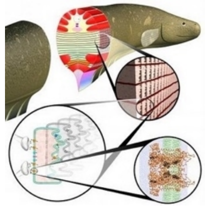
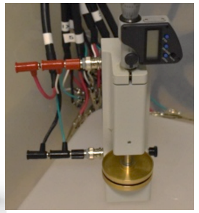
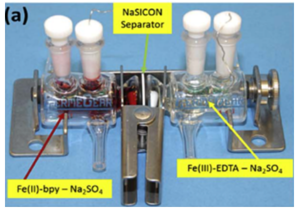
SAND2023-08301C

Sandia National Laboratories

Aqueous Batteries: Transforming Prehistoric Chemistry to Meet Next Generation Storage Needs




Erik D. Spoerke, Ph.D.

Energy Storage Materials Lead
Sandia National Laboratories

American Chemical Society Fall 2023 Meeting

San Francisco, CA
August 13-17, 2023

Erik Spoerke's work at Sandia National Laboratories is supported through the U.S. Department of Energy's Office of Electricity, including the Energy Storage Program, managed by Dr. Imre Gyuk

What is the Ultimate Challenge for Grid-Scale, Long-Duration Storage?

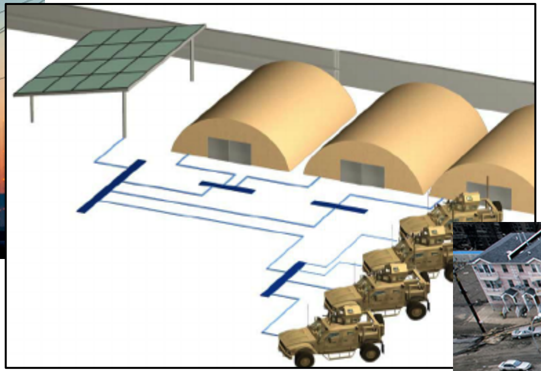
*How can we replace high energy density fossil fuels, not just for generation, but for **storage**?*

greengroundswell.com

A Need for Scalable Stationary Energy Storage

Renewable/Remote Energy

Grid Agility/Reliability



National Defense

Emergency Aid

- Inherent Safety
- Long, Reliable Operational Life
- Functional Energy Density
- Low Cost, Scalable
- *Domestically/Globally Accessible*

A Need for Scalable Stationary Energy Storage

Renewable/Remote Energy

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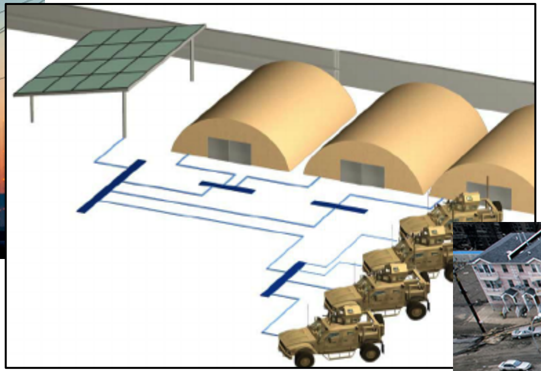


National Defense

Emergency Aid

- Inherent Safety
- Long, Reliable Operational Life
- Functional Energy Density
- Low Cost, Scalable
- *Domestically/Globally Accessible*

Aqueous batteries can meet these needs!

What Are You Going to Hear Today?

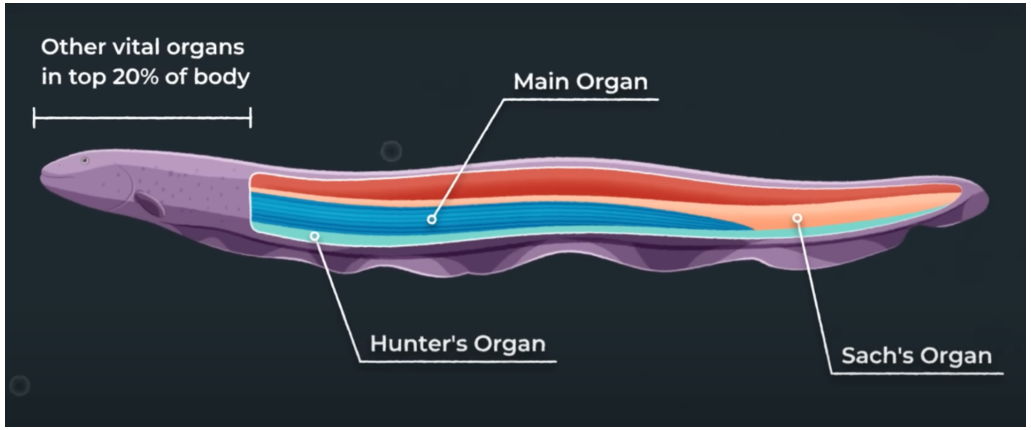
Part I: A High Level Overview of Aqueous Batteries Today

Part II: Creative Materials Chemistry Approaches to Meet Three Battery Challenges

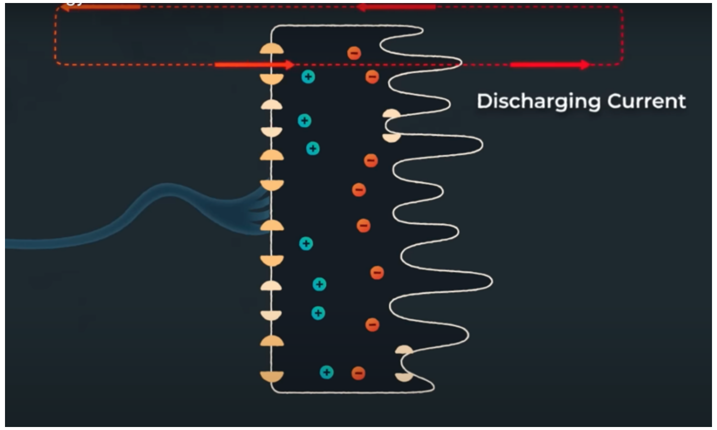
A Prehistoric Battery-Powered Hunters: Electric Fish

Inspiration From "Eelectricity"

Electric Eel Anatomy

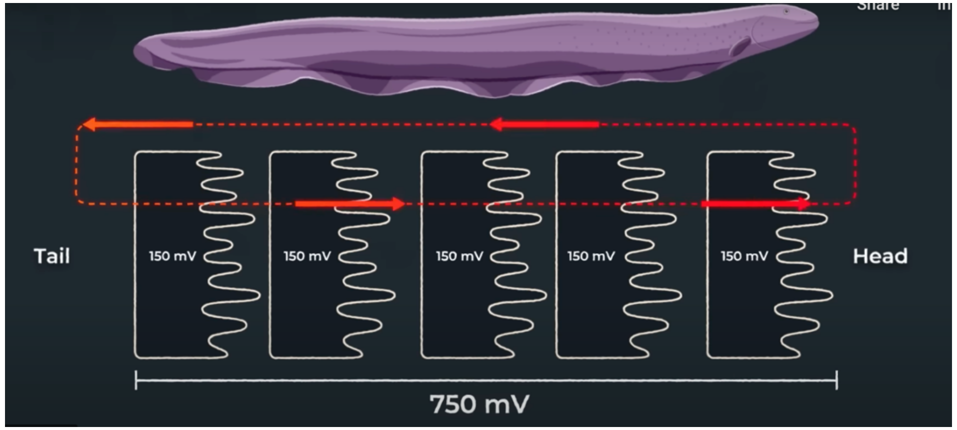


Ionic Dipole in an Electrocyte



By controlling ion-concentration gradients across many electrocyte cell membranes, the cells in electric eels can generate and discharge current and voltage.

Electrocytes are organized in series/parallel to produce high voltage (600-800V) and current (up to an Ampere).



Alessandro Volta

Electrolyte stacks in fish look like coin stacks

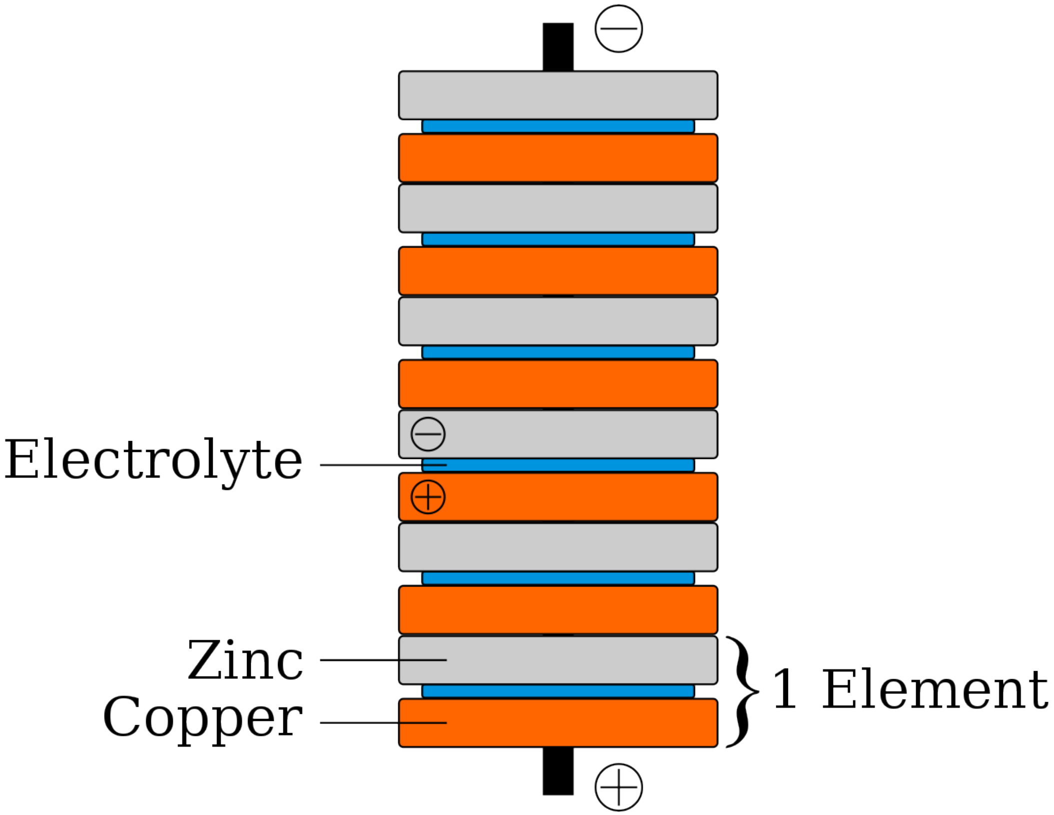
https://www.technologynetworks.com/tn/videos/the-insane-biology-of-the-electric-eel-364591

Batteries in the Beginning?

Pursuing studies of "animal electricity," Alessandro Volta hypothesized that two different metals, separated by a moist material would generate "metallic electricity"

To test this idea, he created voltaic piles from stacks of alternating Zn and Cu.

Alessandro Volta's Original "Pile", exhibited in the Volta Temple, Como, Italy.CC 3.0 - GuidoB



A Long History of Aqueous Batteries

- Low-cost, high energy density, safety, and global availability have made Zn-based batteries attractive for more than 220 years!

- *Alessandro Volta - early 1800s: Voltaic piles from stacks of alternating Zn and Cu.*
- *Zn-Carbon battery – later 1800s (manufactured significantly as primary battery until 1980s)*
- *Zn-CuO battery - late 1800s (primary battery, used in electric submarine (Gymnote, 1889))*
- *Zn-MnO_2 (D, C, AA, AAA) - largely replaced Zn-Carbon*
- *Zn-Ag_2O – Invented in 1920s, used on Apollo missions (still used today as energy dense primary batteries)*
- *Primary Zn-air batteries (button cells) – Originally 1933, widespread use in hearing aids.*
- *Zn-Ni explored in 1970's, 1980s as rechargeable batteries for vehicles (hundreds of cycles, ~1,000 today).*
  - *Other Ni-based, alkaline batteries include Ni-MH, Ni-Cd*

Rechargeable Zn-based Aqueous Batteries

- Low-cost, high energy density, safety, and global availability have made Zn-based batteries attractive for more than 220 years!
- *Diverse* Zn-batteries offer a range of properties to meet growing demand across varied applications:

✓ Renewables integration (including microgrids)

✓ Backup power (assurance for data centers, telecom, etc.)

✓ Grid stability and resilience

✓ Behind-the-meter applications for residential and commercial applications (Lower energy cost, power quality, etc.)

Zn-MnO_2

URBAN ELECTRIC POWER

1 MWh UEP alkaline battery backup system for the San Diego Supercomputer Center (CA).

ZĒLOS

Zn-Ni

ZincFive

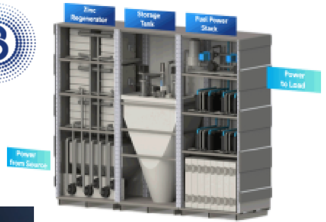
ZAF Energy Systems

Æsir Technologies, Inc.

ENZINC

Zn-Air

ZINC8

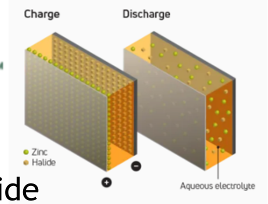


ZAF Energy Systems

e-zinc

Zn-Br

eos



35 MWh EOS Zn-Br system planned to provide 10 hour storage for solar-plus-storage microgrid with Indian Energy (CA).

redflow

Zn-Br flow battery installation

Zn-ion

SALIENT ENERGY

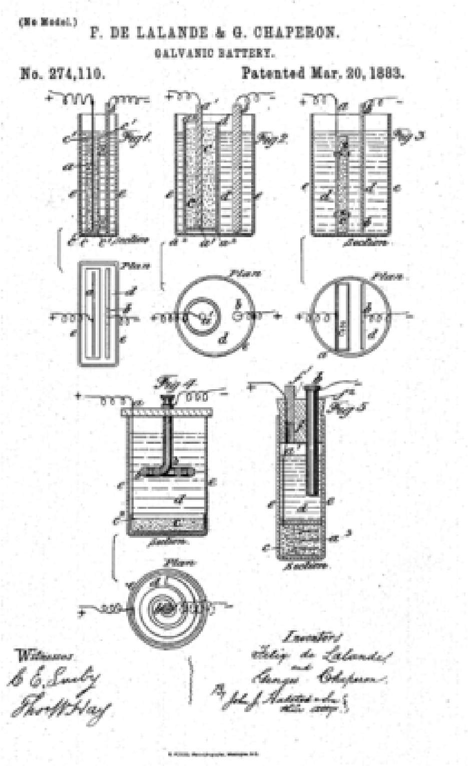
enerpoly

Zn-CuO Batteries (674 mAh/g)

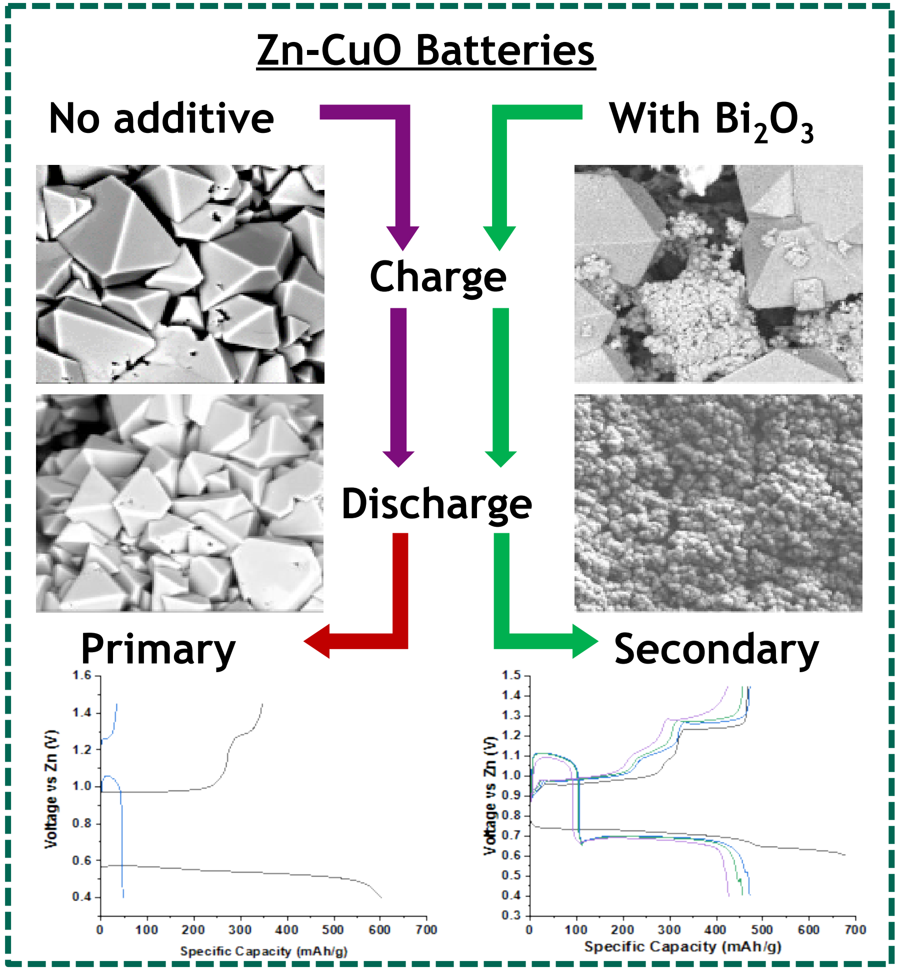
Anode: $Zn^0 + 4OH^- \rightarrow [Zn(OH_4)]^{2-} + 2e^-$ $E^o = 1.285$ V

Cathode: $CuO + H_2O + 2e^- \rightarrow Cu^0 + 2OH^-$ $E^o = -0.29$ V

$Zn^0 + CuO + H_2O + 2\ OH^- \rightarrow [Zn(OH_4)]^{2-} + Cu^0$ Cell Voltage: 0.995 V



Edison-LaLande Battery.
PAT. Mar. 20, 1883.
OTHER PATENTS APPLIED FOR



Almost 140 years of no reported rechargeable CuO cathode

1883 → **2021**

Publication:
N. Schorr et al. *ACS Appl. Energy Mater.* 2021, 4, 7, 7073-7082.

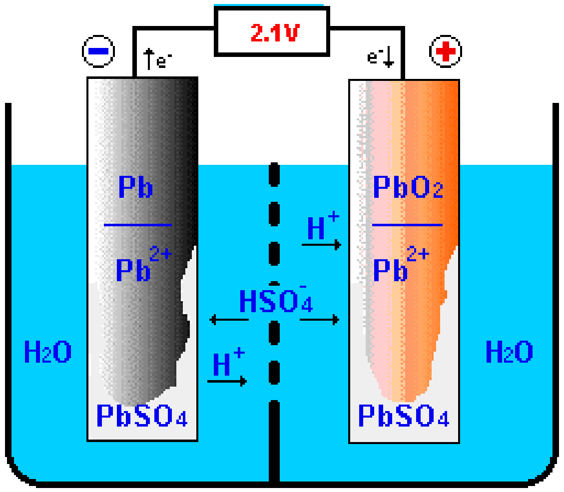
Tim Lambert: Zn-CuO

Lead Acid Batteries

- Invented in 1859 by Gaston Planté
- Energy Density ~30-50 Wh/kg
- Typically hundreds of cycles

- The 2020 global market for PbA batteries was ~500 GWh (70% of global energy storage) and $40 billion*

- Automotive/mobile applications
- Off-grid use (e.g., traffic signal and lighting, railroad communications, uninterruptable power supply (UPS), and telecommunications)
- Grid-integrated applications (e.g., renewable integration, load smoothing, time-shifting, etc.)



S.R. Salkuti, DOI:10.11591/ijece.v11i3.pp1849-1856

Battery Operation
- Anode: Pb
- Cathode: PbO_2
- Electrolyte: H_2SO_4

- During discharge, oxidation and reduction reactions at each electrode produce $PbSO_4$.

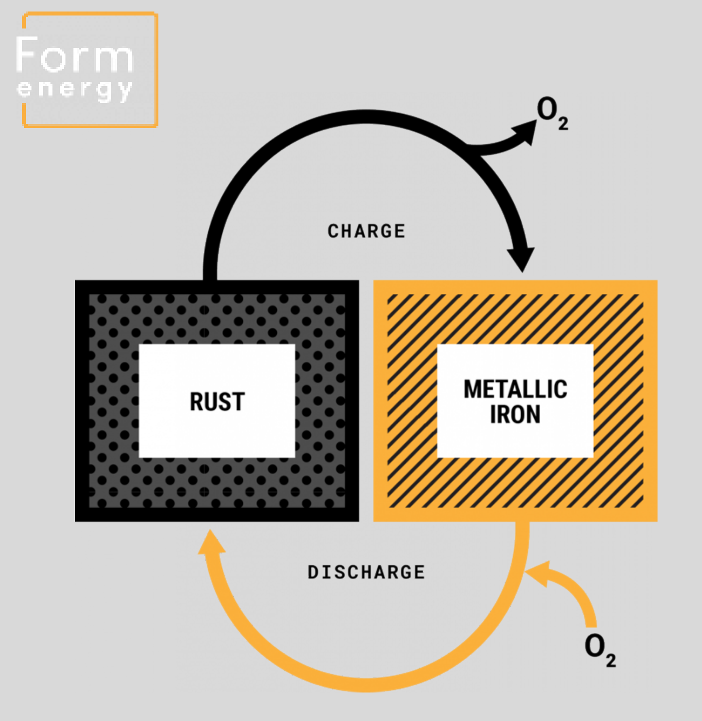
*DOE SI 2030 Technology Assessment on Pb-Acid Batteries (Sue Babinec)

Air-Based Batteries

- Utilize air-based cathode and earth-abundant metal anode.
- Challenges around reversible, fast kinetics of oxygen evolution reaction (OER) or oxygen reduction reaction at cathode(s).
- Air-breathing cathodes also must address side reactions with variable atmospheric conditions.

Zn-Air Batteries targeting scalable storage up to 24 hours.

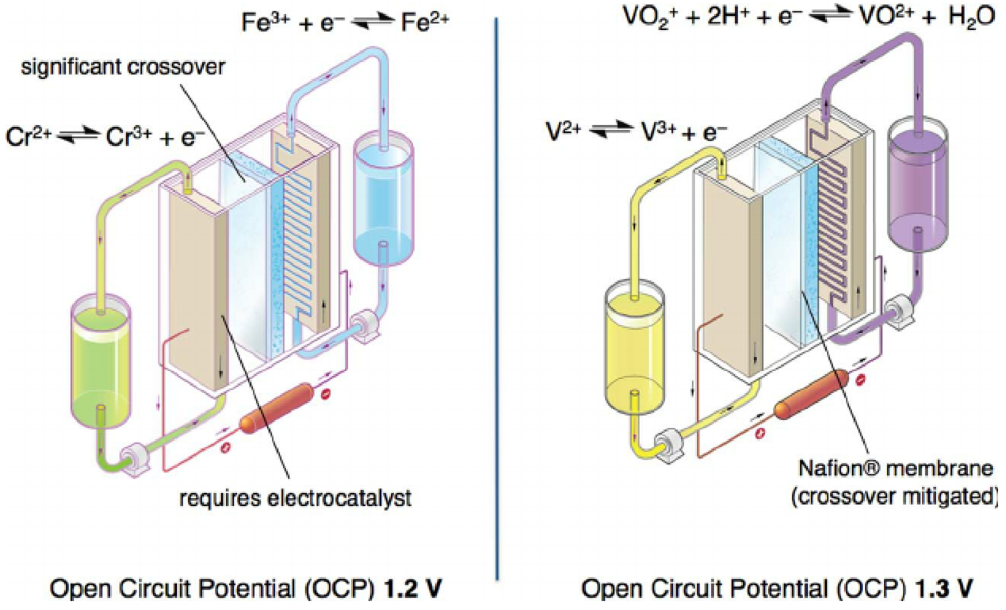
Fe-Air: Targeting 100 hour storage



Form Energy’s large-scale manufacturing facility in Weirton, WV

Redox Flow Batteries

- Widely commercialized (>100 companies)
  - **Vanadium** (Largest: 100MW / 400MWh (Dalian, China))
  - Zn-Br (~500kW/2MWh) – RedFlow
    - 2,959 MWh stored energy
    - 285 active deployments
  - Fe-Cr (~250kW / 1MWh)
  - Fe-Flow (ESS, Inc.)
  - Transition Metal-Chelate Chemistry
  - Non-aqueous RFBs?
    - Higher voltages possible, but more expensive



- Independently tunable power and energy
- Challenges
  - Energy Density
  - Cost
  - Reliability

- Dalian Flow Battery Energy Storage Peak-shaving Power Station
- Power up to 200,000 residents per day

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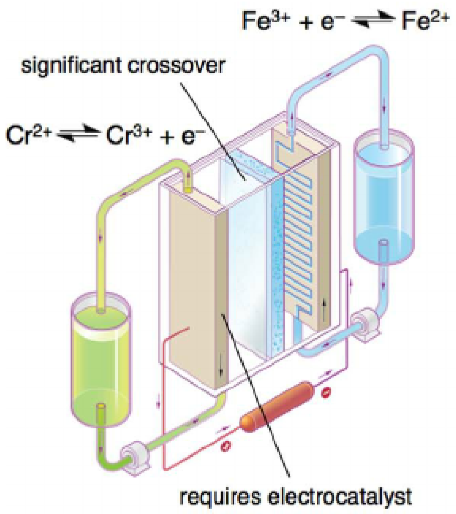
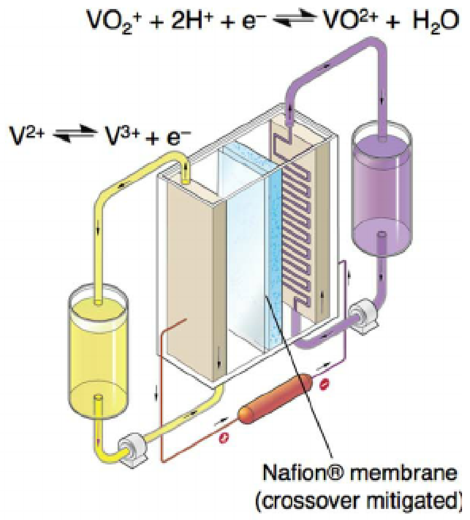


Open Circuit Potential (OCP) **1.2 V**



Open Circuit Potential (OCP) **1.3 V**

- Independently tunable power and energy
- Challenges
  - Energy Density
  - Cost
  - Reliability

What Are You Going to Hear Today?

Part I: A High Level Overview of Aqueous Batteries Today

Part II: Creative Materials Chemistry Approaches to Meet Three Battery Challenges

Challenge 1: A limitations for the cycle life of flow batteries is crossover of anolyte and catholyte species.

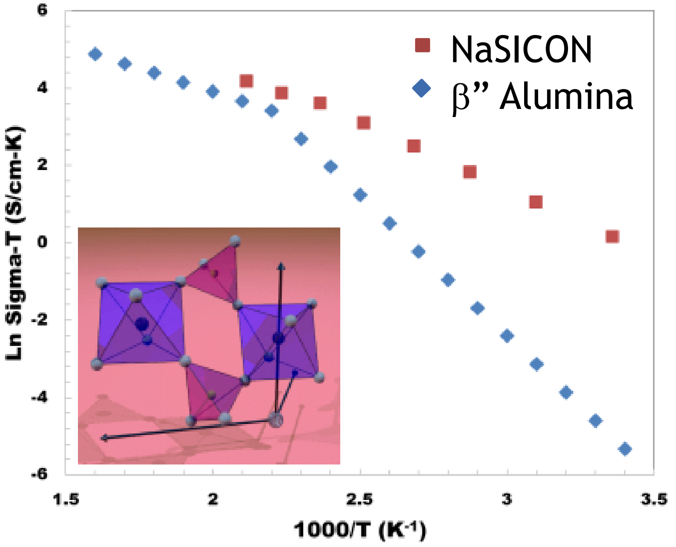
Could we implement a “zero crossover” solid state separator for use in a flow battery?

Materials Chemistry to Address a Flow Battery Crossover

Challenge 1: A limitations for the cycle life of flow batteries is crossover of anolyte and catholyte species.

Could we implement a "zero crossover" solid state separator for use in a flow battery?

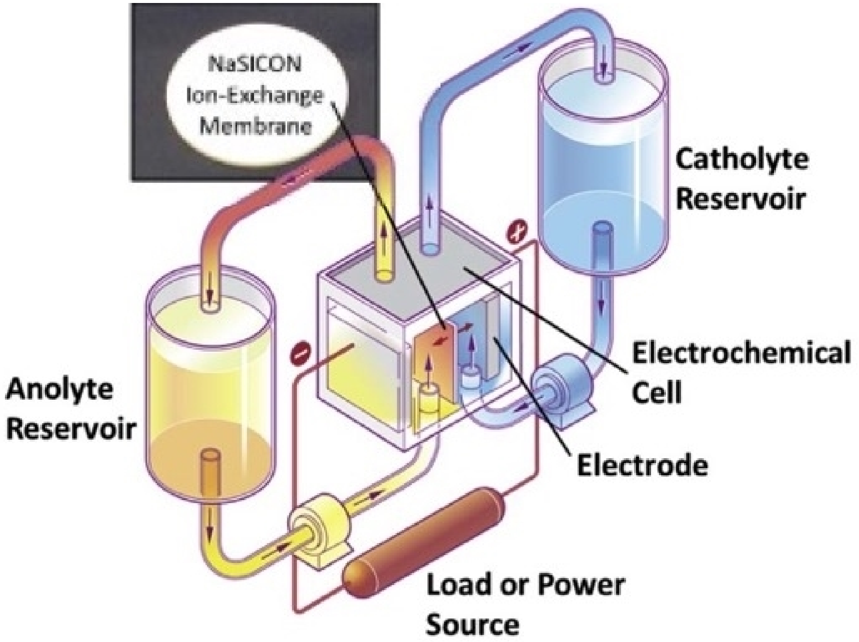
(NaSICON (Na Super Ion CONductor): $Na_3Zr_2PSi_2O_{12}$



Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

NaSICON with >98% bulk density has conductivity of ~3-4x10^{-3} S/cm at 25°C.

NaSICON cylinder and sectioned pellets.



As a stable solid-state ion conductor, NaSICON could serve as a zero-crossover separator…

Allcorn and Spoerke, *et al. J. Power Sources*. **378**. 353-361.

Initial Tests of Zero-Crossover Flow Battery

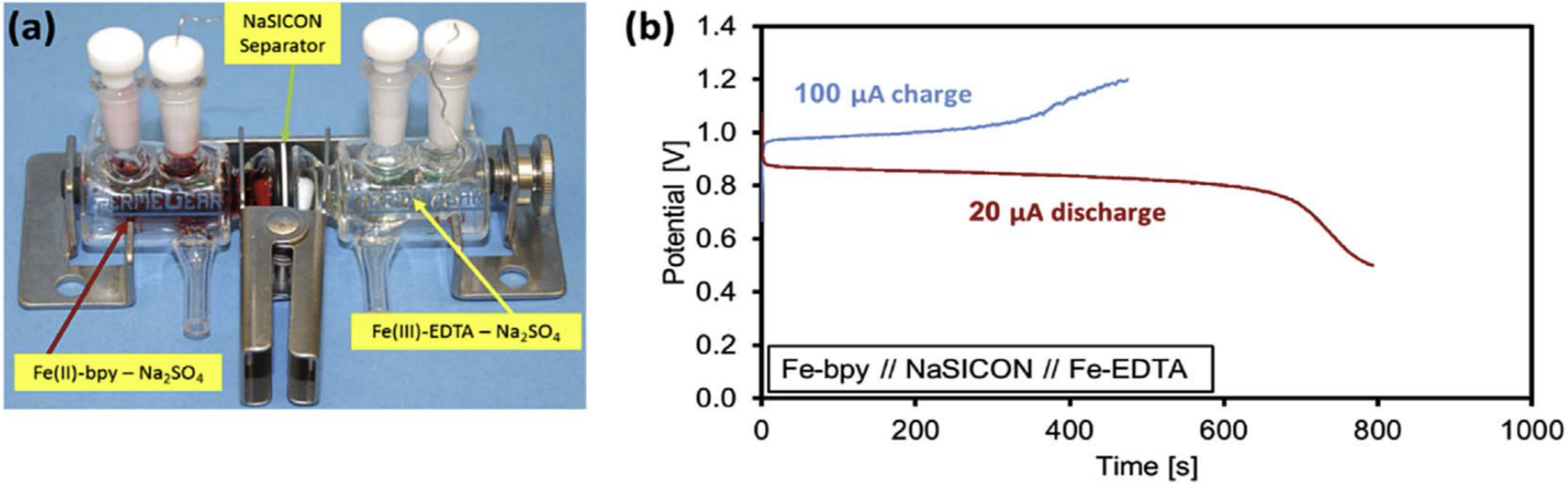
Cell Setup:
- 4 mM Iron-2,2’-bipyridyl (Fe-bpy) catholyte
- 4 mM Iron ethylenediaminetetraacetic acid (Fe-EDTA) anolyte
- 0.4M Na_2SO_4 supporting electrolyte

NaSICON separator

$$Cathode: [Fe(bpy)_3]^{3+} + e^- \rightarrow [Fe(bpy)_3]^{2+}$$

$$Anode: Na_2^+[Fe(EDTA)]^{2-} \rightarrow Na^+[Fe(EDTA)]^- + e^- + Na^+$$

$$Overall: [Fe(bpy)_3]^{3+} + Na_2^+[Fe(EDTA)]^{2-} \rightarrow [Fe(bpy)_3]^{2+} + Na^+[Fe(EDTA)]^- + Na^+$$

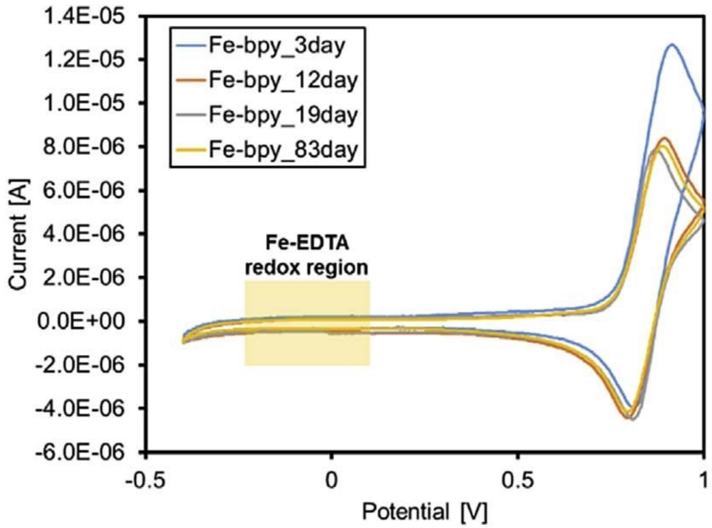


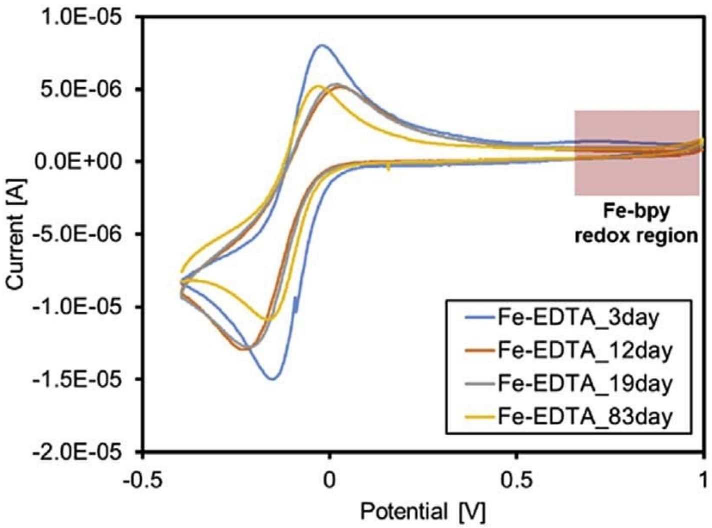
Allcorn and Spoerke, *et al*. *J. Power Sources*. **378**. 353-361.

Demonstration of Zero Crossover

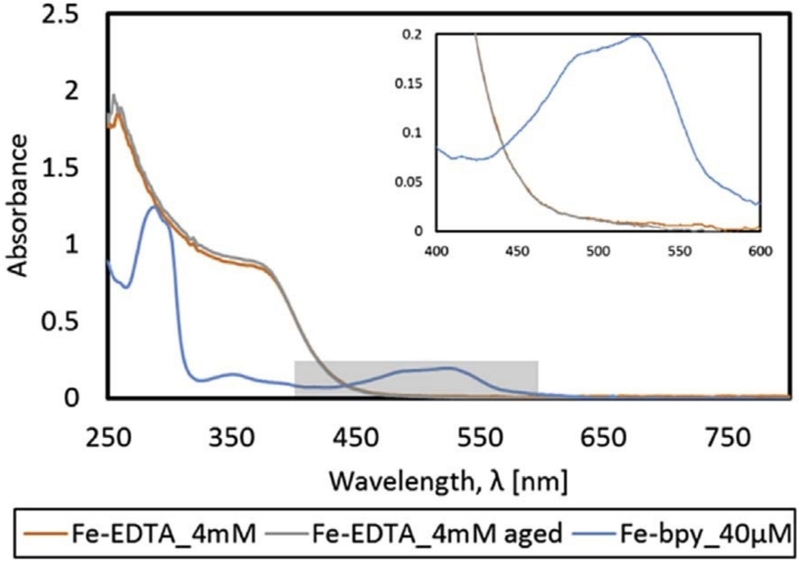
Combined Electrochemical (CV) and Spectroscopic (UV-Vis) characterization shows no trace of crossover in H-Cell tests over time.

Cyclic Voltammetry (CV)





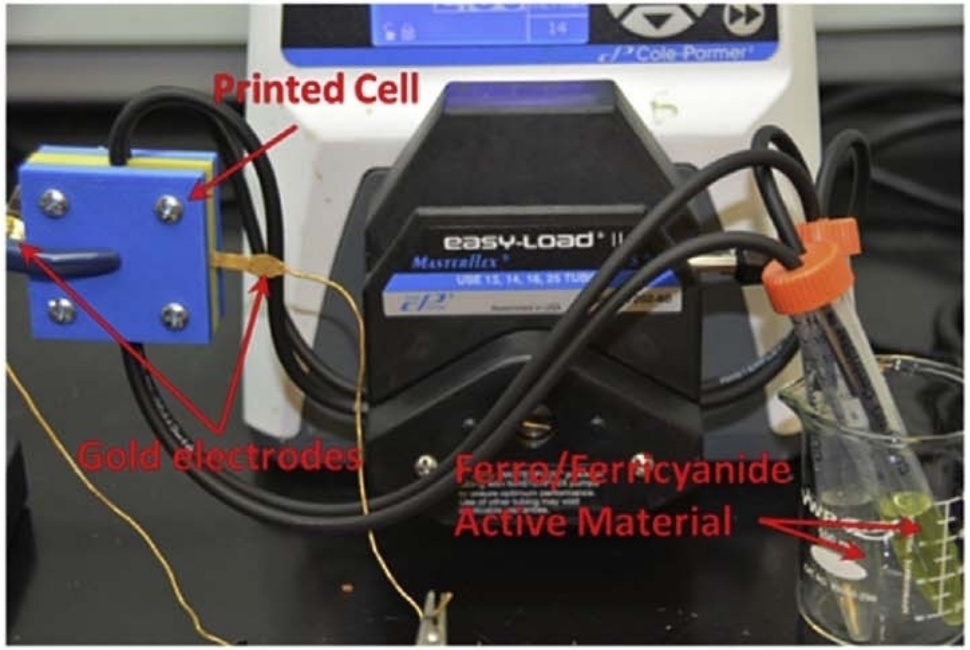
UV-Vis Spectroscopy

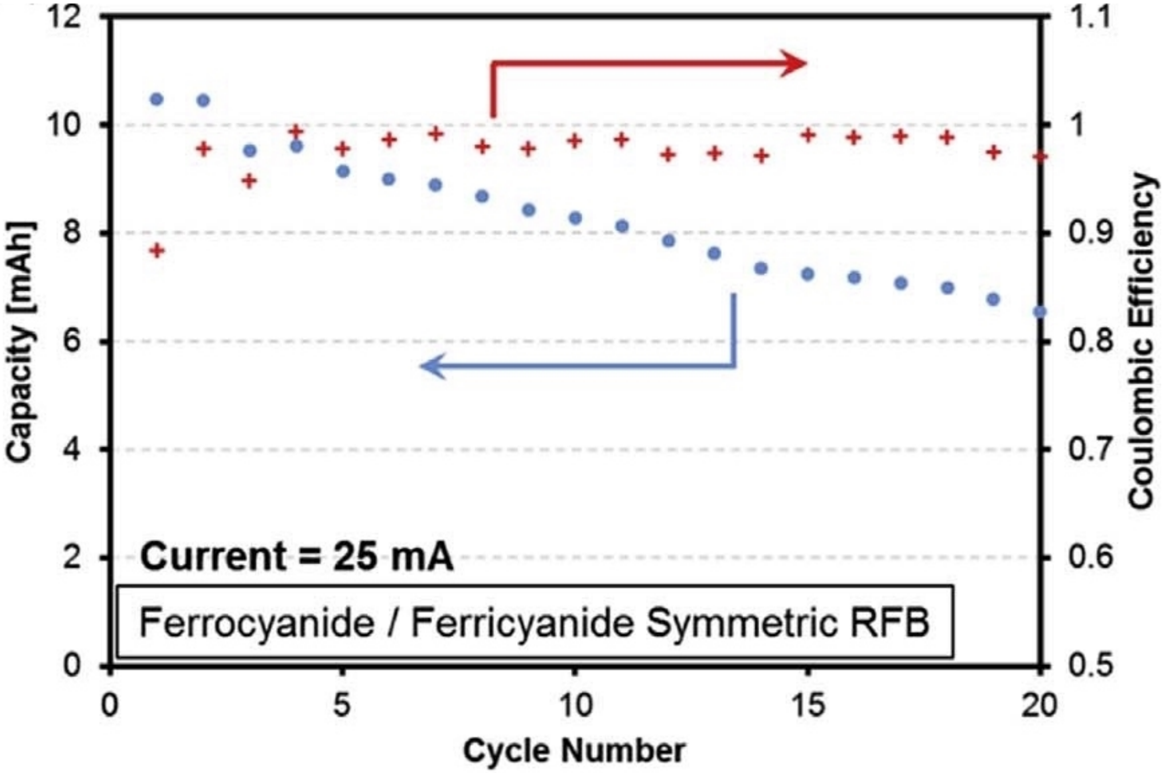


CVs of aged Fe-bpy and Fe-EDTA electrolytes from −0.4 to +1.0 V vs. Ag/AgCl at a rate of 10 mV/s.

Allcorn and Spoerke, *et al. J. Power Sources*. **378**. 353-361.

Testing in a Flow Cell Configuration





Electrochemical cycling in a flow cell configuration using a symmetric ferryocyanide/ferricyanide symmetric RFB allowed utilization of 88.4% of theoretical capacity at 8.6 mA/cm^2 across the NaSICON with high coulombic efficiency.

Allcorn and Spoerke, *et al. J. Power Sources*. **378**. 353-361.

Challenge 2: NaSICON can be expensive and challenging to synthesize well. (Is NaSICON ”Good Enough”?)

Could we identify a less expensive, easier-to-produce alternative to NaSICON?

A Skier's Perspective on Ion Transport Materials Design

- ✓ Rapid transport on well-defined paths (conductive)

A Skier's Perspective on Ion Transport Materials Design

✗ Impeded transport (resistive)

Skimaven.com

✓ Rapid transport on well-defined paths (conductive)


SFChronicle.com

A Skier's Perspective on Ion Transport Materials Design

✗ Impeded transport (resistive)

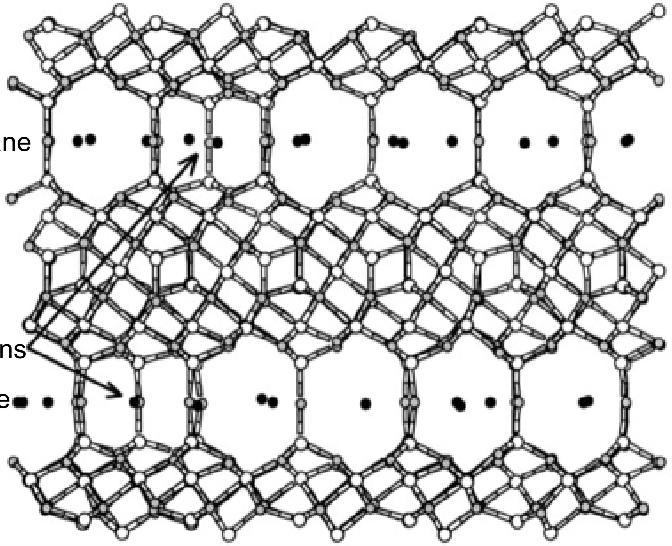
✓ Rapid transport on well-defined paths (conductive)

✓ Selective transport

Inspiration from β"-Al_2O_3

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.



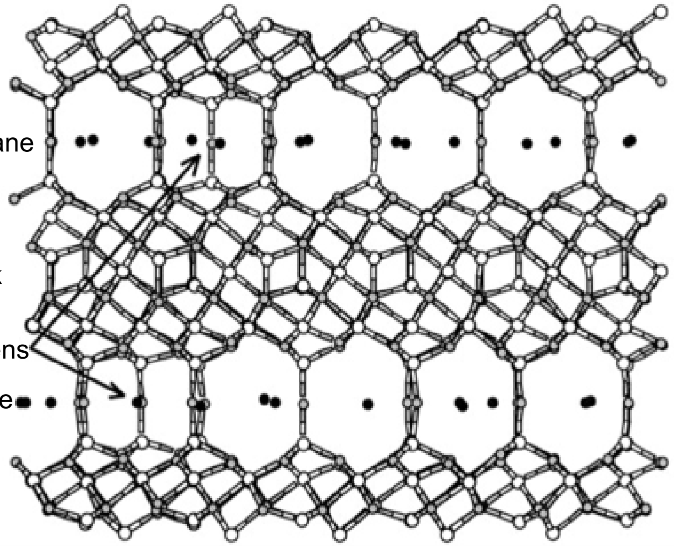
Beckers, van der Bent, and Leeuw. *Solid State Ionics* **133**(3-4)(2000), p217-231.

Dirt: A "Dirt Cheap" Alternative Solid State Separator?

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

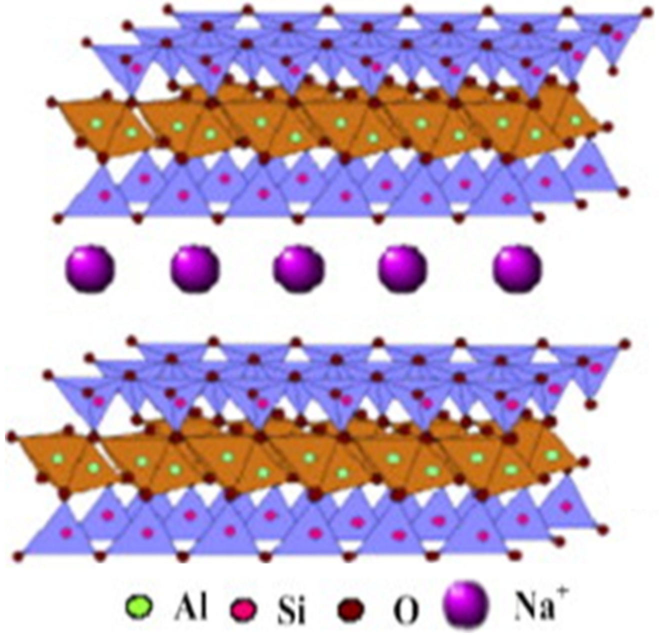
In the known Na-ion conductor β"-Al_2O_3, Na^+ conduction follows ordered conduction planes.

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.

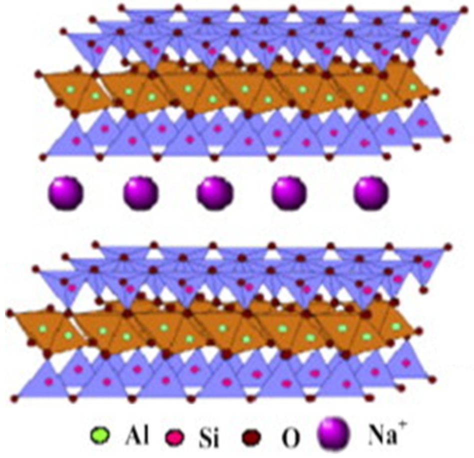
Challenge: Can we utilize MMT to create a low cost Na^+ ion conductor?



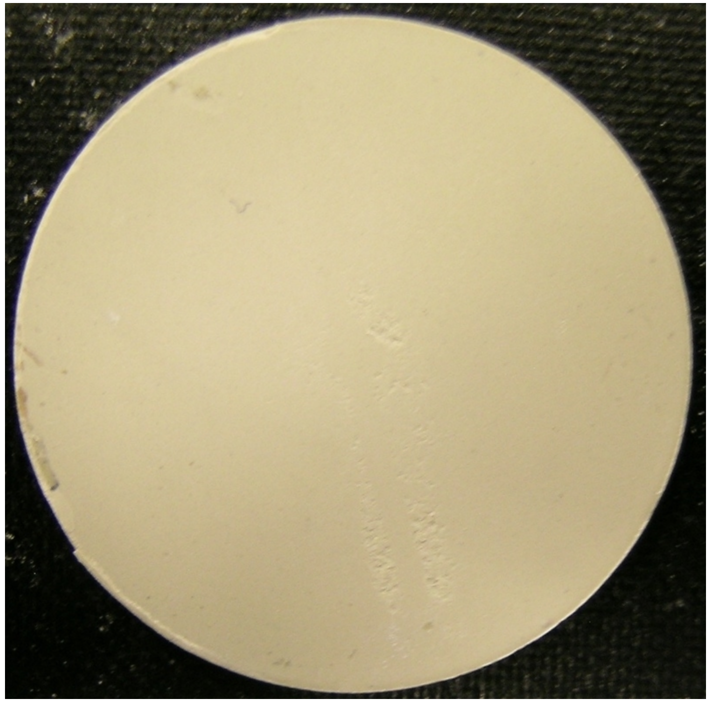
Motawie, *et al. Egypt. J. Petroleum* **23**(3)(2014), p331-338.

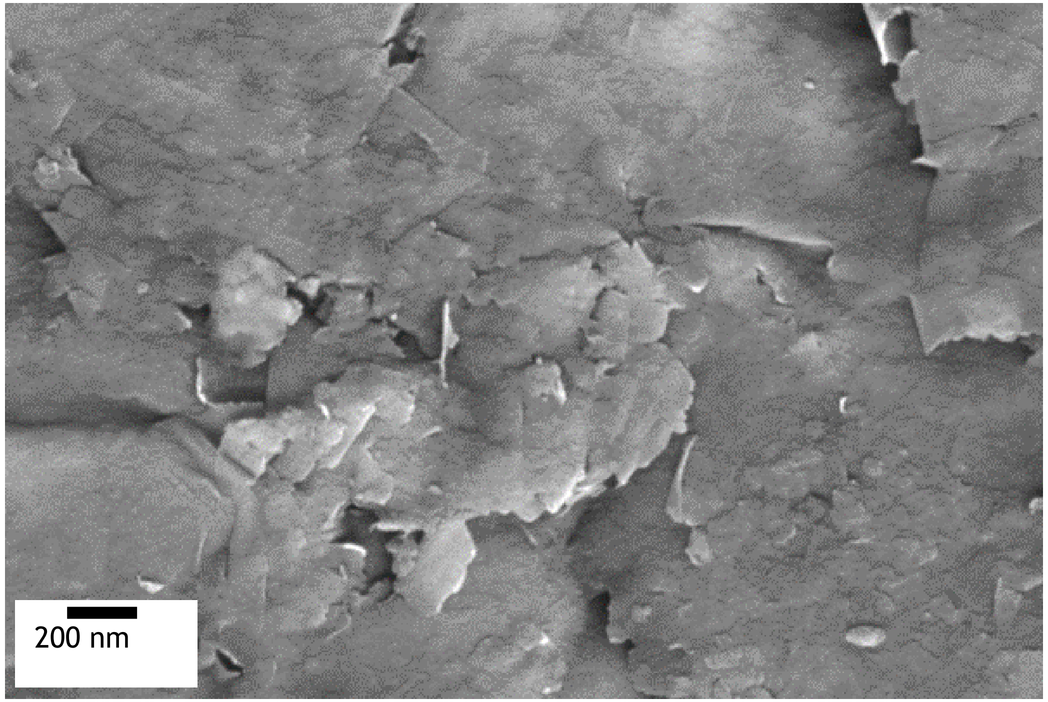
"Kitty Litter Konductors"?

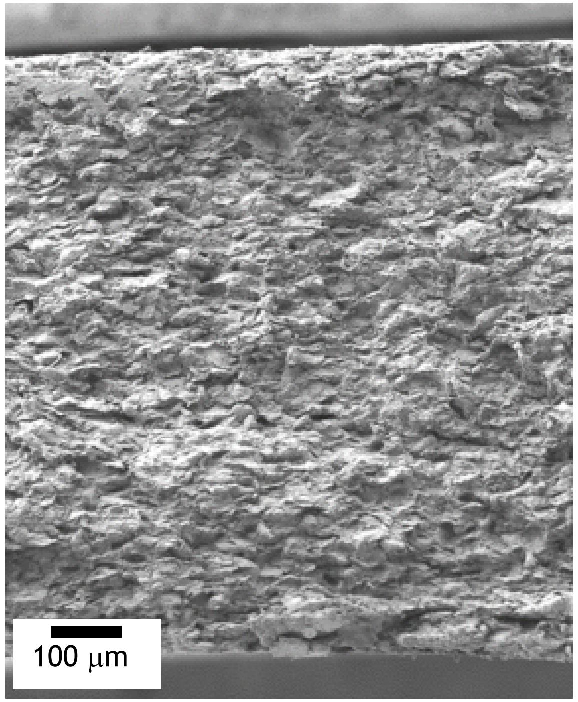
- MMT can be pressed into pellets suitable for assessment of ionic conductivity.
- Clay structure clearly evident in bulk pellet.



MMT Pellet (1")



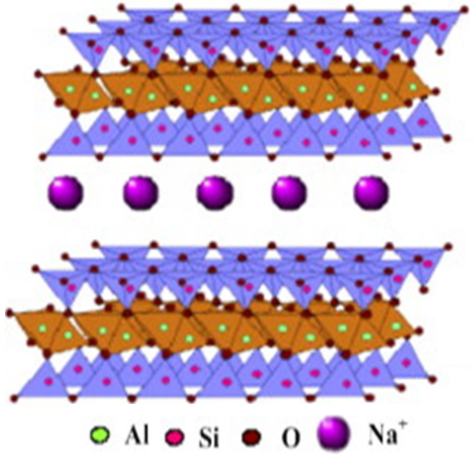




Spoerke, et al. In Preparation

Multilayered Structure and Composition Matter!

- MMT pellets exhibit 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 pellet.



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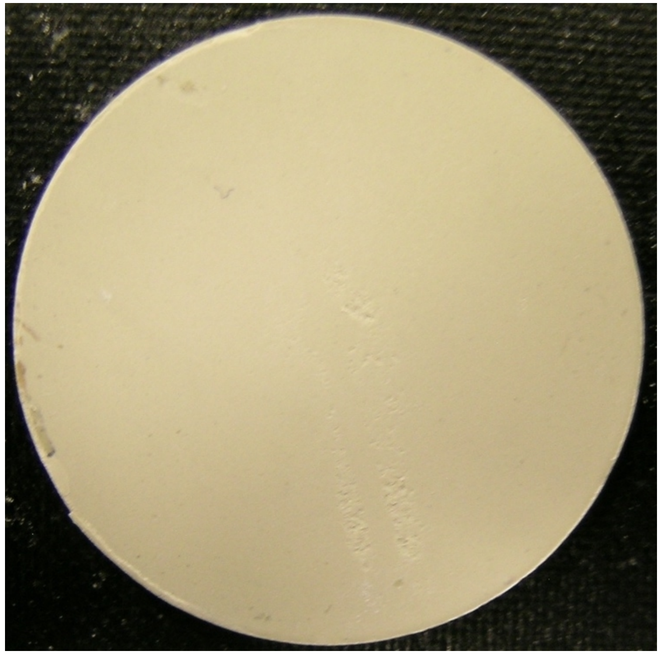

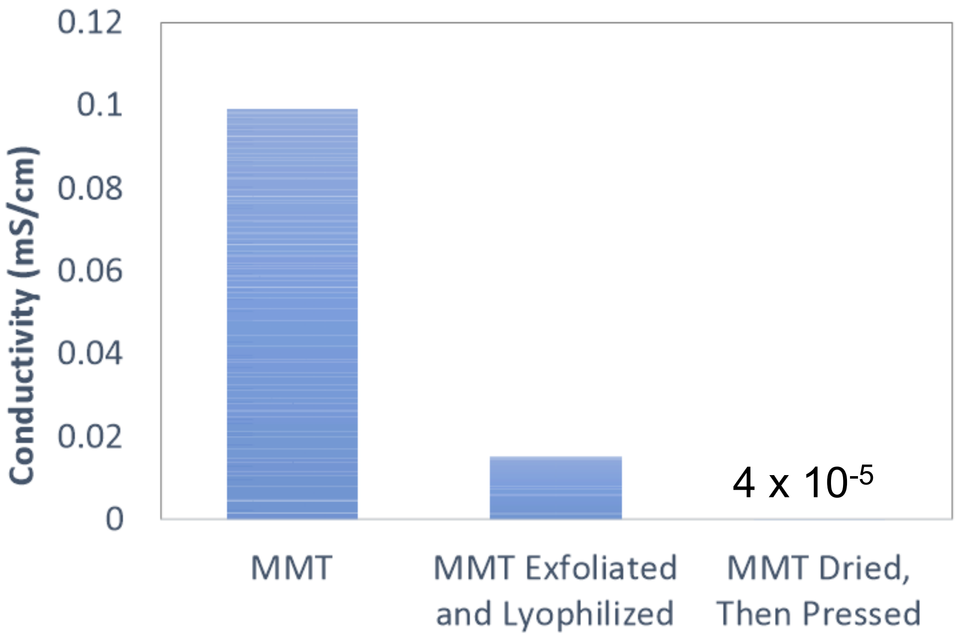

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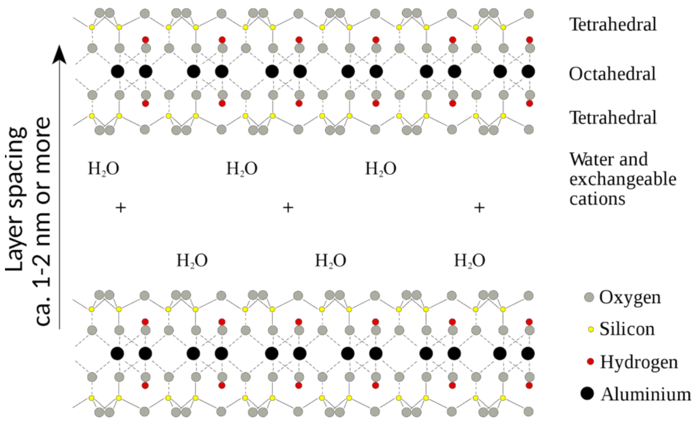
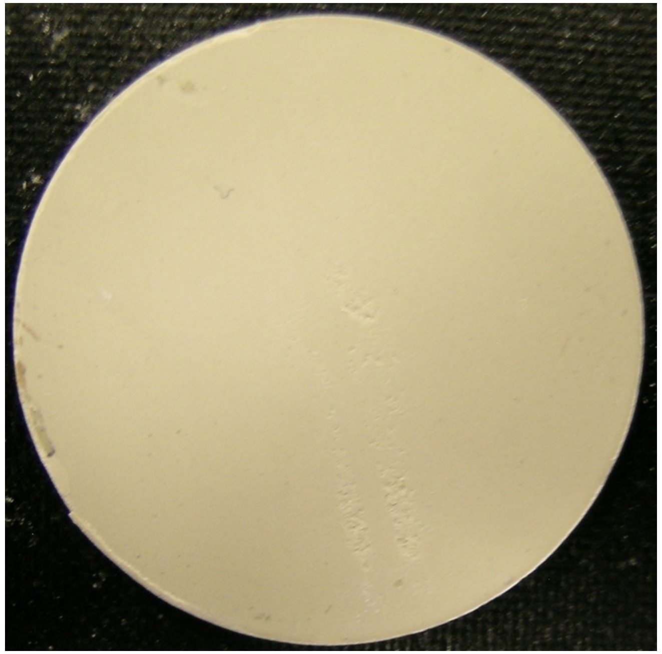
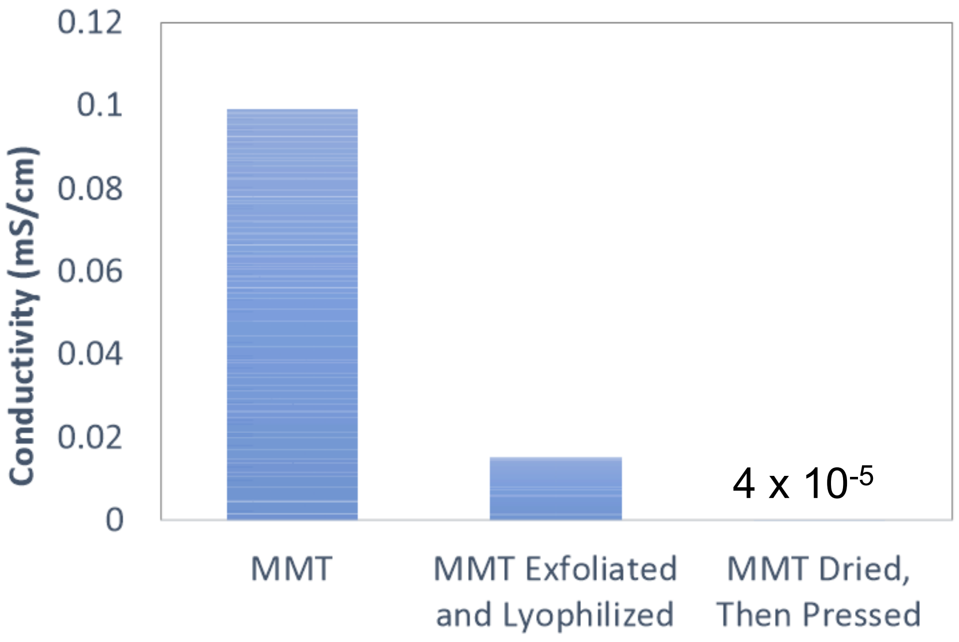


Image by Andreas Trepte, Wikipedia Commons

MMT Pellet (1")





Spoerke, et al. In Preparation

Confirming Na Conductivity

- Na-MMT pellets exhibit excellent ionic conductivity!
  (0.3 - 1 x 10^{-4} S/cm)
- Al-MMT: 8 x 10^{-11} S/cm
- K10-MMT (Acid-substituted): 7 x 10^{-9} S/cm
- Water content in each clay at least as high as in Na-MMT

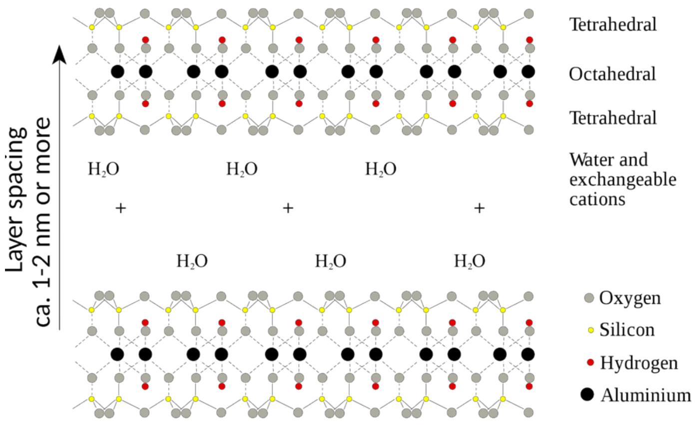
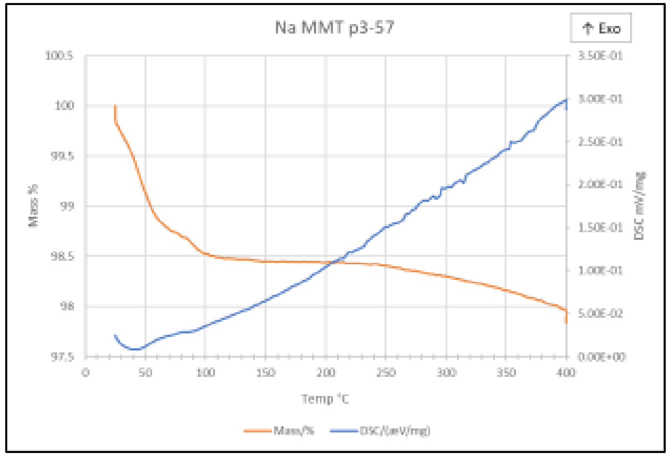


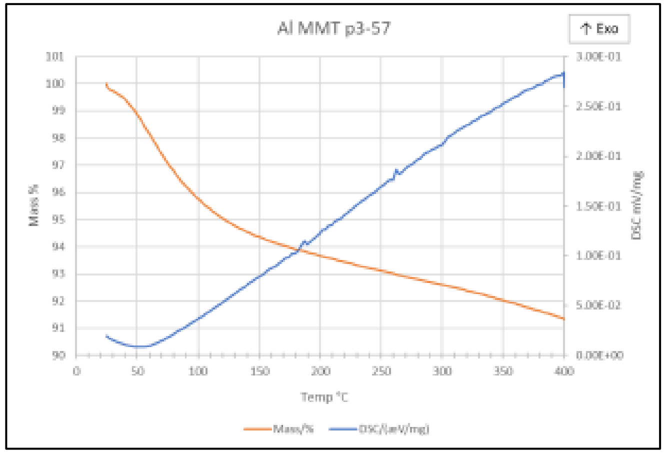
Image by Andreas Trepte, Wikipedia Commons

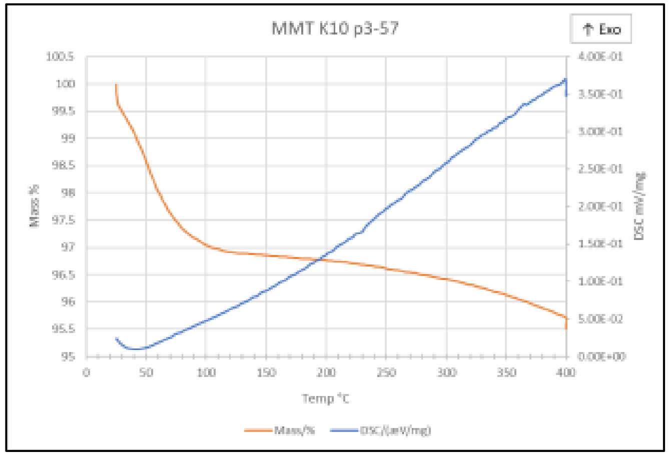
Na: ~1.5% H_2O

Al: ~6% H_2O

K10: ~3% H_2O





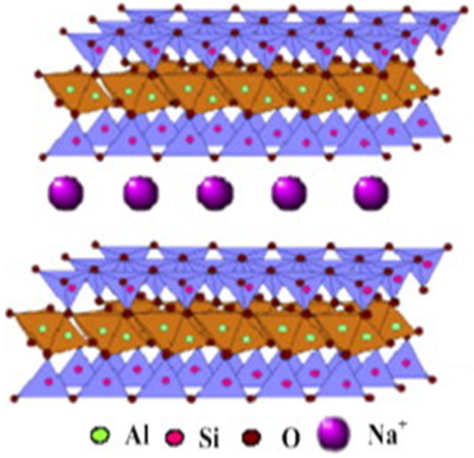


Spoerke, et al. In Preparation

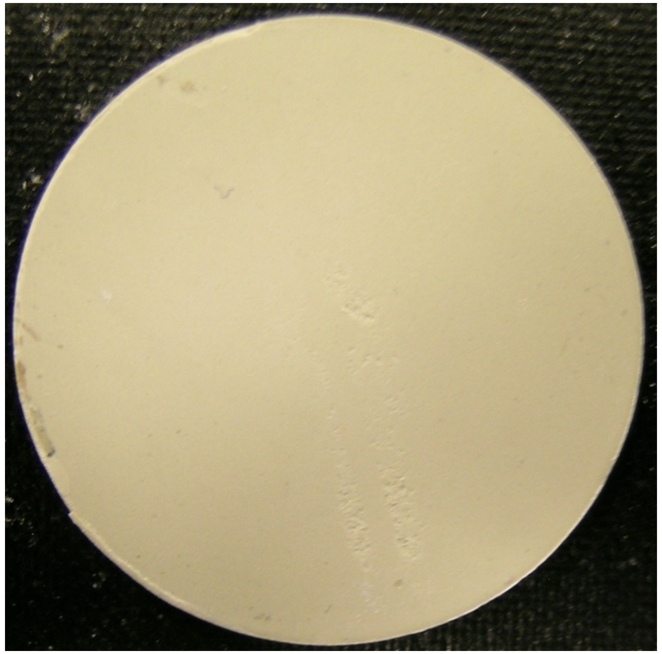
Humpty Dumpty's Separators…

Despite promising conductivity…

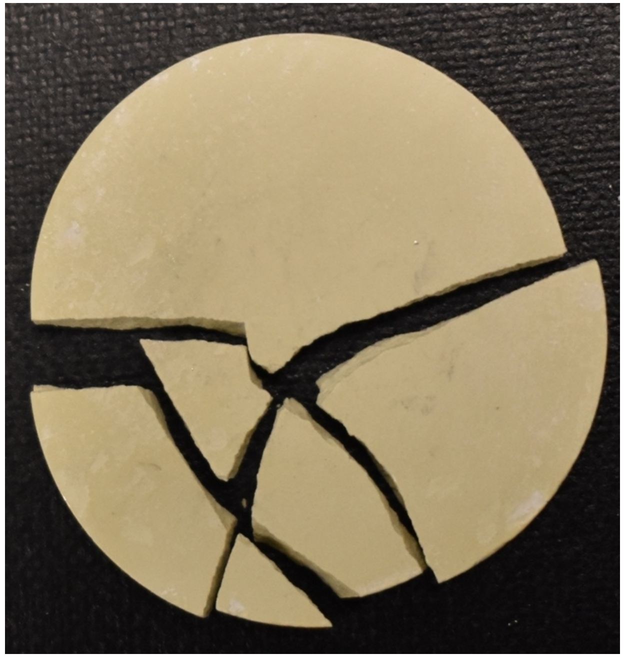
- MMT pellets can be very fragile
- MMT is soluble in…well…everything useful!



MMT Pellet (1")



Broken MMT Pellet



R. Hill, A.S. Peretti, L.J. Small, E.D. Spoerke, and Y-T. Cheng. "Characterizing Mechanical and Microstructural Properties of Novel Montmorillonite-based Sodium Ion Conductors." (2022) *J. Mater. Sci.* **57**(4), 1-10.

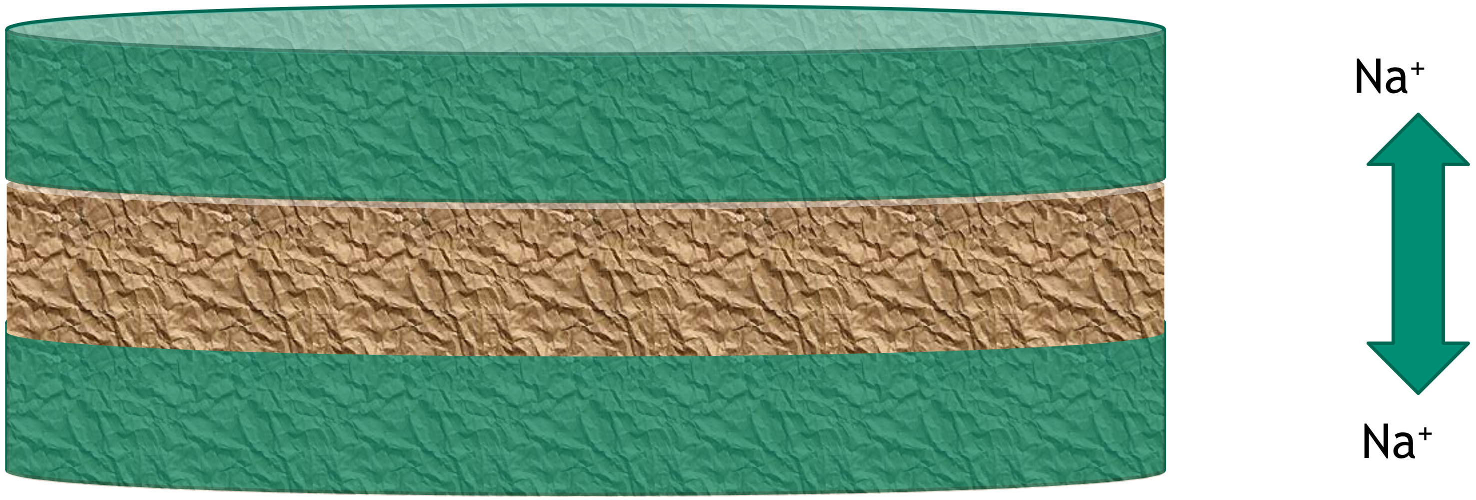
Dirt Pseudocapacitor: Proof of Concept

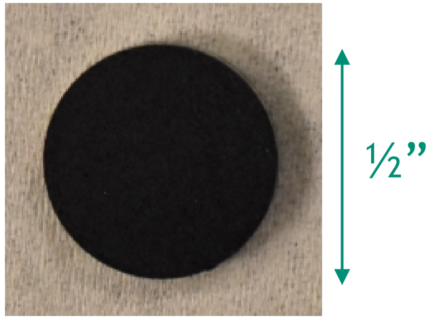
Using MMT as a solid state separator, we can press a sandwich an Na-MMT solid electrolyte between two MnO_2-based electrodes.

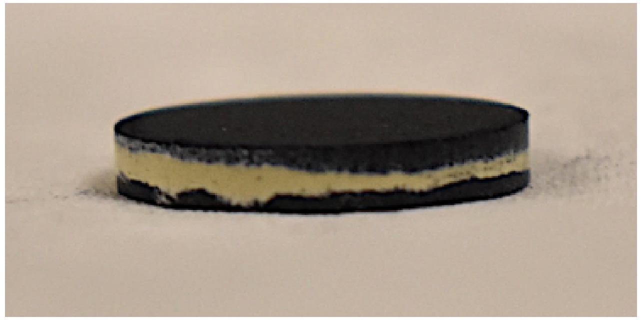
"Anode":
Na_xMnO_2 + Carbon + MMT

Solid State Electrolyte:
Na-MMT

"Cathode":
Na_xMnO_2 + Carbon + MMT







Spoerke, et al. In Preparation

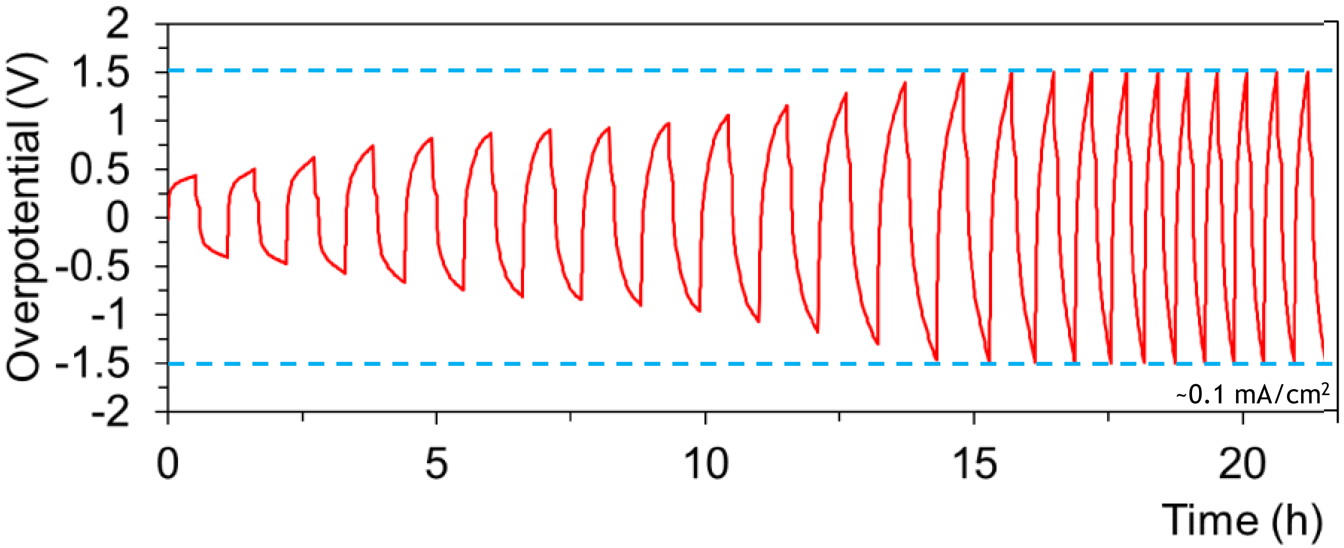
Promise, but a Materials Challenge!

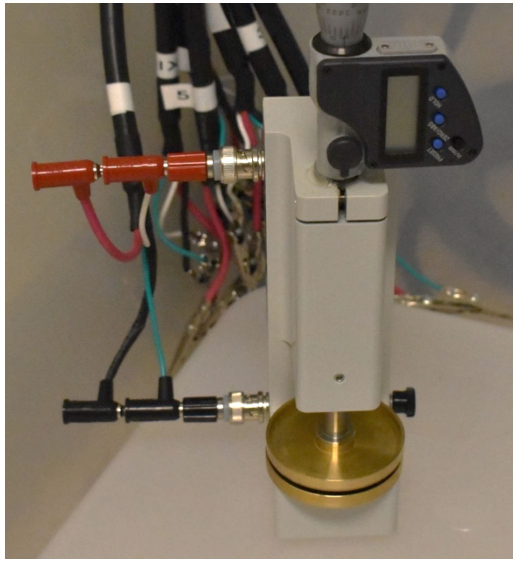
Electrochemical cycling shows promise!

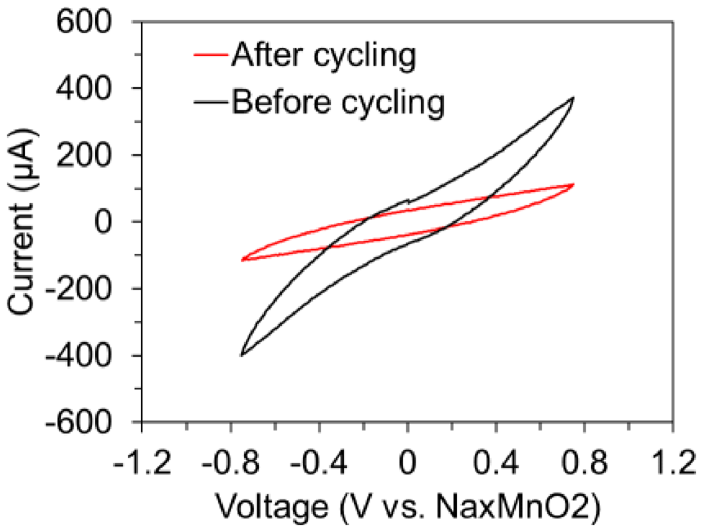
Cell cycling and cyclic voltammetry show signs of electrode degradation.

Need to improve electrode composition and interfaces.

Symmetric Galvanostatic Na_xMnO_2 cycling data. 1.5V limits (marked in blue dashed line)



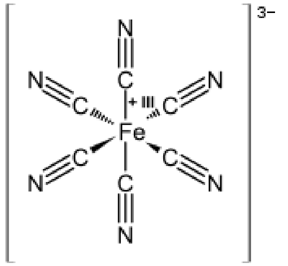


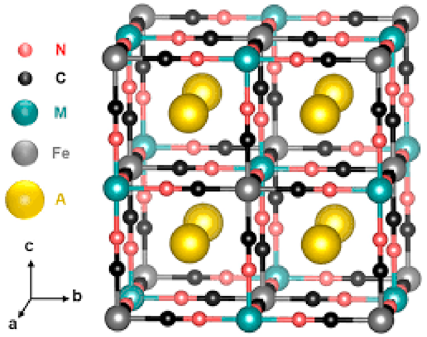


Cyclic voltammetry before and after testing shows loss of faradaic capacitance, indicating irreversible active material degradation.

Dirt Pseudocapacitor: Moving in the Right Direction?

Consider a different active sodium ion intercalation material: **Prussian Blue (PB)**



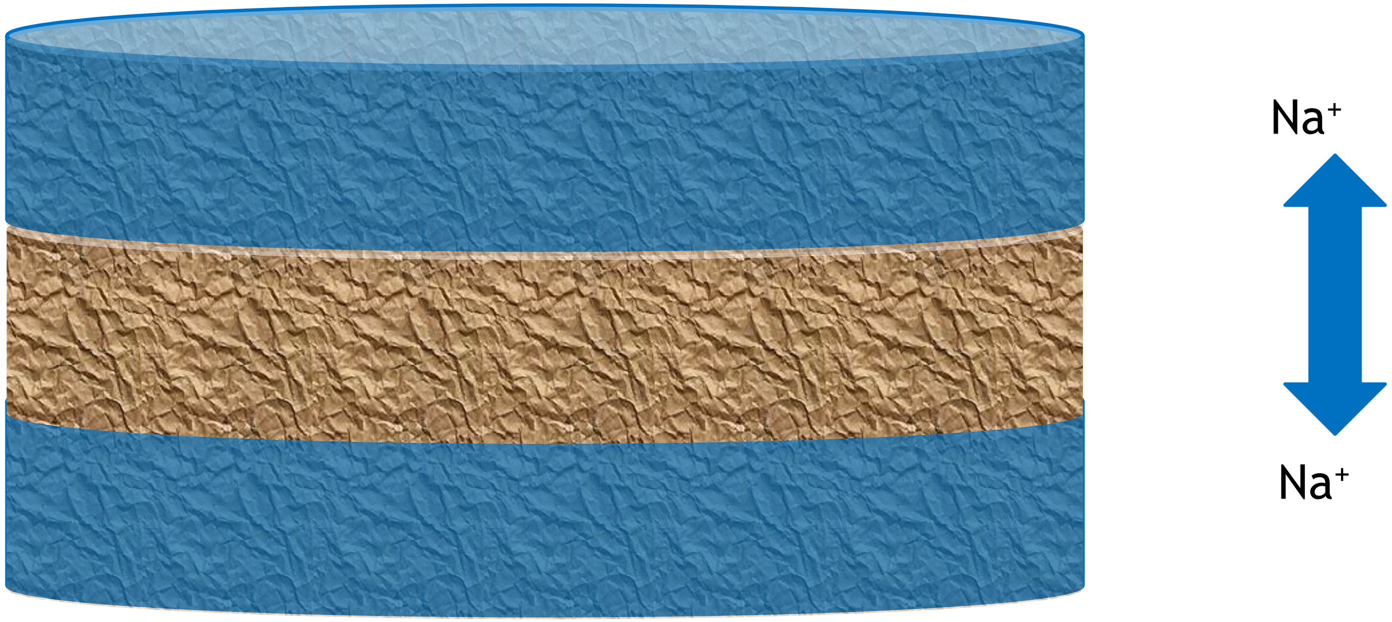


Lumley, et al., https://doi.org/10.1021/acsami.0c08084

“Anode”:
Prussian Blue + Carbon + MMT

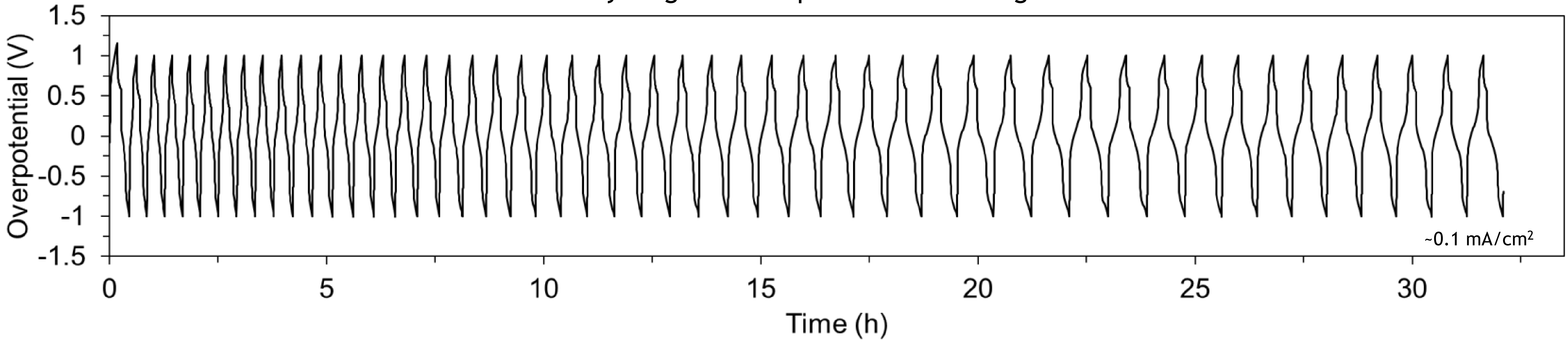
Solid State Electrolyte:
Na-MMT

“Cathode”:
Prussian Blue + Carbon + MMT

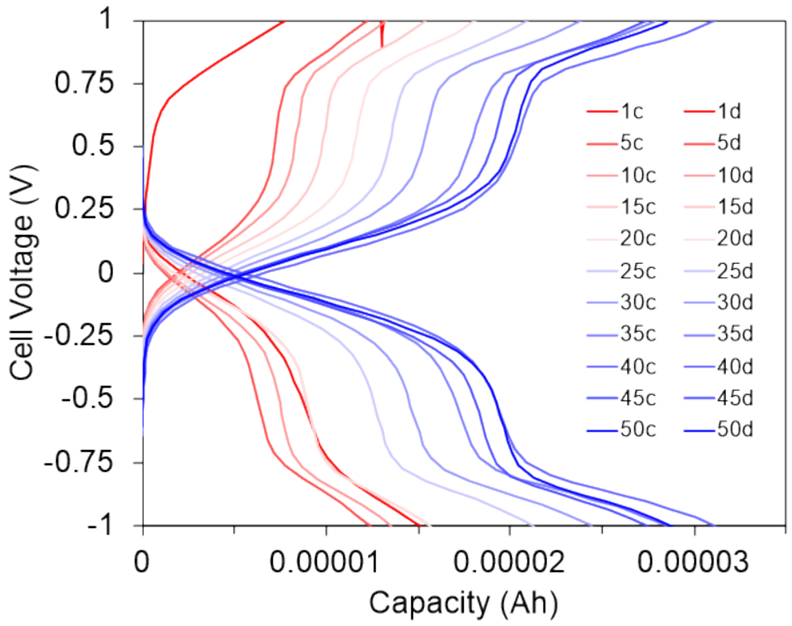


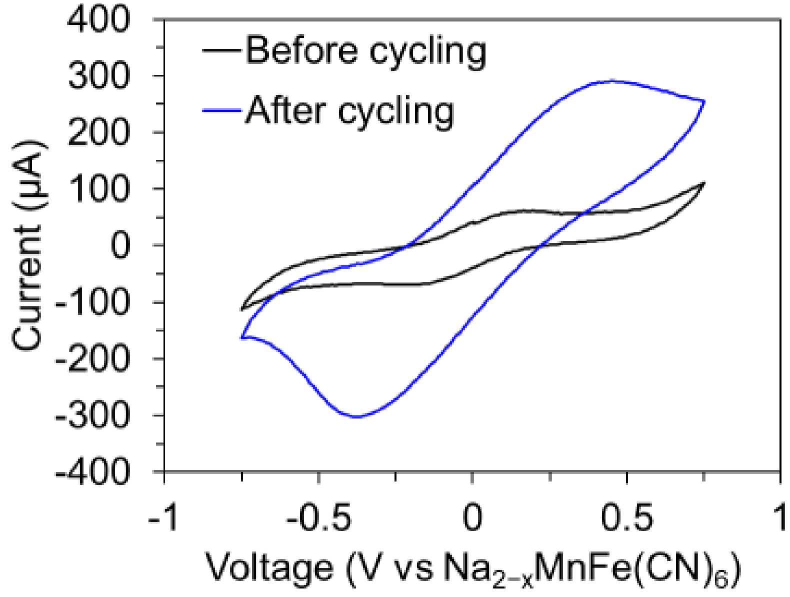
PB Improves Electrochemical Cycling!

Galvanostatic PB cycling shows improvements…and gets better over time!



Charge-Discharge curves and cycling profile show two electrochemical plateaus (high and low iron spin states) and improvements over time.





Cyclic voltammetry before and after testing shows increase in faradaic capacitance, indicating increased activity in PB material.

Challenge 3: Battery materials are costly and complicated to assemble at scale.

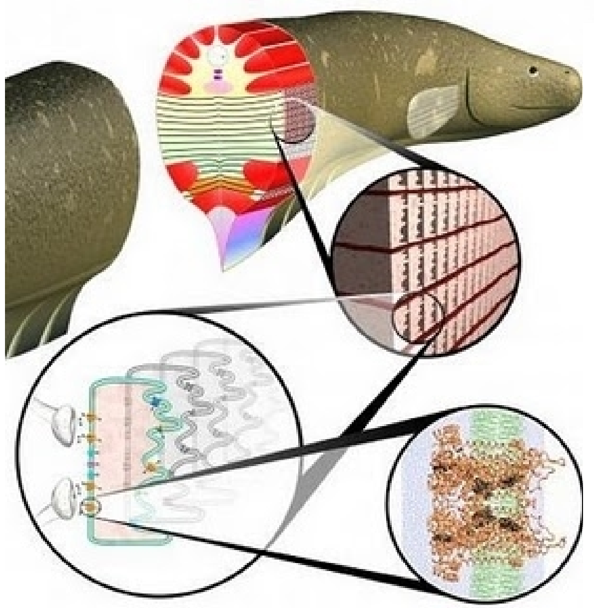
Can we realize a water-based electrical energy storage system inspired by biology?

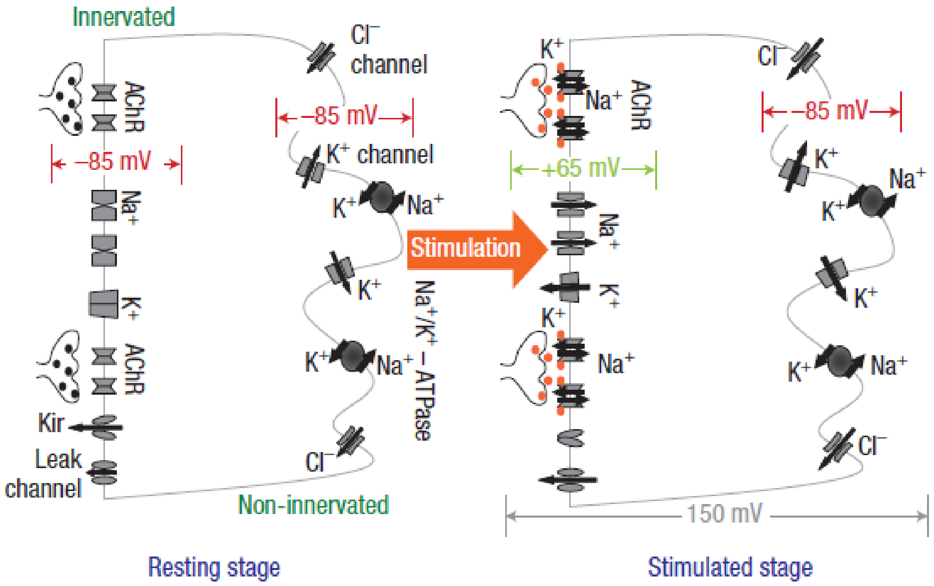
Harnessing Bio-Electricity

Returning to the original inspiration for batteries – we sought inspiration from bio-electricity!

Electric Eels: “Potential Inspiration”

Nature uses ion concentration gradients to control a wide range of critical electrical functions.





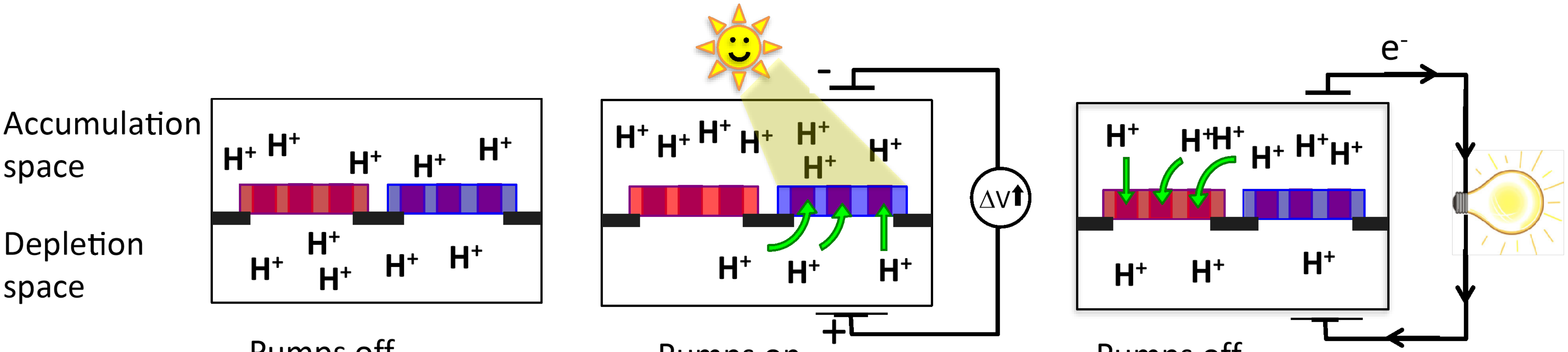
Electric eels can repeatedly generate 1A at 600V with millisecond discharge rates!

- *Key to electric eel function is the ability to control ion concentration gradients across cellular membranes.*
- *Series-Parallel connection of many cells provides scalability and resilience!*

Xu and Lavan, Nature Nanotech (2008) **3**, p666-670.

A Simplified Scheme for Bio-Inspired Energy Storage

Two chambers, separated by a membrane capable of selective ion transport



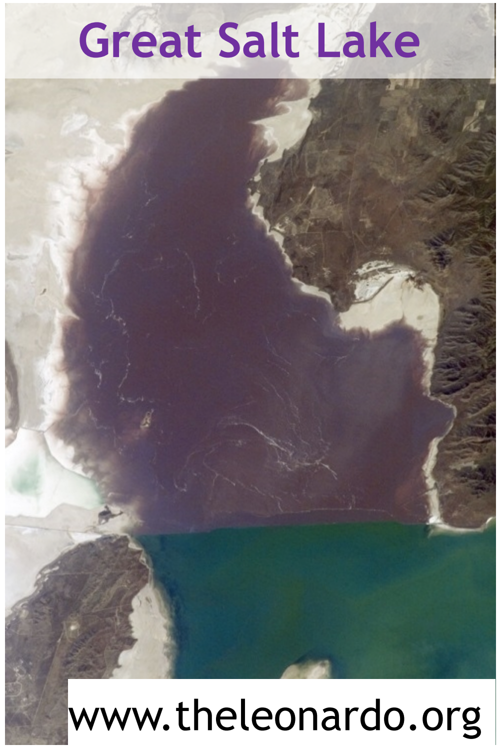
Pumps off
Gates closed
System static

Pumps on
Gates closed
System charging

Pumps off
Gates open
System discharging

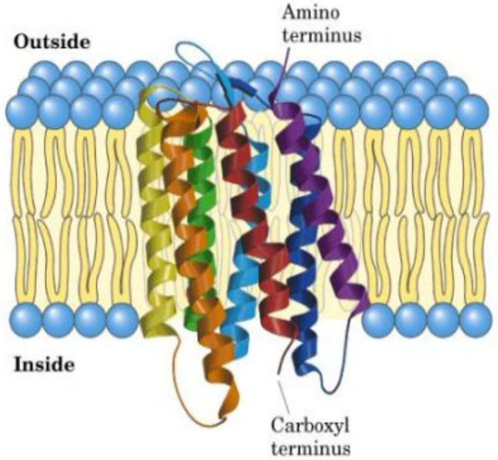
How to Control Ion Transport to Create a Concentration Gradient?

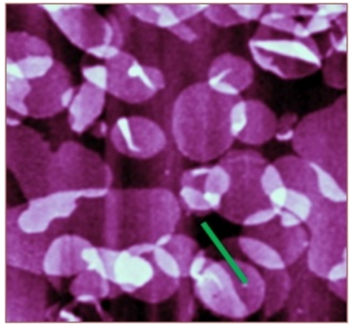
Bacteriorhodopsin (BR) (Halobacterium salinarum)



- Light driven, *selective* proton pump (1 photon = 1 proton)
- Up to ~10,000-fold proton gradient possible (~300 mV) on a millisecond timescale!
- Exceptionally stable
  - 140^{o}C (dry)
  - pH 3-10
  - > 10^6 pumping cycles
  - Stable for over **5 years**

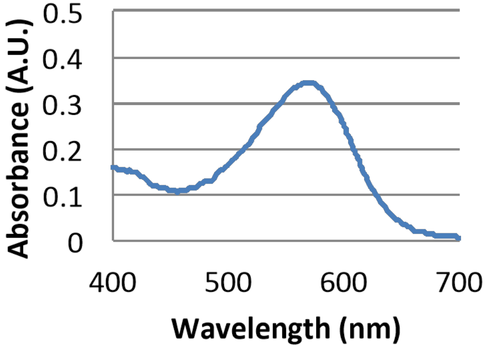
BR in a cell membrane





Purple Membrane containing BR

Extracted Purple Membrane containing BR

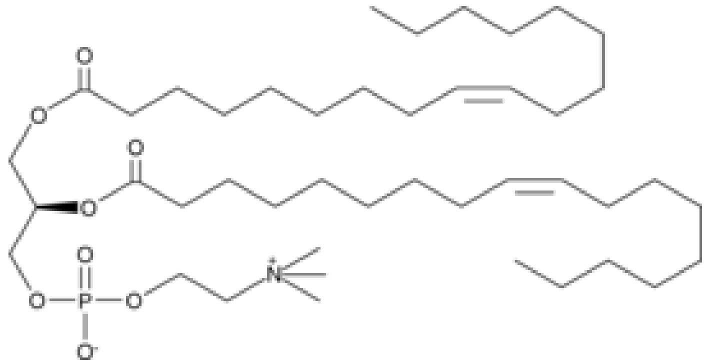


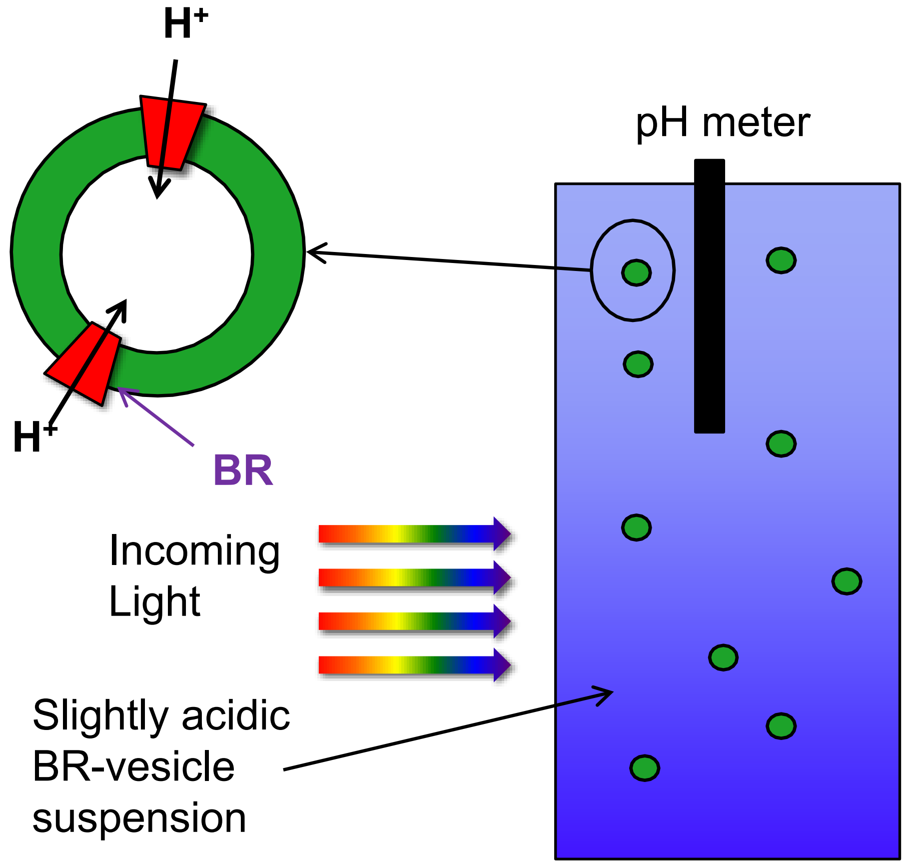
George Bachand and Virginia Vandelinder

Creating a Synthetic BR Cell Membrane

BR in DOPC vesicles

DOPC = 1,2-Dioleoyl-*sn*-glycero-3-Phosphatidylcholine





Creating a Synthetic BR Cell Membrane

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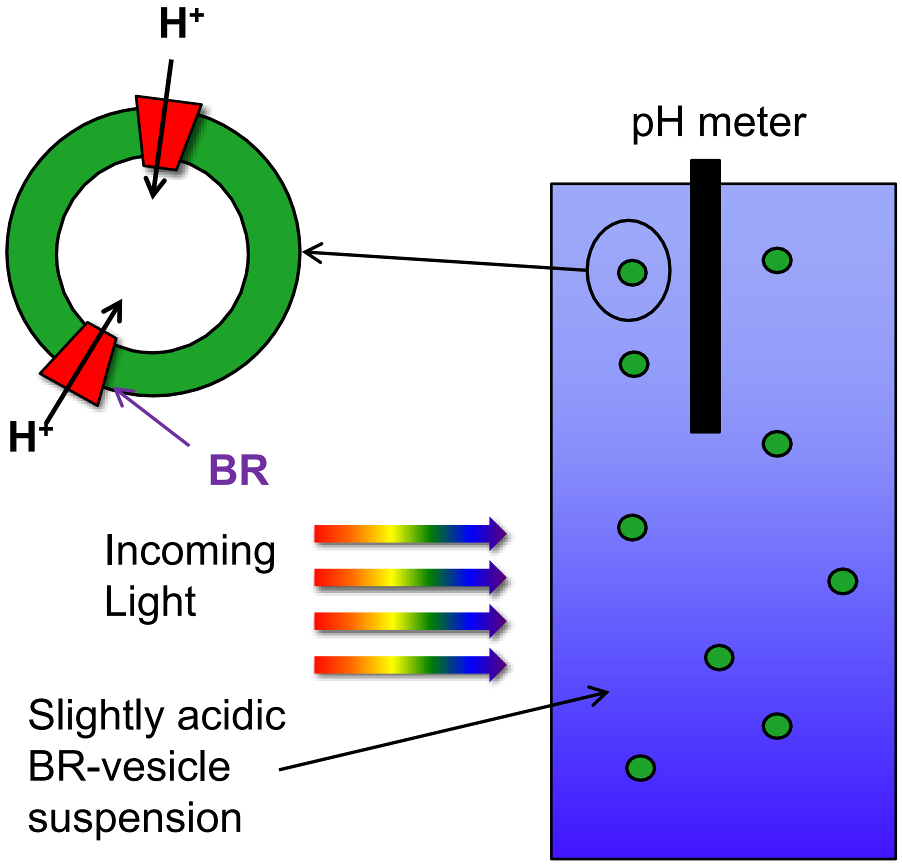
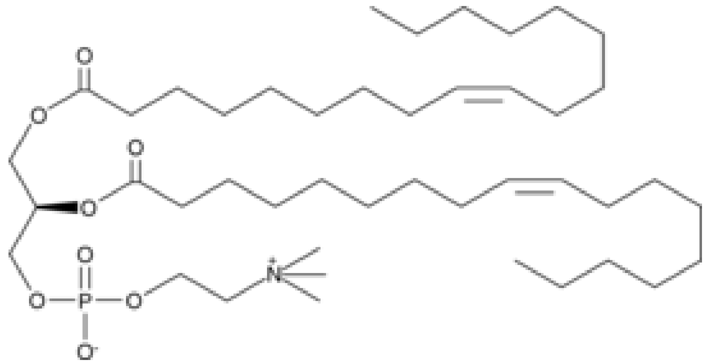
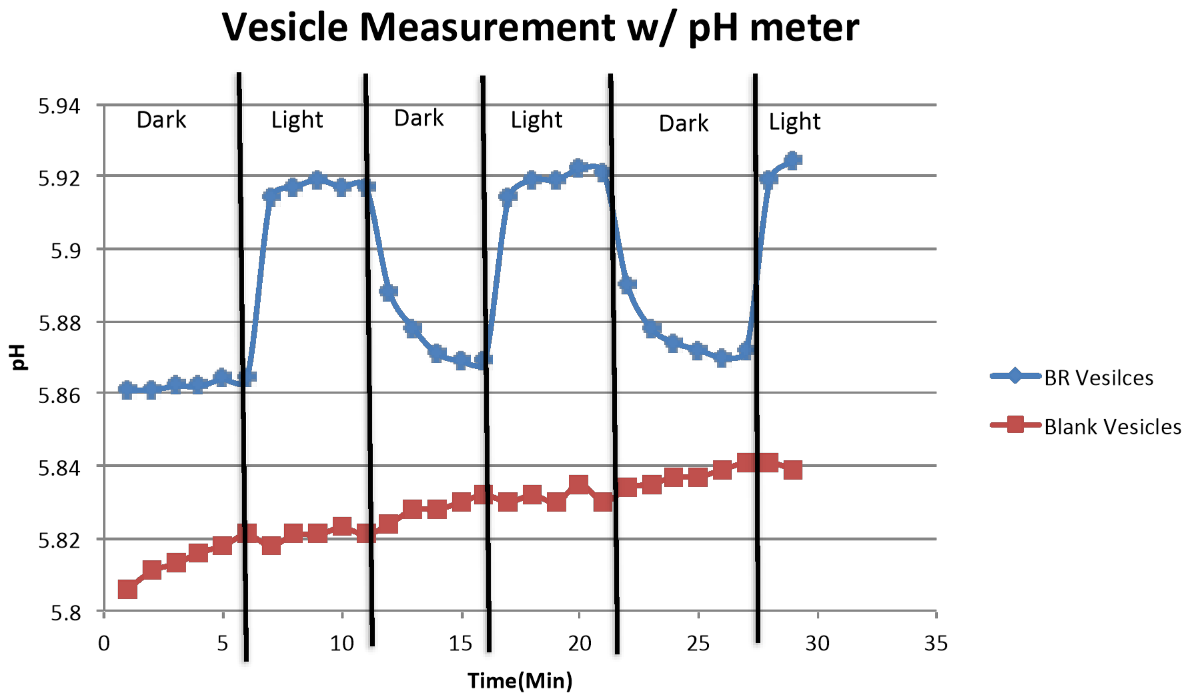




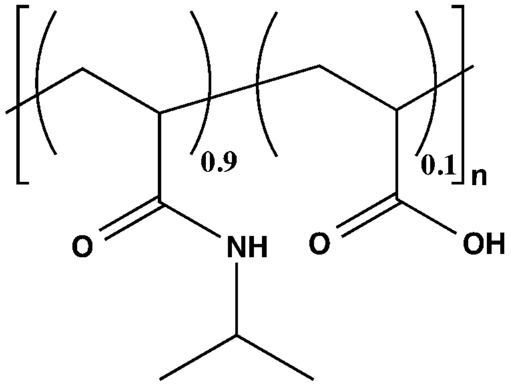


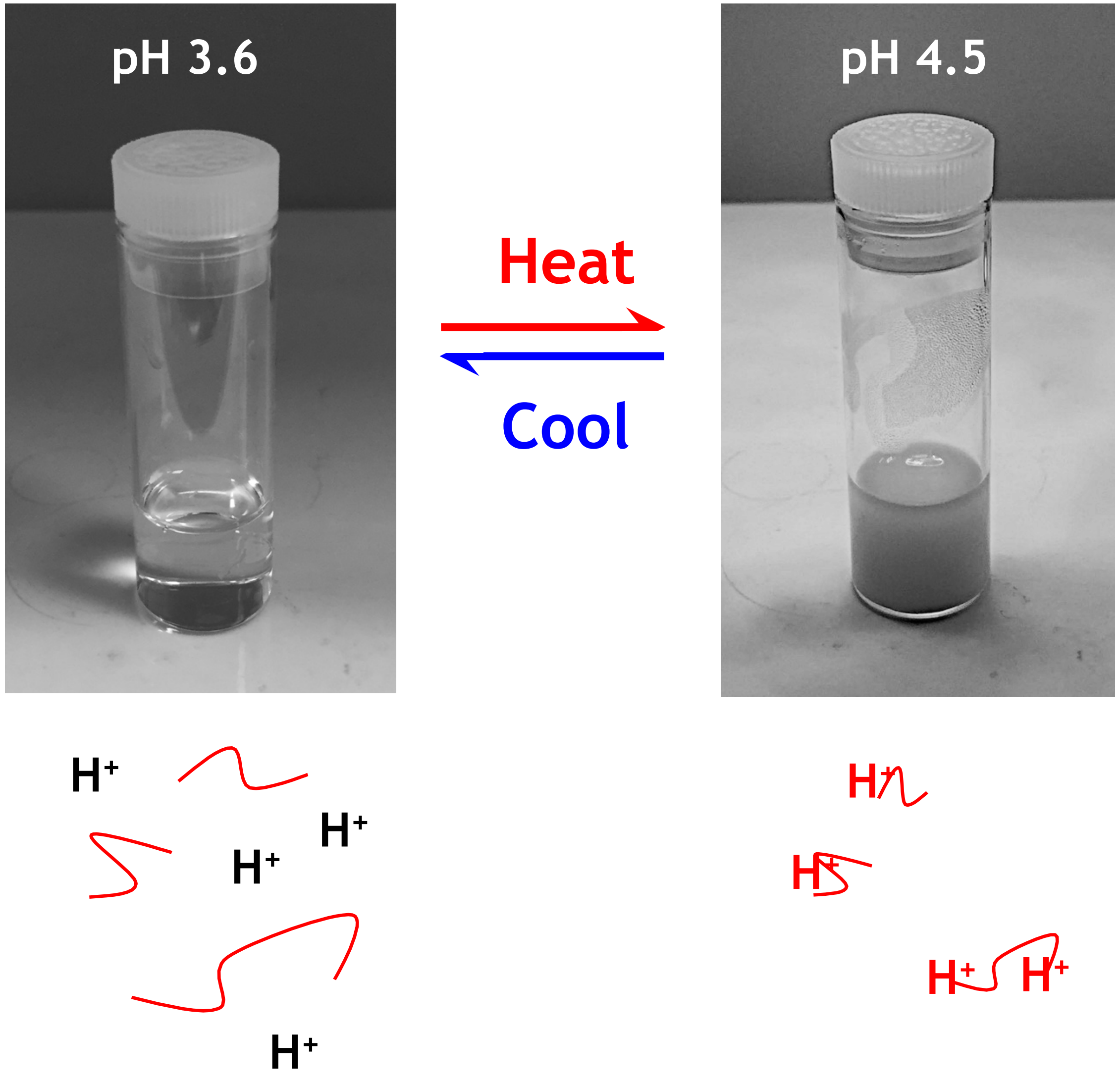
George Bachand and Virginia Vandelinder

Controlling Ion Concentrations with a Thermally Responsive Acidic Copolymer

NIPAM copolymers undergo a thermally reversible phase transformation that induces a change in solution pH.

Poly(NIPAM-co-AA)



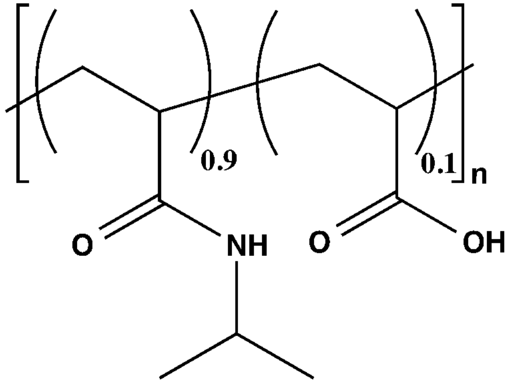


Synthesis acknowledgement:
Dara Gough

Concept for Polymer-Mediated Voltage Generation

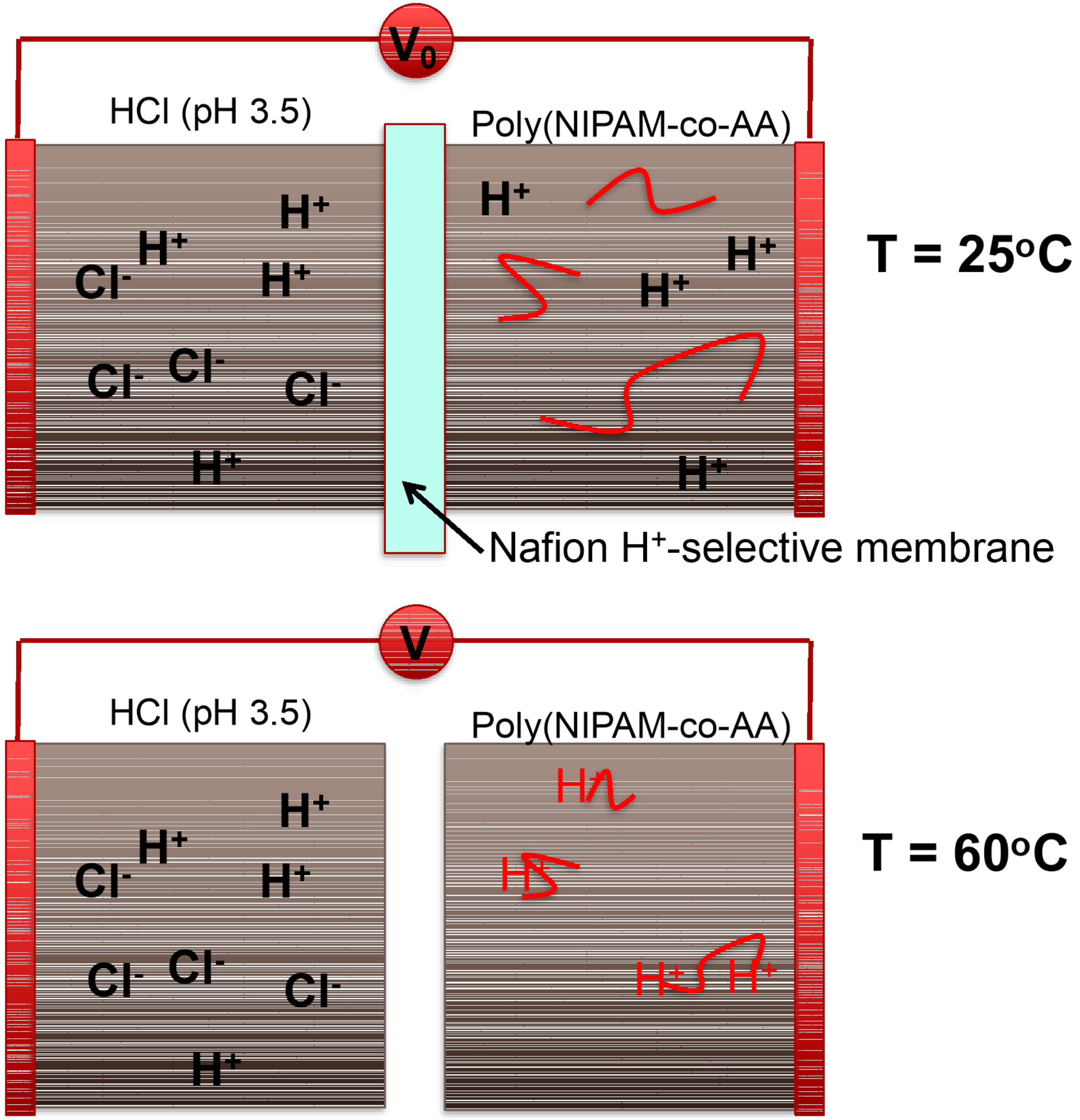
Polymer-mediated changes in pH can be used to generate voltage!

Poly(NIPAM-co-AA)



Open Circuit

Open Circuit

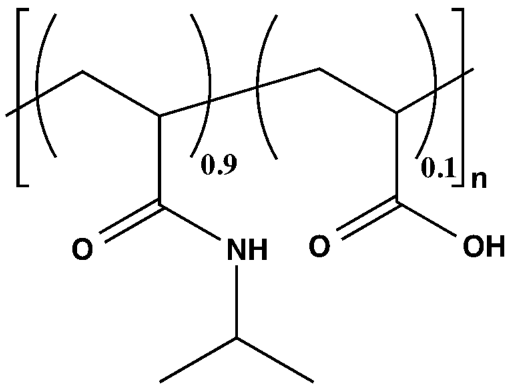


Synthesis acknowledgement:
Dara Gough

Concept for Polymer-Mediated Current Generation

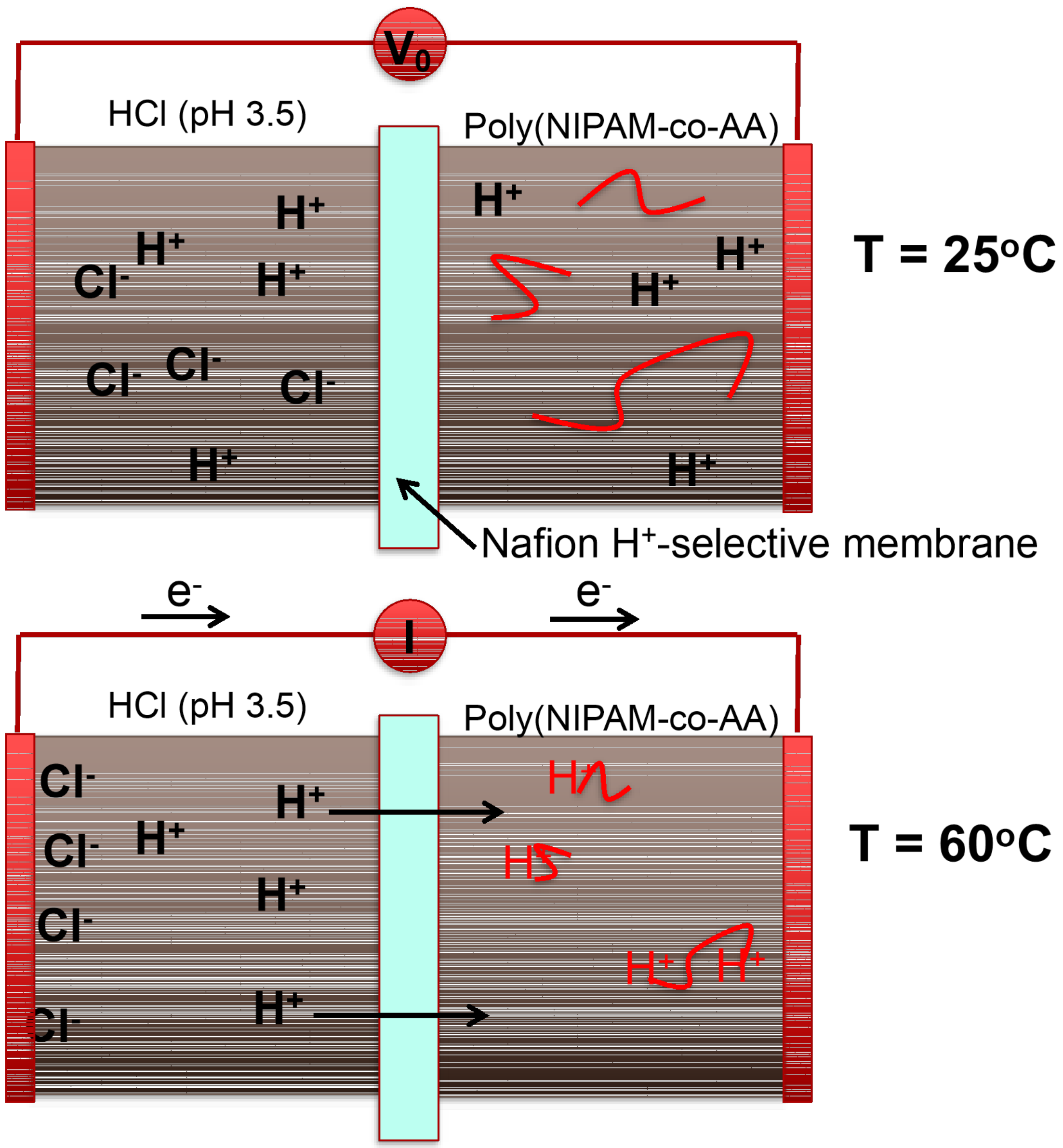
Under closed circuit conditions, polymer-mediated changes in pH can be used to induce current!

Poly(NIPAM-co-AA)



Open Circuit

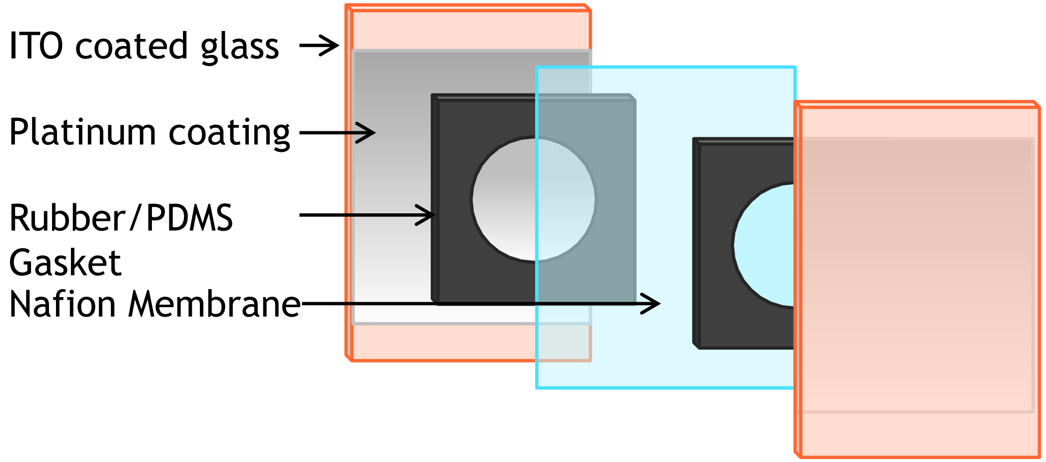
Closed Circuit



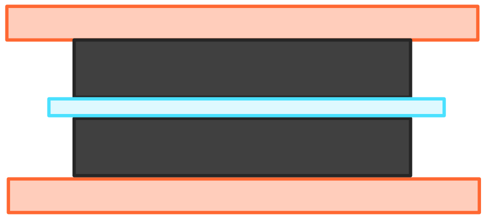
Synthesis acknowledgement:
Dara Gough

Testing Electrochemical Behavior of Polymer-Mediated Electrical Energy Storage

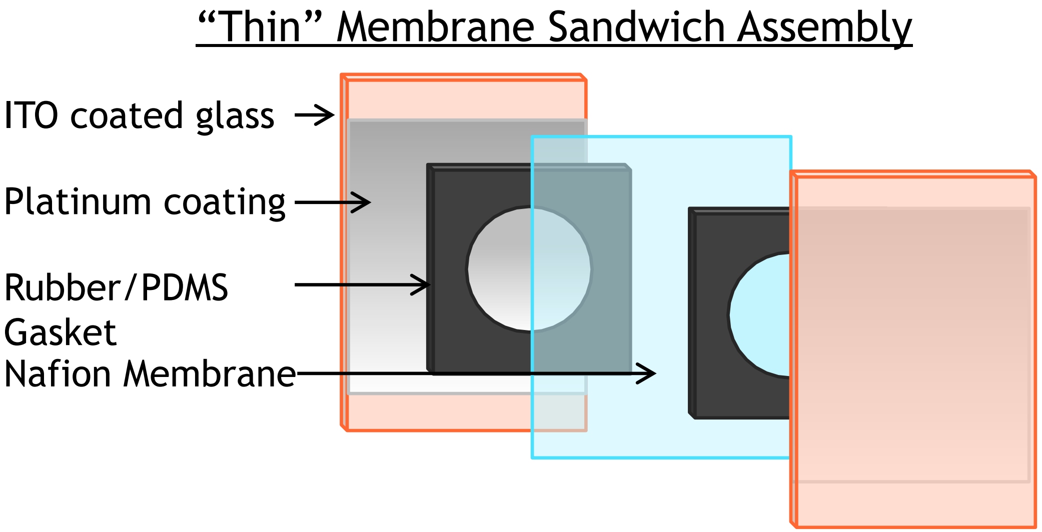
"Thin" Membrane Sandwich Assembly

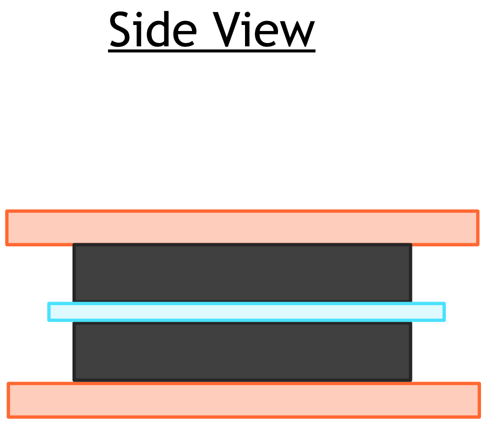


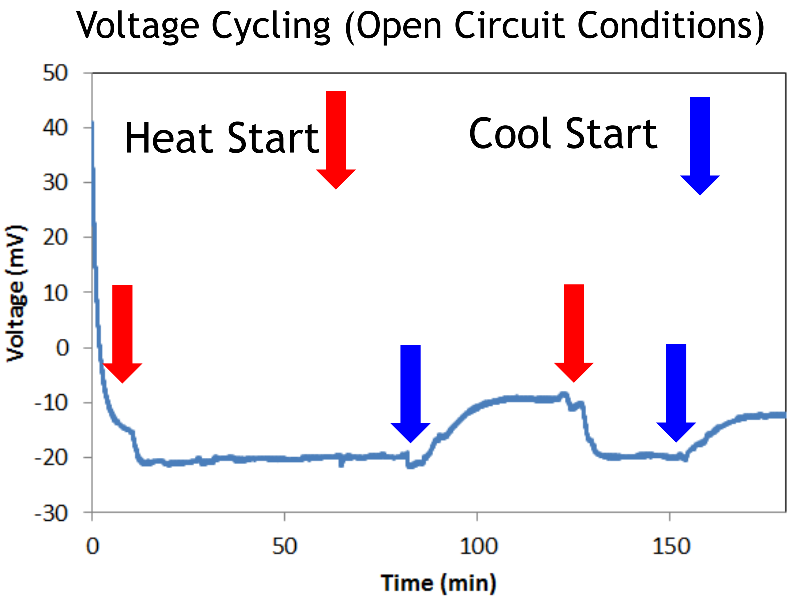
Side View

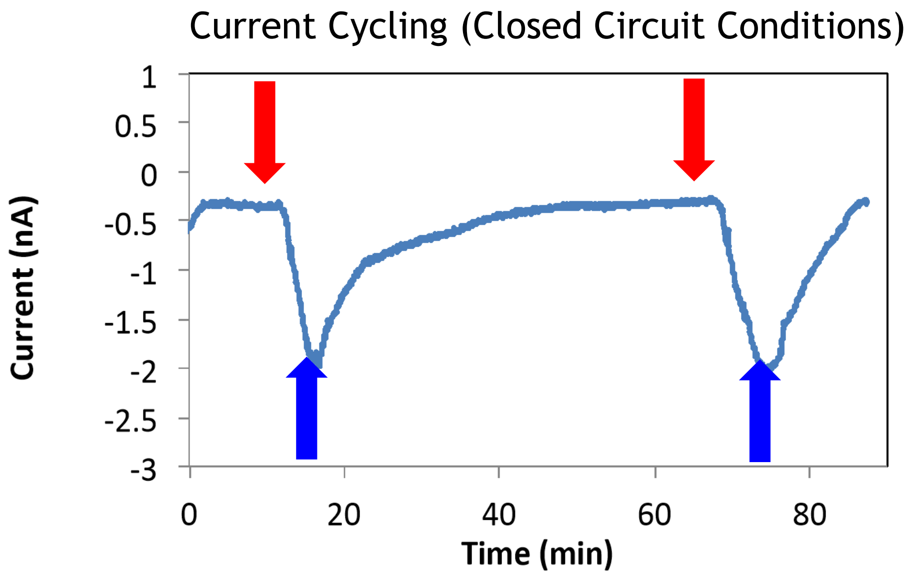


Testing Electrochemical Behavior of Polymer-Mediated Electrical Energy Storage









Recap and Final Thoughts

- Born from bio-inspired research, aqueous batteries have been a mainstay of energy storage for over 2 centuries!

- Modern developments have the potential to address vital needs for renewables integration, grid services, backup power, and other large-scale applications
  - Diverse Zn and Ni Chemistries
  - Pb-Acid
  - Metal-Air
  - Redox Flow

- Today's examples highlight opportunities for new, innovative water-based materials chemistries to provide non-conventional solutions to energy storage challenges.
  - Zero-crossover separators (e.g., solid state ion conductors)
  - Earth abundant "dirt cheap" materials with high functionality (clay conductors)
  - Bio-inspired ionic membranes and materials systems

We are at the beginning of a global energy revolution!

Continued creativity, enthusiasm, and passion for energy storage will help create a new generation of safe, cost-effective, and highly efficient energy storage technologies, needed to enable a much-needed energy infrastructure transformation.

Thanks!

Flow Batteries:
Eric Allcorn
Ganesan Nagasubramanian
Harry Pratt III
David Ingersoll
Travis Anderson
Leo Small

Clay Conductor:
Amanda Peretti
Martha Gross
Stephen Percival
Leo Small
Prof. Y-T Cheng (U. Ky)
Ryan Hill (U. Ky)

Electric Eel:
Leo Small
David Wheeler
Alina Martinez
Virginia Vandelinder
George Bachand
Susan Rempe

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Center for Integrated Nanotechnologies (CINT)

U.S. DEPARTMENT OF ENERGY

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Contact: Erik Spoerke (edspoer@sandia.gov)

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