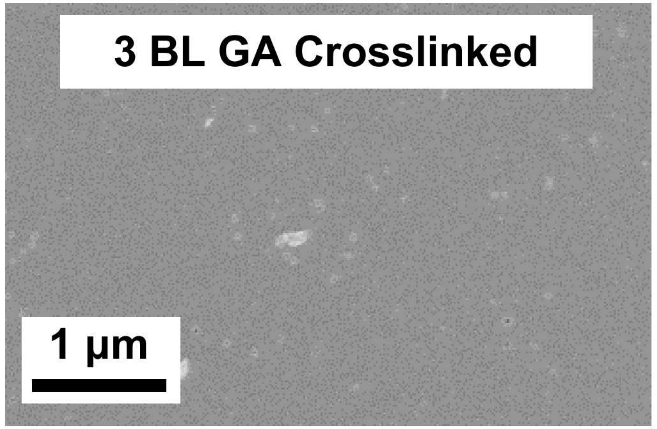


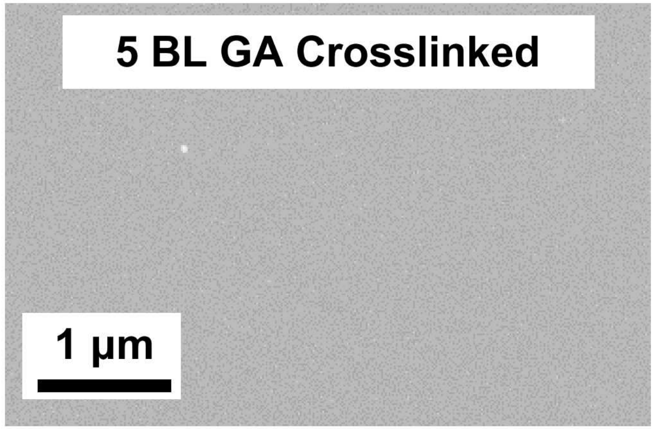
Polyelectrolyte pore filling observed inside nanopores.



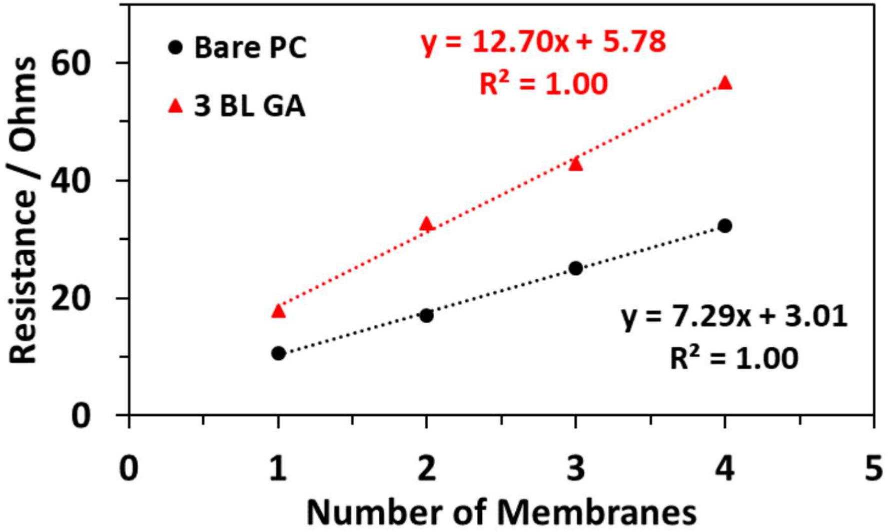




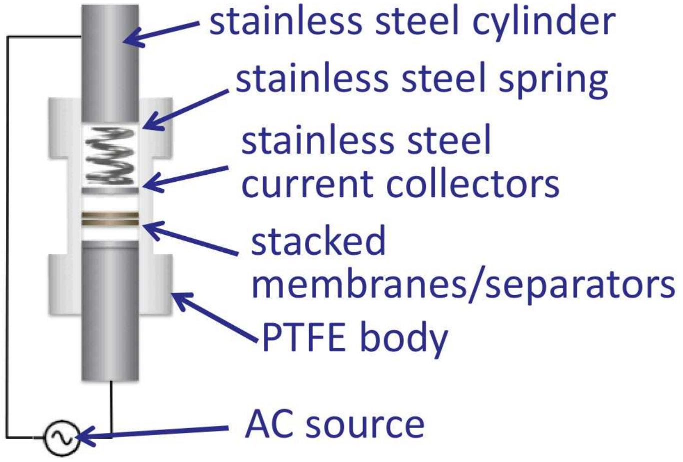


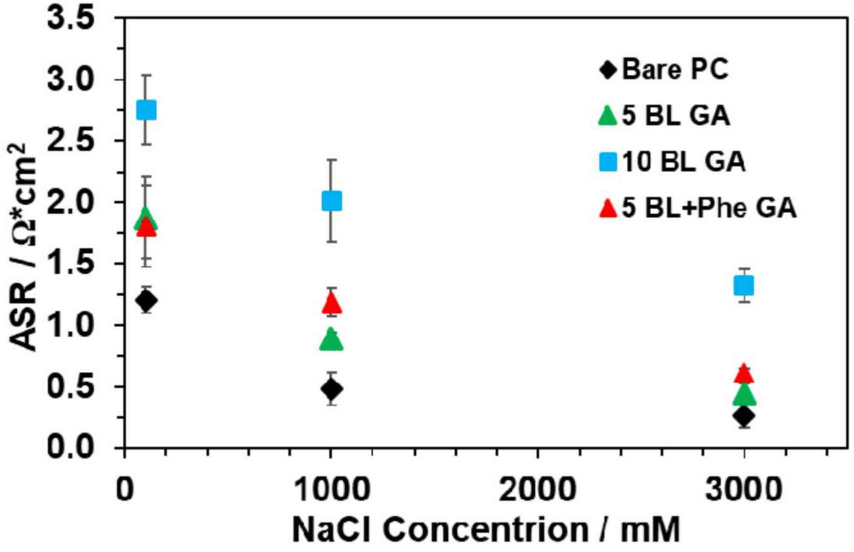


Membrane Ionic Resistance



1-4 membranes were stacked in a Swagelok style cell and resistance measured in different ionic strength NaCl solutions.





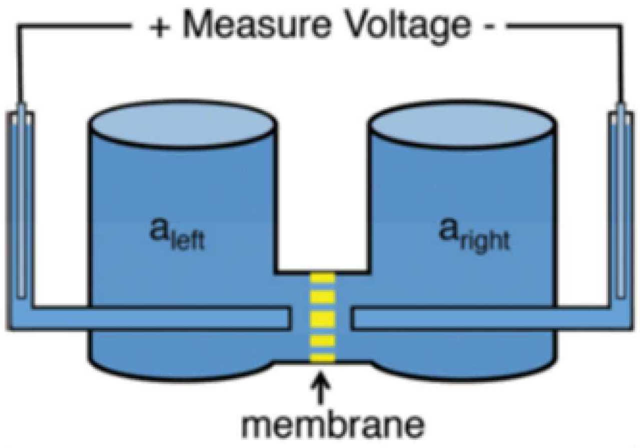
Polyelectrolyte increased Area Specific Resistance (ASR) compared to bare PC.

Thicker polyelectrolyte further increases the ASR.

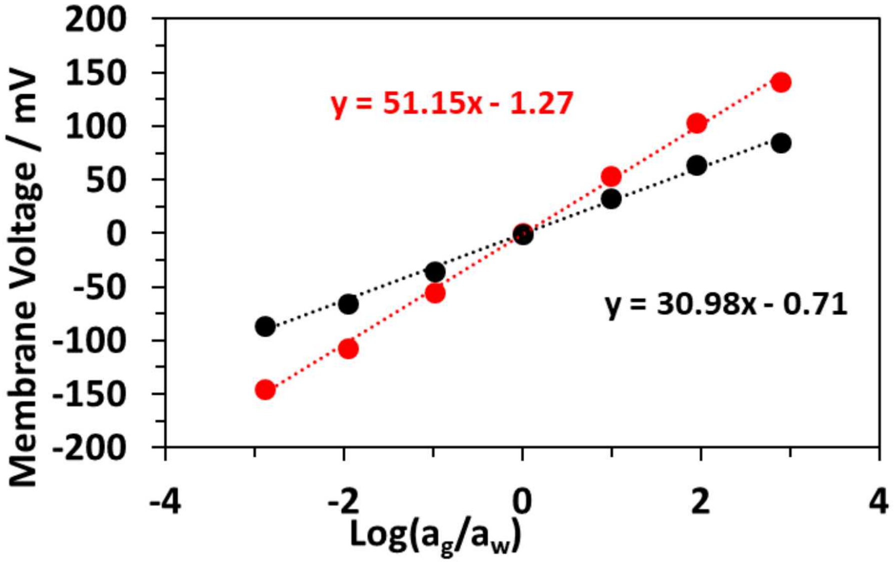
ASR shows little change with amino acid additives.

ASR for polyelectrolyte modified films are on par or lower than commercial ion exchange membranes (~1-2 Ω*cm^2 in 1 M NaCl).

Determining Transmembrane Ionic Selectivity



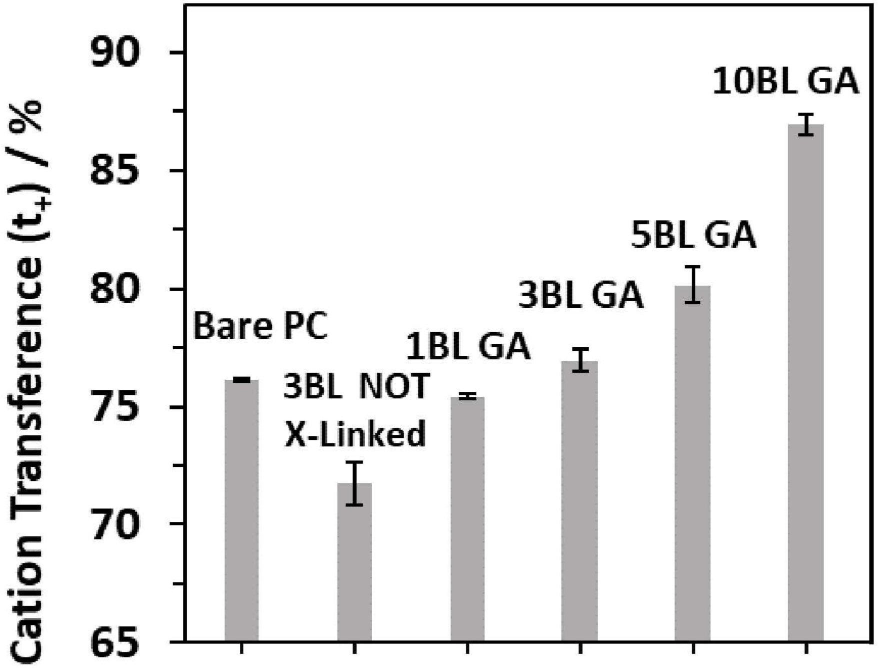
$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$



Cation transference number (t_+) calculated by measuring the potential difference when the membrane separates different NaCl concentrations. Higher slope indicates higher cation selectivity.

Demonstrating Ionic Selectivity of LbL Polyelectrolytes

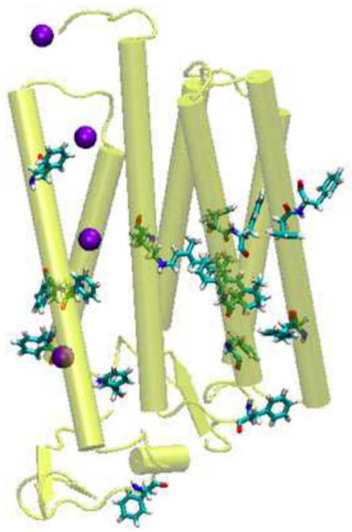
Increasing number of bilayers results in increasingly cation-selective transport, and crosslinking is critical to retaining selectivity.

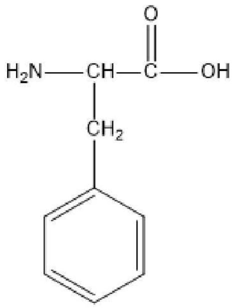


Demonstrating Ionic Selectivity of LbL Polyelectrolytes

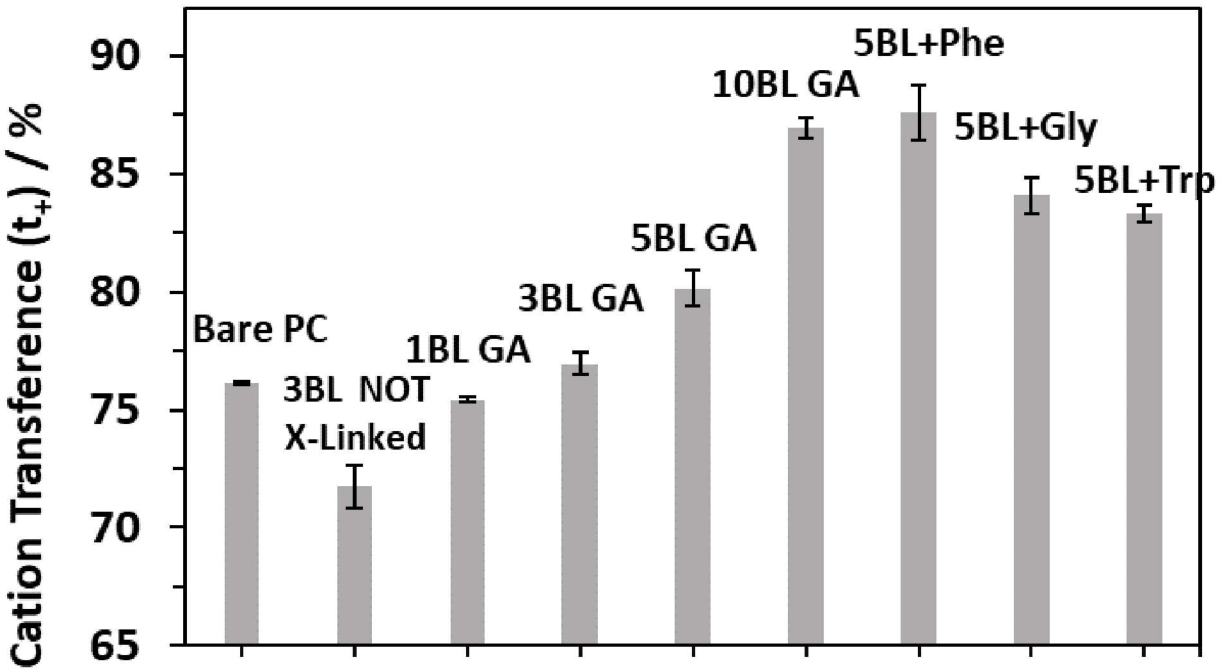
Increasing number of bilayers results in increasingly cation-selective transport, and crosslinking is critical to retaining selectivity.

Addition of bio-inspired amino acid additives significantly increases the selectivity without increasing thickness.





Phenylalanine (Phe)



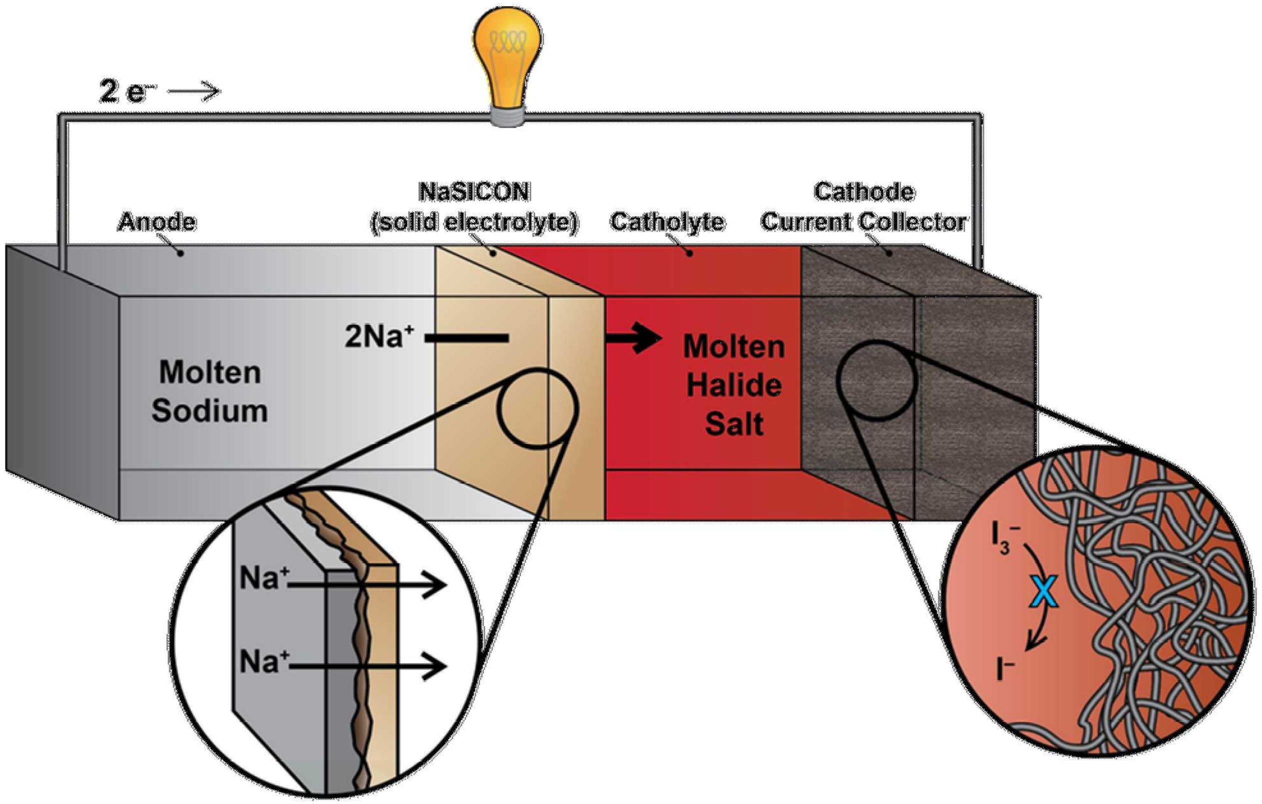
Na^+ (purple) transport in biological ion channels is facilitated by phenylalanine (blue) in channelrhodopsin chimera C1C2.

Low Temperature Molten Sodium (Na-NaI) Batteries

Realizing a new, low temperature molten Na battery requires new battery materials and chemistries.

Ingredients for Success

- Molten Na anode
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)
- 25 mol% NaI in AlX_3 catholyte
- *No complications from solid state electrodes!*



Na-NaI battery:

$Na \rightarrow Na^+ + e^-$ $E^0 = 0V$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

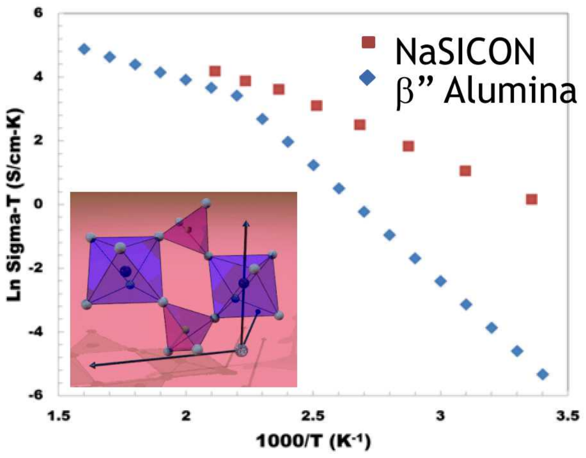
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

Martha Gross

NaSICON Separator

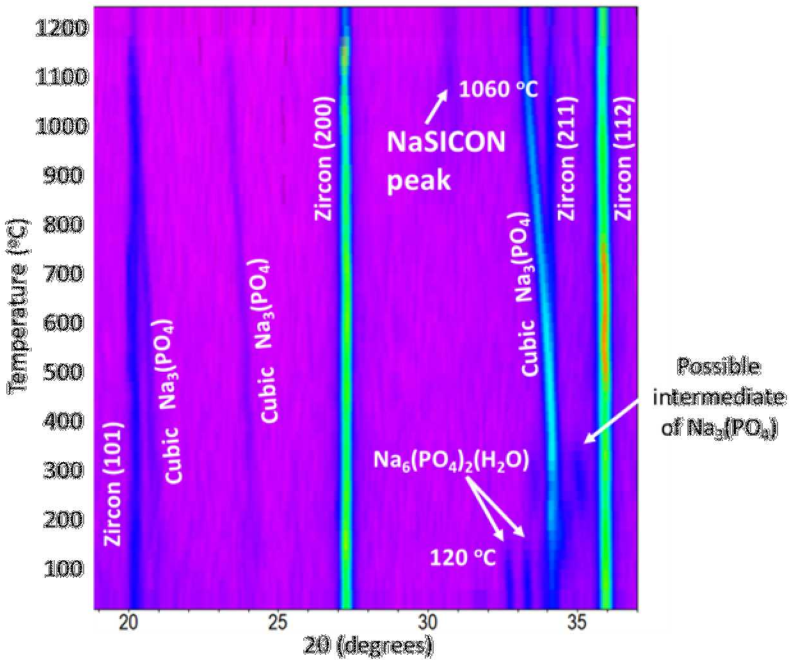
Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>10^{-3} S/cm at 25°C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover



NaSICON calcined to remove hydrates, sintered at 1230°C, yields >94% density and >0.4 mS/cm at 25°C.

These ceramics are suitable for lab-scale testing of molten sodium batteries.



- VTXRD shows conversion of Zircon and cubic $Na_3(PO_4)$ to NaSICON starting near 1100°C
- Hydrate form of $Na_3(PO_4)$ up to 120°C, converts to cubic $Na_3(PO_4)$ at ~300°C.

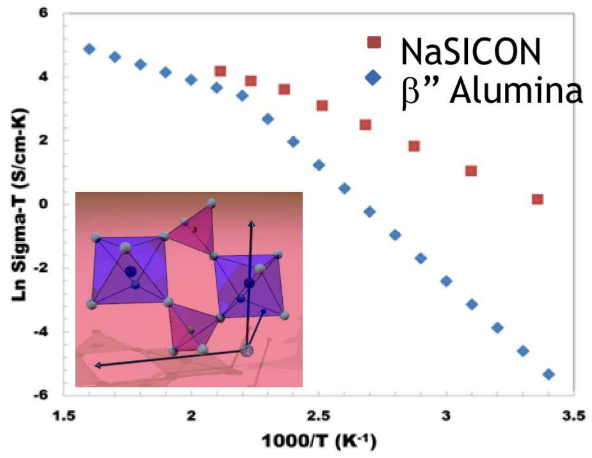
NaSICON Separator

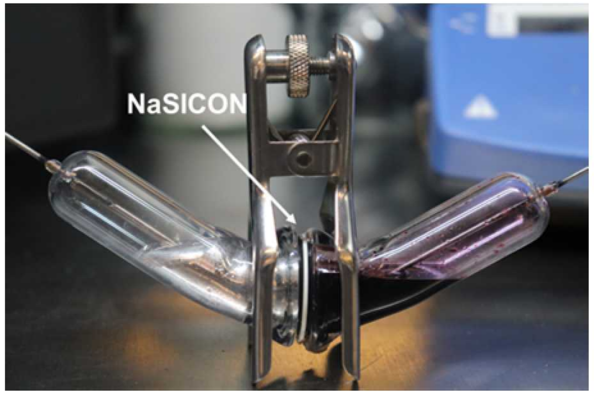
Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>10^{-3} S/cm at 25^{o}C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover

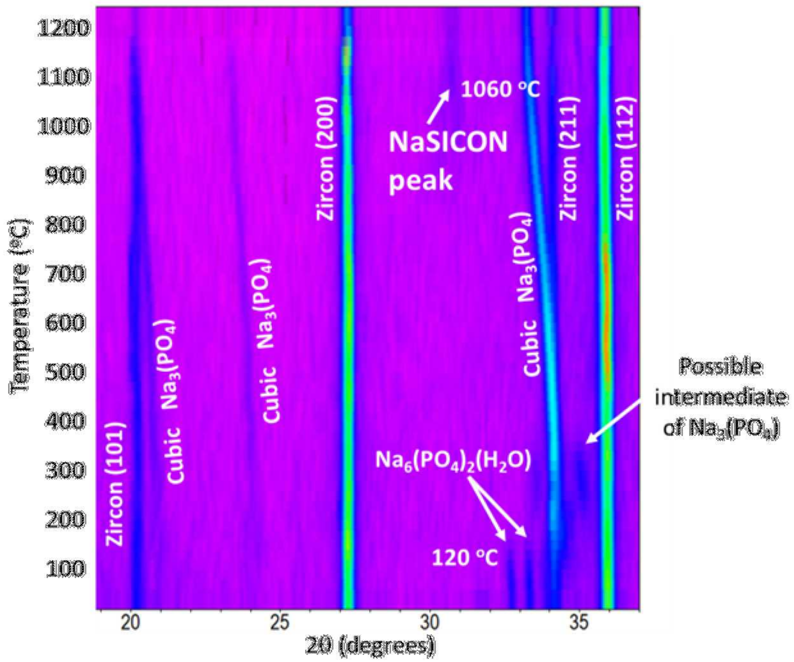
NaSICON calcined to remove hydrates, sintered at 1230°C, yields >94% density and >0.4 mS/cm at 25°C.

These ceramics are suitable for lab-scale testing of molten sodium batteries.





Molten Na Battery Cell Set-Up



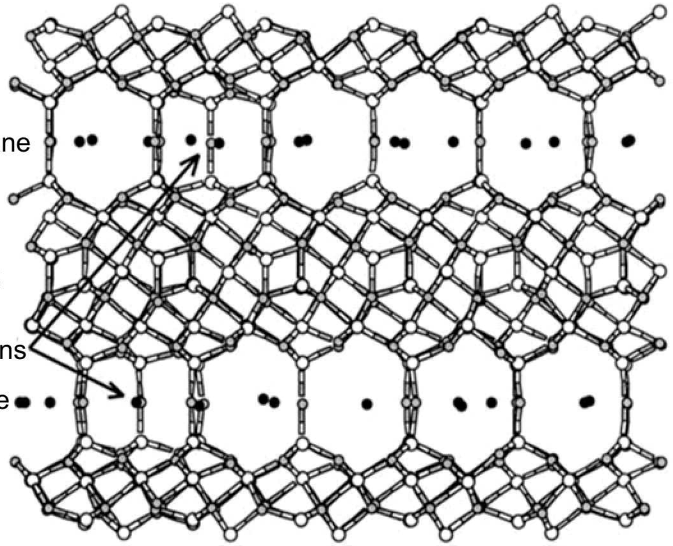
- VTXRD shows conversion of Zircon and cubic $Na_3(PO_4)$ to NaSICON starting near 1100°C
- Hydrate form of $Na_3(PO_4)$ up to 120^{o}C, converts to cubic $Na_3(PO_4)$ at ~300^{o}C.

An Alternative Solid State Separator?

Goal: Identify new, highly conductive, low cost sodium ion conductors for energy storage applications.

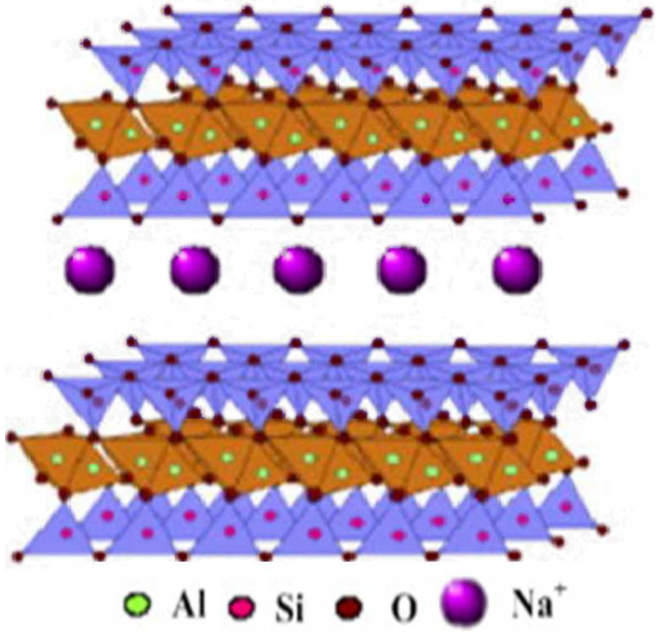
In the known Na-ion conductor β”-Al_2O_3, Na^+ conduction follows ordered conduction planes.

The ordered layers in low-cost montmorillonite (MMT) clay create similar Na-rich conduction planes.



Beckers, van der Bent, and Leeuw. *Solid State Ionics* **133**(3-4)(2000), p217-231.

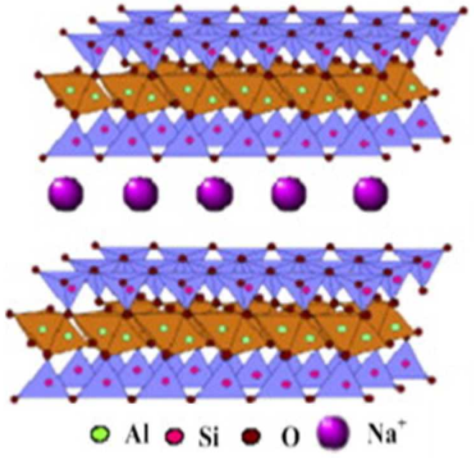
Challenge: Can we utilize MMT to create a low cost Na^+ ion conductor?

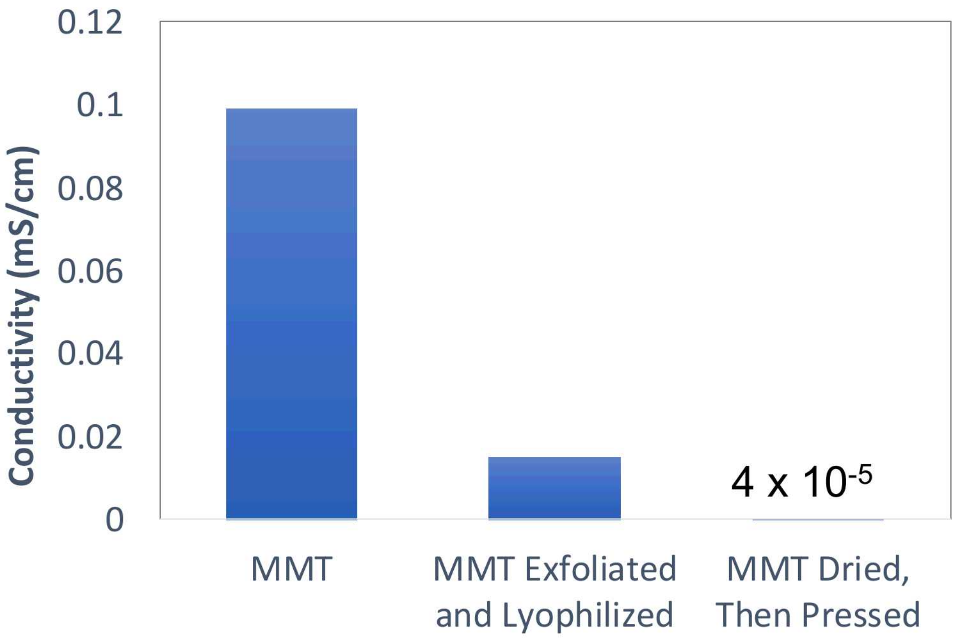


Motawie, *et al. Egypt. J. Petroleum* **23**(3) (2014), p331-338.

"Kitty Litter Konductors"

- MMT can be pressed into pellets with excellent ionic conductivity! (~ 0.1 mS/cm)
- The layered structure of the clays plays a key role Na^+ mobility through the separator..
- H_2O content increases conductivity of composite.

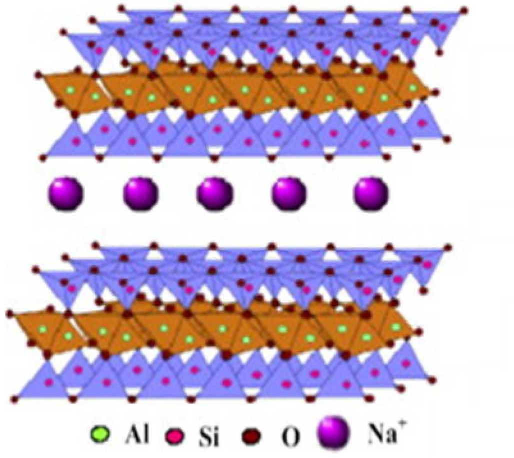


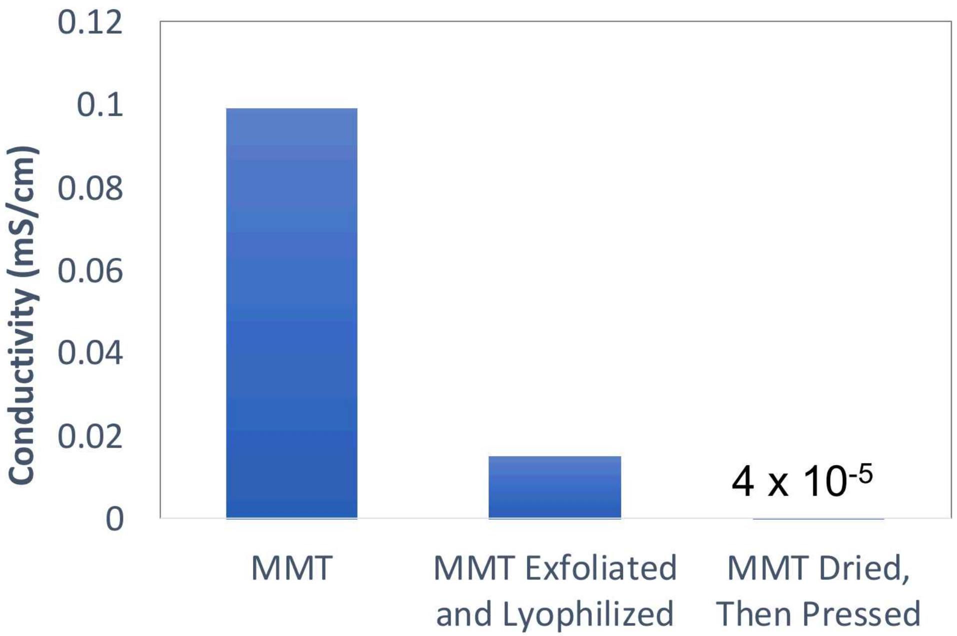


MMT Pellet (1")

"Kitty Litter Konductors"

- MMT can be pressed into pellets with excellent ionic conductivity! (~ 0.1 mS/cm)
- The layered structure of the clays plays a key role Na^+ mobility through the separator..
- H_2O content increases conductivity of composite.
- MMT can be fragile, though!





MMT Pellet (1")

Broken MMT Pellet

Creating MTT-Based Composites

Can we integrate MMT into a composite with high conductivity and improved mechanical integrity?

Initial Composite Assessment

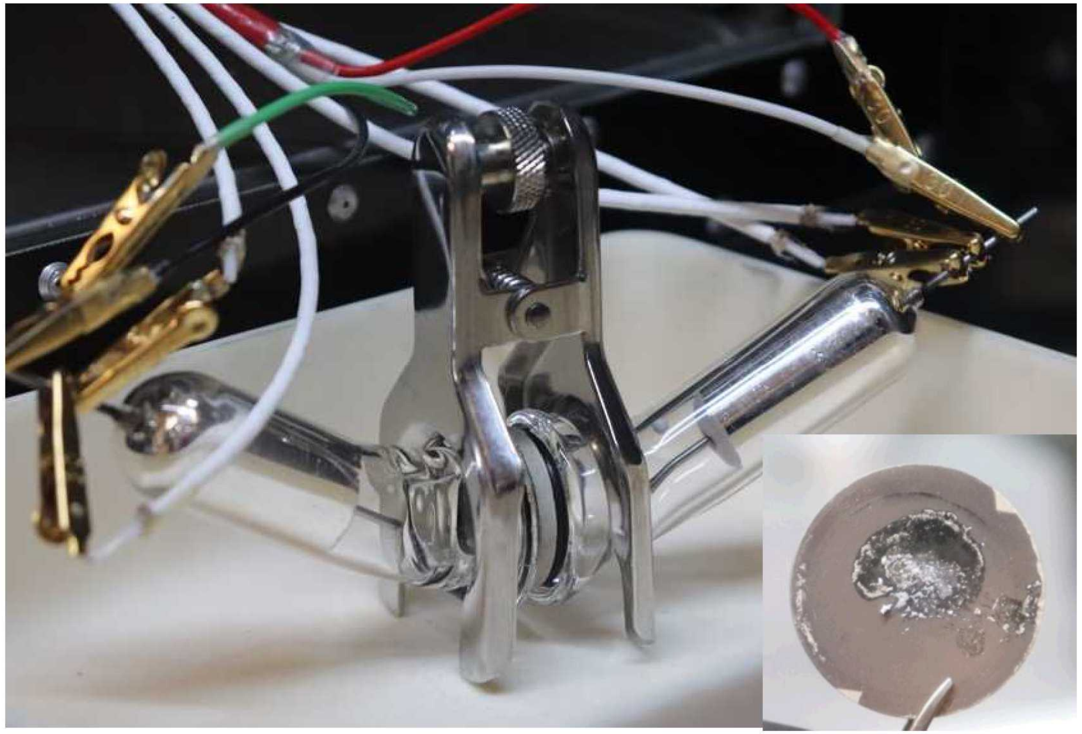
	σ (S/cm)	Qualitative Mechanical Properties
MMT	1×10^{-4}	Brittle, breaks with little effort
MMT: PE-block-PEG (1:1)	9×10^{-11}	Soft, crumbly
MMT:PEG (1:1)	5×10^{-8}	Pliable, but crumbly
MMT: PEG:NaTFSI (1:1:0.05)	4×10^{-6}	Pliable, but crumbly
MMT pressed at 150°C	5×10^{-5}	Very fragile
MMT: HDPE (3% HDPE, 150°C)	6×10^{-5}	Rigid and stronger

Adding a small amount of HDPE *significantly improves pellet integrity*, without significant impact to conductivity, beyond what is normally degraded by heating to 150°C.

- Doping with sodium trifluoromethanesulfonimide (NaTFSI) can recover some of the conductivity lost through addition of insulating polymer matrix.
- Low temperature, functional polymers (e.g., PEG), do not significantly improve pellet integrity and are not suitable for molten Na-batteries, but inform composite design.

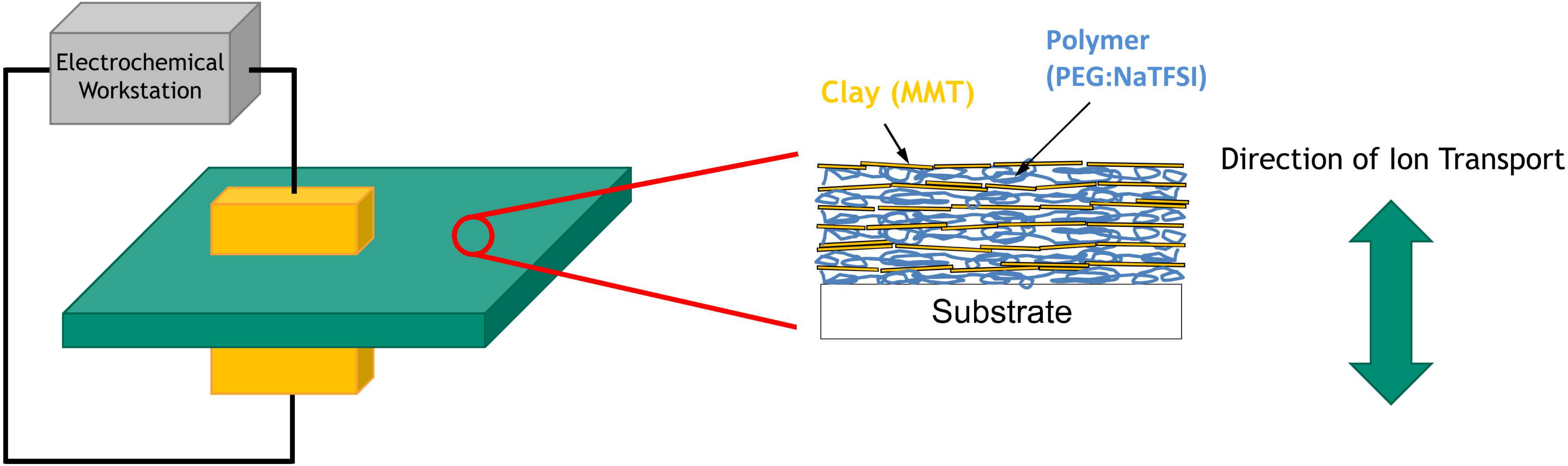
Are These Useful?

- Alternatively, increasing pellet thickness and application of protective surface coatings stabilize MMT pellets for battery testing.
- Initial tests show promise, but reveal high impedance across separator interfaces with Na.



Symmetric molten Na cell with MMT separator (w/ Sn-based coating). Inset: separator after test.

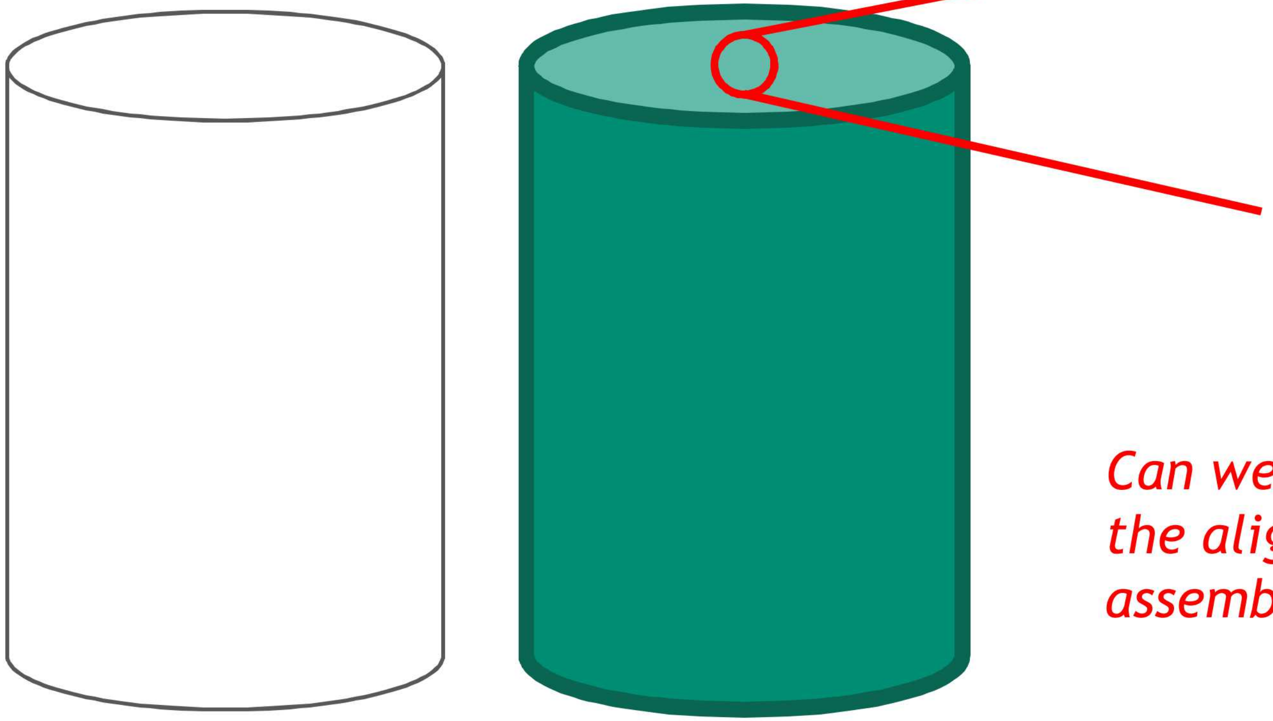
"Through Plane" Ionic Conduction in Clay Composites

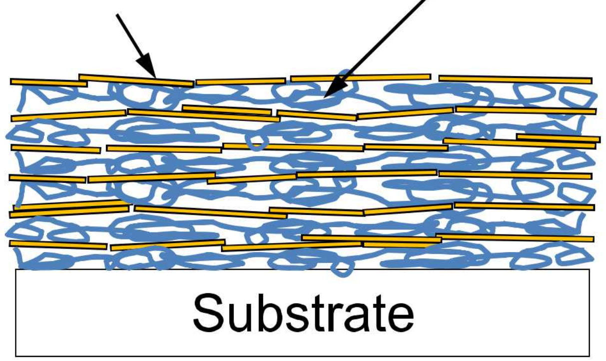


Conductivity measures ~10^{-10} S/cm. Poor conductivity is inconsistent with

"In-Plane" Ionic Conductivity

Longitudinal Coating

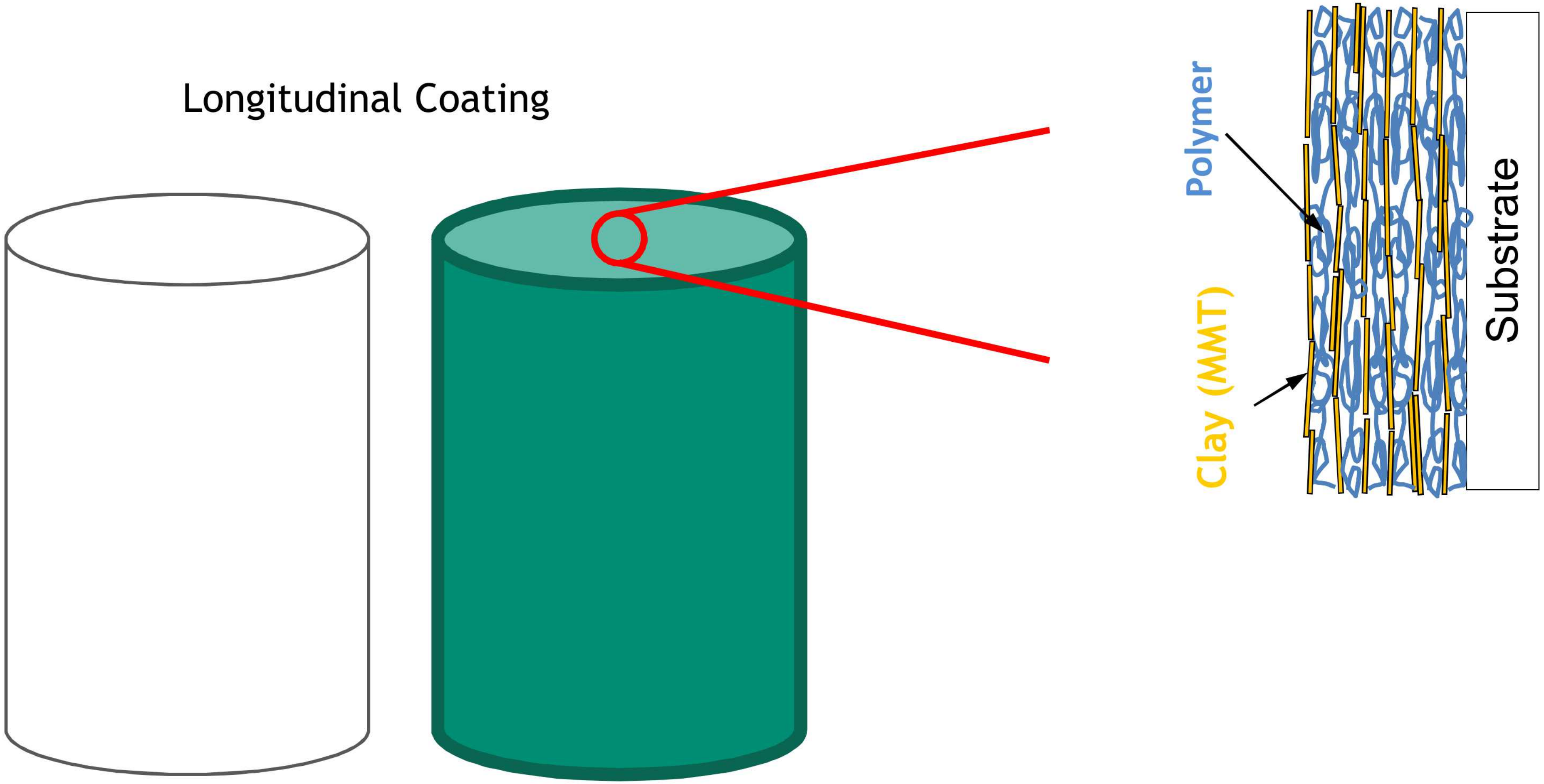




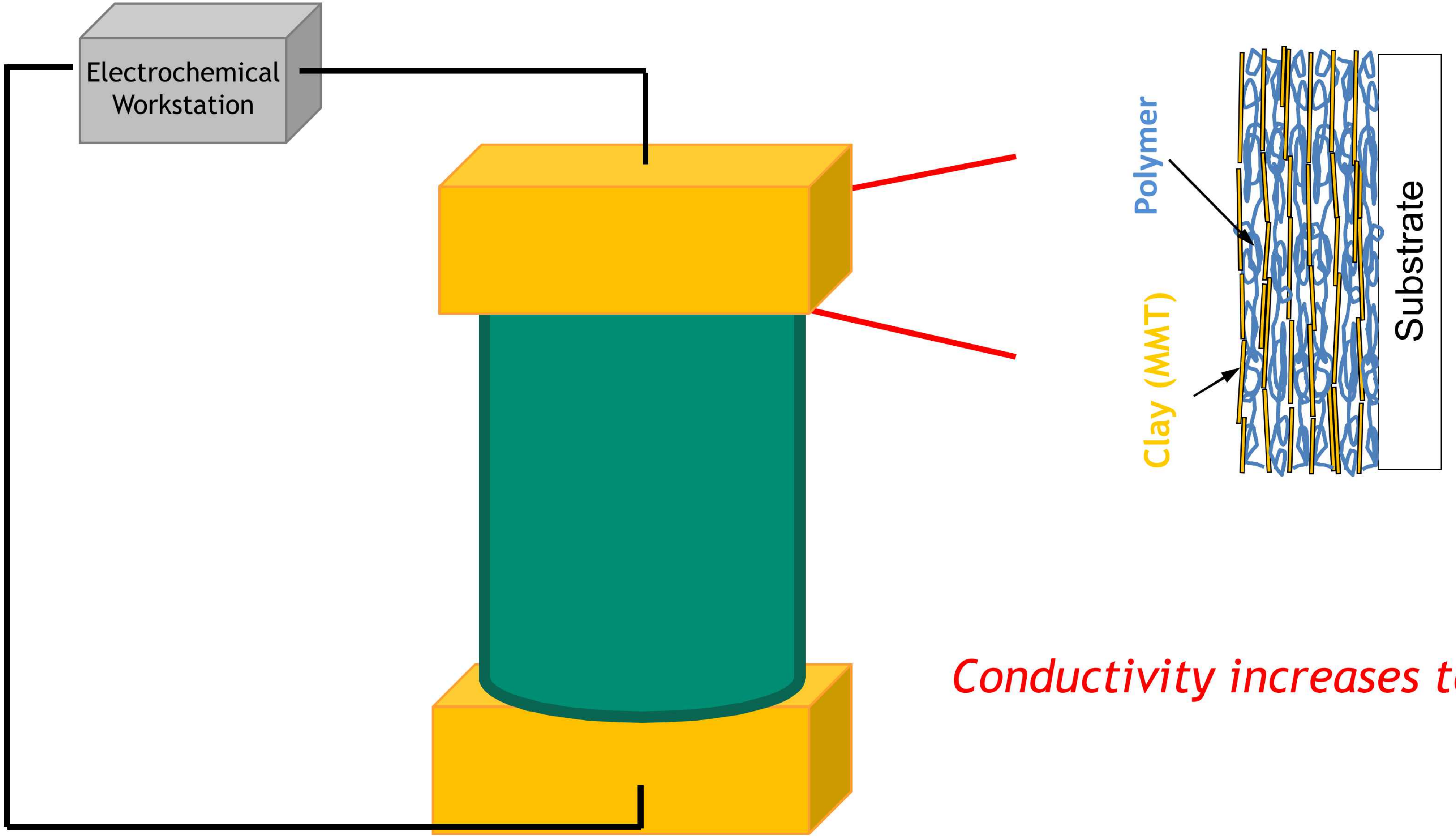
Can we evaluate the conductivity along the aligned planes of the clay in an assembled composite film?

Assessing Directional Ionic Conductivity

Longitudinal Coating



Assessing Directional Ionic Conductivity



Conductivity increases to ~10^{-4} S/cm!

Summary

Multilayered materials provide opportunities for manipulation of ion transport!

- ✓ Anti-Corrosion coating
  - Chemical stabilization of coatings enables corrosion inhibition in solution by increasing charge transfer resistance.
  - Increasing clay aspect ratio decreases ionic transport, improving corrosion inhibition.

- ✓ Ion-Selective Membranes
  - Using LbL techniques and selective chemical crosslinking, stable, cation-selective membranes can be created.
  - Bio-inspired addition of amino acids can improve ionic selectivity.

- ✓ Solid State Ion Conductors
  - Using layered, sodiated clay, new ion-conducting separators are feasible.
  - Clay structure and water content are important to ion conduction.
  - Thin film analogs illustrate strongly anisotropic ion conduction in clay-based materials.

Acknowledgments and Thanks

THANK YOU!

Polymer clay nanocomposites and polyelectrolyte thin film work were supported through Sandia's Laboratory Directed Research and Development (LDRD) Program.

Na-battery work at Sandia National Laboratories is supported through the Energy Storage Program, managed by Dr. Imre Gyuk in the U.S. Department of Energy Office of Electricity.

Questions?

Erik Spoerke

edspoer@sandia.gov

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

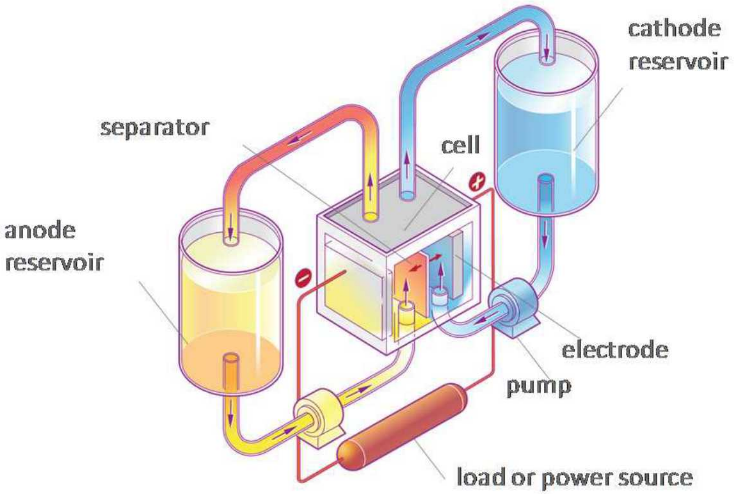
Backup Slides

Grid-Scale Research at SNL

Renewable/Remote Energy Grid Reliability National Defense Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability



SNL work in collaboration with University of Washington/Texas, Davidson College, LANL, WattJoule, UET.

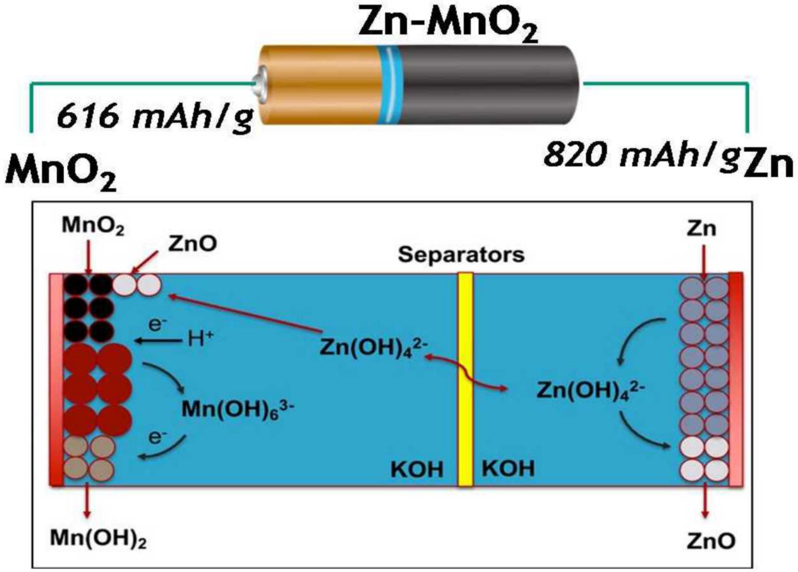
SNL PI: Dr. Travis Anderson
SNL Membrane PI: Dr. Cy Fujimoto

Grid-Scale Research at SNL

Renewable/Remote Energy Grid Reliability National Defense Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability



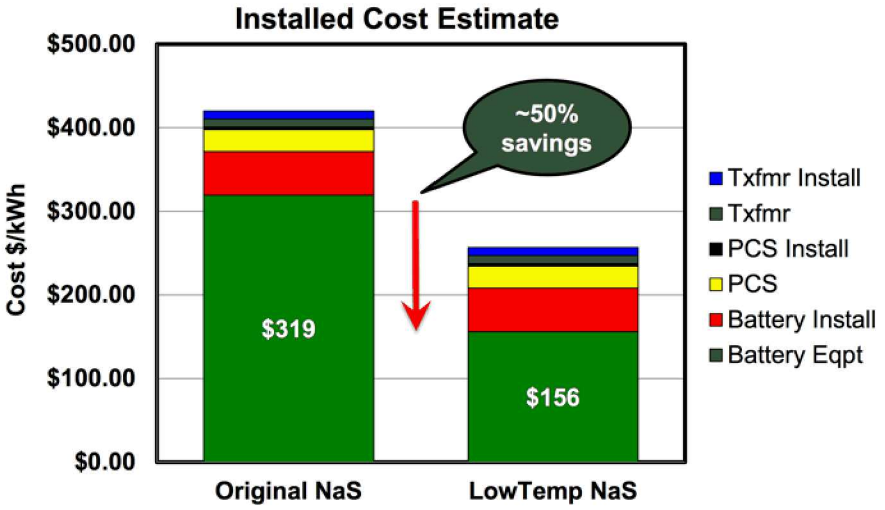
SNL work In collaboration with CUNY, Northeastern University, New Mexico State, Stony Brook University, Urban Electric Power.

SNL PI: Dr. Tim Lambert

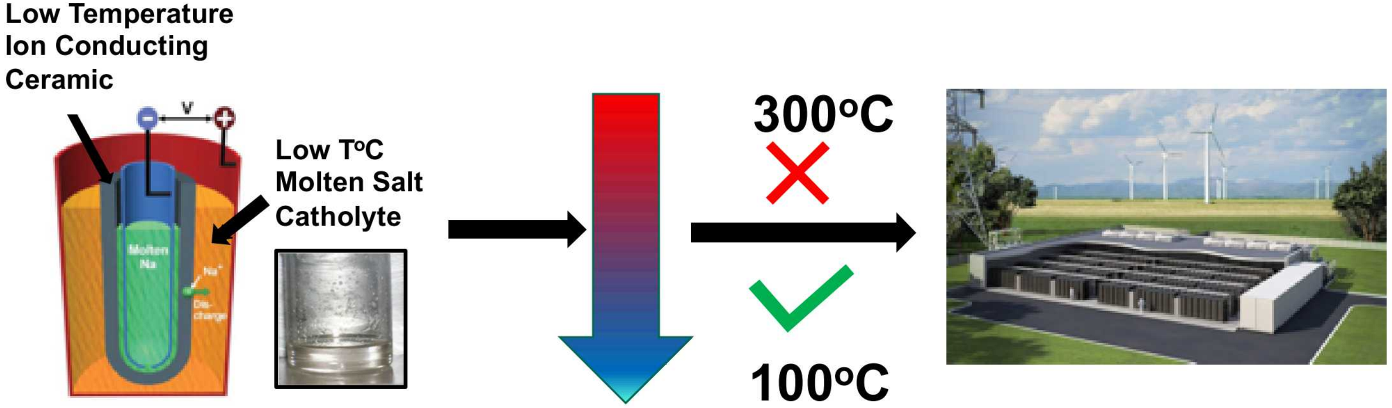
Lowering Battery Operating Temperature to Drive Down Cost

<u>Our Objective:</u> A safe, reliable, molten Na-based battery that operates at drastically reduced temperatures (near 100ºC).

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Separators
  - Cell body
  - Polymer components?
- Reduced operating costs
- Simplified heat management costs
  - Operation
  - Freeze-Thaw



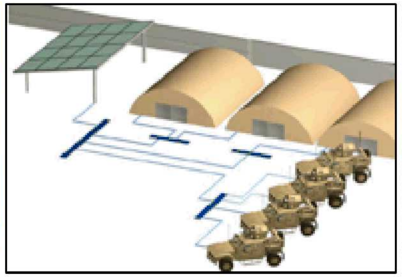
Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online): https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf



A Need for Grid-Scale Energy Storage

Renewable/Remote Energy

Grid Reliability

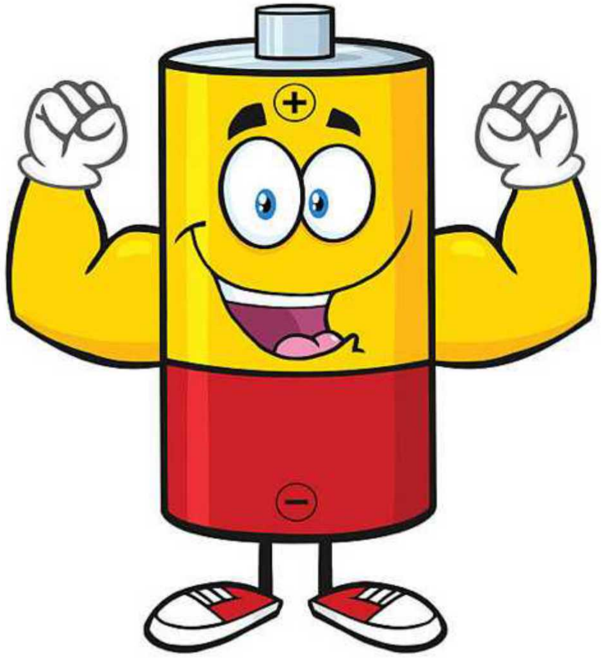


National Defense

Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

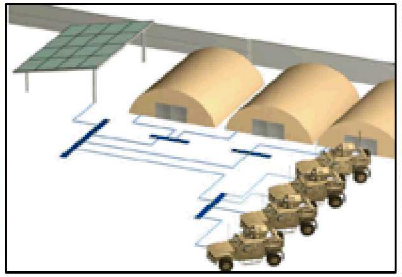
- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability



Sodium Batteries


Renewable/Remote Energy

Grid Reliability



National Defense

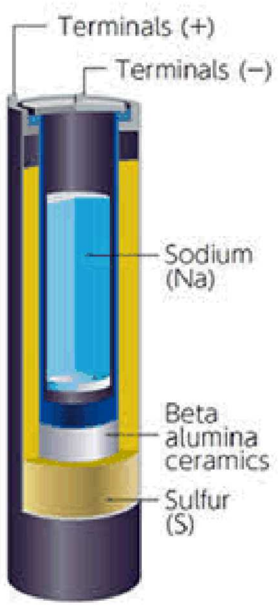
Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability

<u>Sodium-based batteries</u>

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA ($Na\text{-}NiCl_2$) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).



<u>Na-S (E_{cell} ~ 2V)</u>

$2Na + 4S \leftrightarrow Na_2S_4$

<u>$Na\text{-}NiCl_2$ (E_{cell} ~ 2.6V)</u>

$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

Sodium Batteries

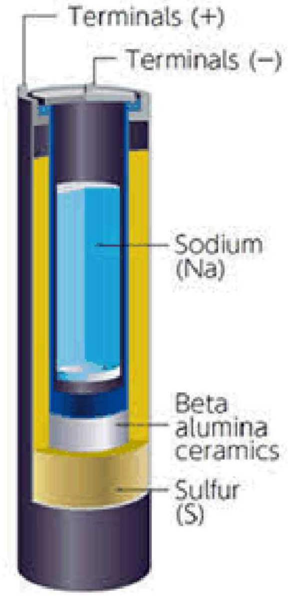
Renewable/Remote Energy | Grid Reliability | National Defense | Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability

Sodium-based batteries

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA (Na-$NiCl_2$) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).

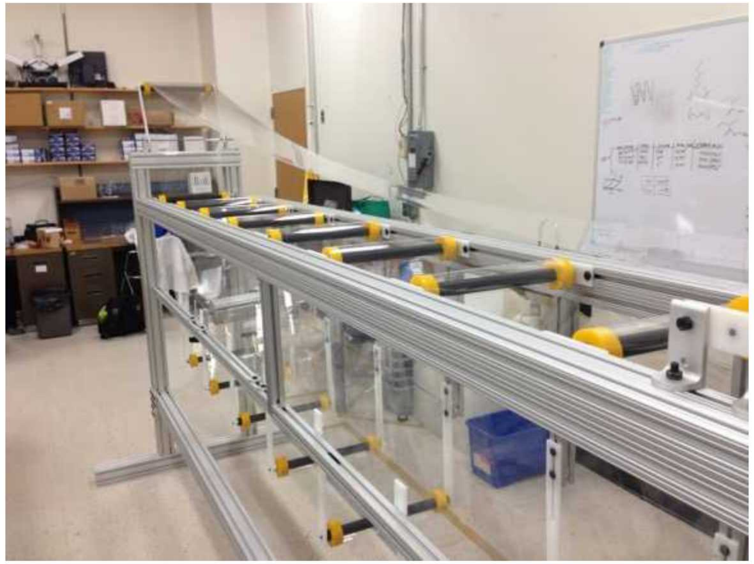


Na- … **6V)**

~300°C Operation!

2Na … $Na^+ + 2Cl^- + Ni(s)$

Large Scale Assembly Capability



Reel to reel coating at TAMU

~60ft of EVA coated by reel-to-reel process at TAMU (Prof. J. Grunlan)

TAMU Reel to Reel system capable of 11” x ~50’ of coating.

- Suitable for lamination onto coatings for:
  - Nature Power 3W and 5W Modules (single crystal Si, < 8”x 12”)
  - Uni-Solar US-3 (amorphous Si, ~8”x 11”)