Oak Ridge National Laboratory

Nonaqueous Sodium-Based Catholytes for Redox Flow Batteries

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Project Team

Ethan Self

Ernesto (Camilo) Zuleta Suarez

Guang Yang (Presentation 604)

Michelle Lehmann (Poster 10/24)

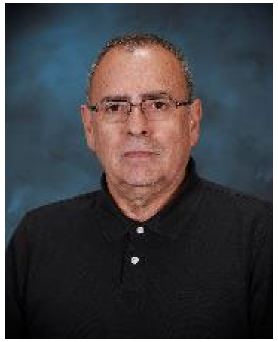
Tomonori Saito

Thomas Zawodzinski

David Mitlin (UT-Austin)

Recent ORNL Team Members

Jagjit Nanda (SLAC-Stanford)



Frank Delnick (Retired 6/22)

Landon Tyler (Graduated 6/22)

Core Expertise and Focus Areas

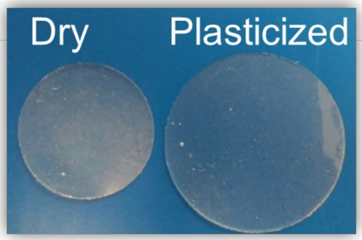
- High energy flow battery chemistries based on earth-abundant active materials
- Polymer electrolytes with high Na^+ conductivity and selectivity (Yang, Lehmann, Saito)
- Advanced characterization and prototype evaluation

Acknowledgments

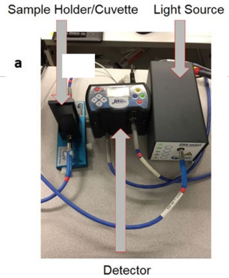
This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity, Department of Energy.

Additional thanks to Michael Starke, Mali Balasubramanian, program managers, and Gabriel Veith at ORNL.

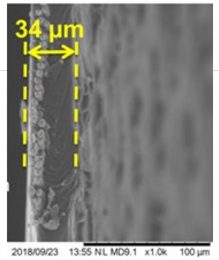
Timeline of ORNL Research on Nonaqueous Redox Flow Batteries



Crosslinked PEO Membranes



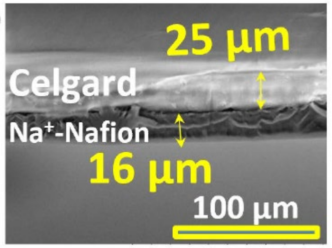
In-Situ UV-Vis Crossover Setup



Glass Fiber/PEO Composites

Nexar Membrane Single-Ion Conductor

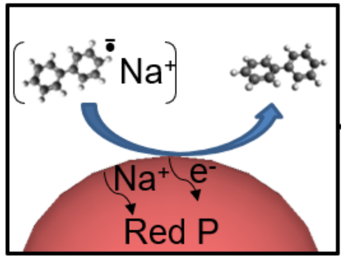
Bettergy Corp. Benchmarking



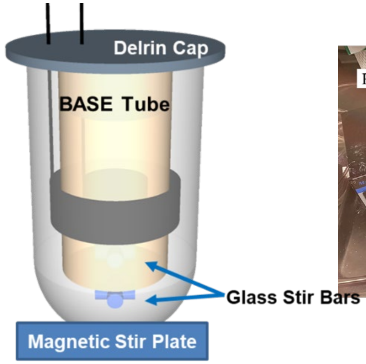
PFSA Composites

2018 2019 2020 2021 2022 2023

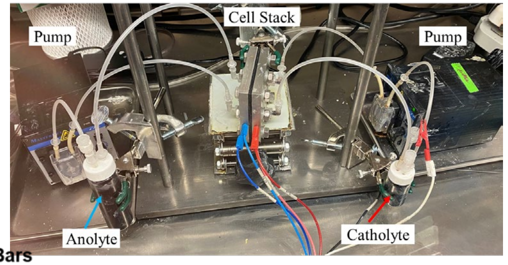
Mediated Red Phosphorus Anode



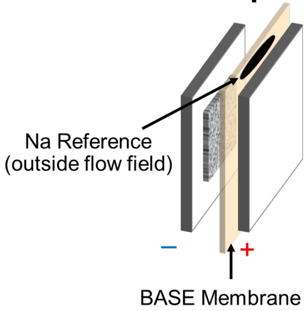
Biphenyl/Na_2S_x Cylindrical Cell



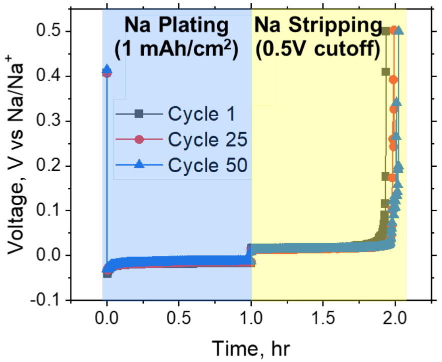
Nonaqueous Flow Cell Testbed



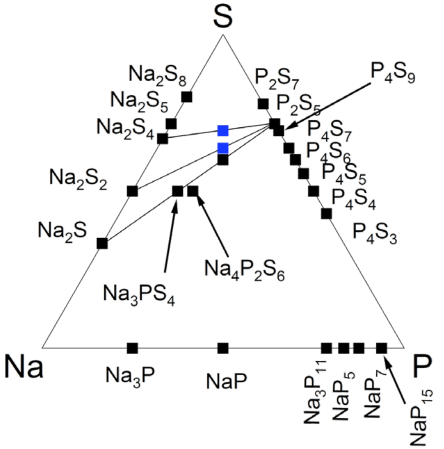
3 Electrode AC Impedance Method Development



Reversible Na Metal Anodes



Thiophosphate Catholytes



*references to these works are available upon request

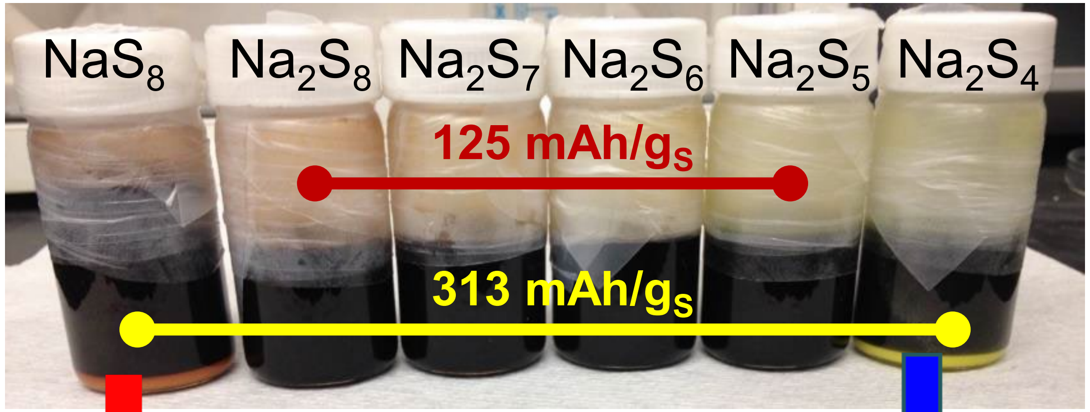
FY23 Research Focus Areas

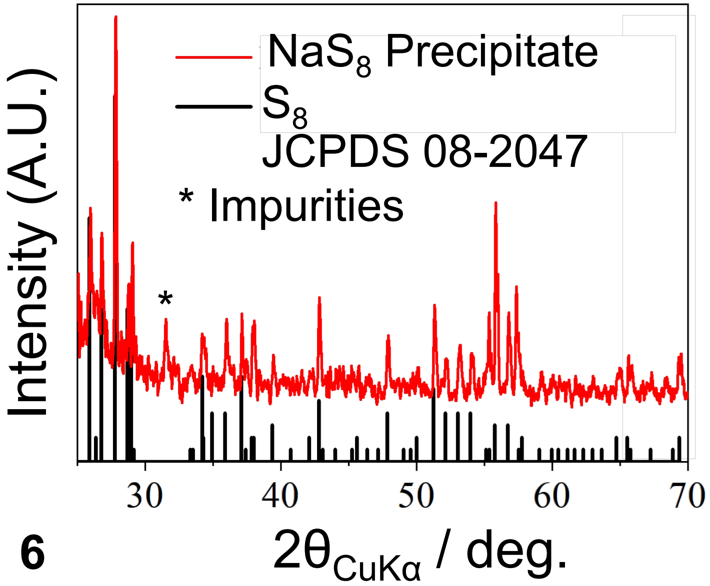
I: Structure and Electrochemistry of Na-(P)-S Catholytes

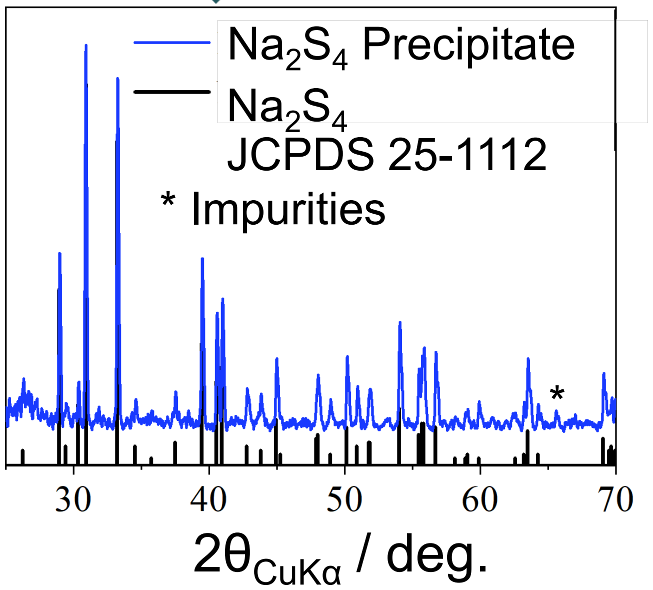
II: AC Impedance Method Development (Battery Diagnostics)

Recap: Na_2S_x is promising catholyte for nonaqueous flow batteries due to low cost and outstanding cycling stability

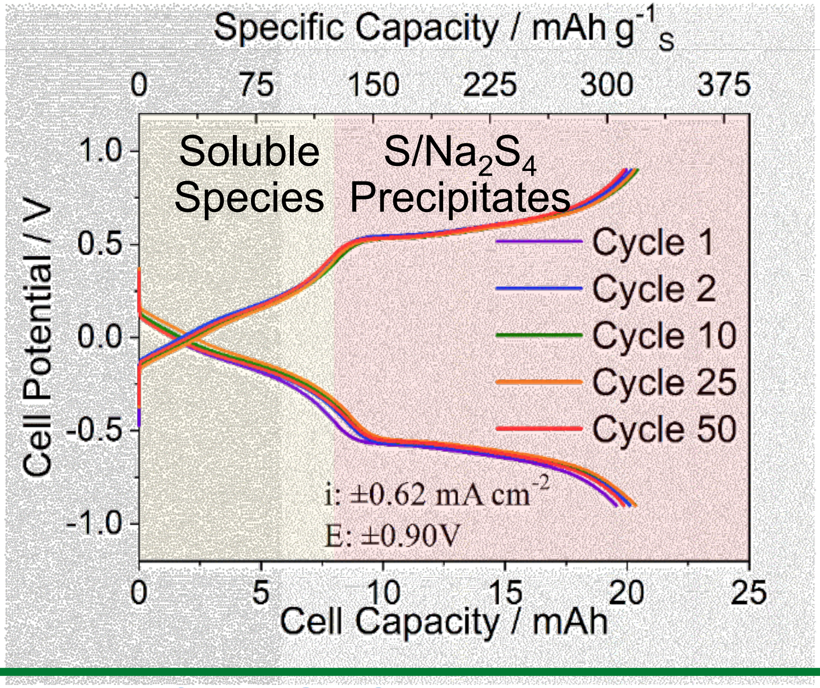
Na_2S_x in Diglyme (2EGDME)







Na_2S_x|BASE|Na_2S_x Symmetric Flow Cell



Overview of Na_2S_x Catholytes

- ✓ Low cost, earth-abundant active material
- ✓ Outstanding reversibility and cycling stability (symmetric and full cells)
- ✗ Low solubility (<<0.1m) when x<5
- ✗ Low sulfur utilization (125 mAh/g) when only soluble Na_2S_x species are cycled.
- ✗ Cycling insoluble species (e.g., Na_2S_4, S) is only viable for small lab-scale prototypes.

E. C. Self et al. *J. Electrochem. Soc.* **2021**, 168, 080540.

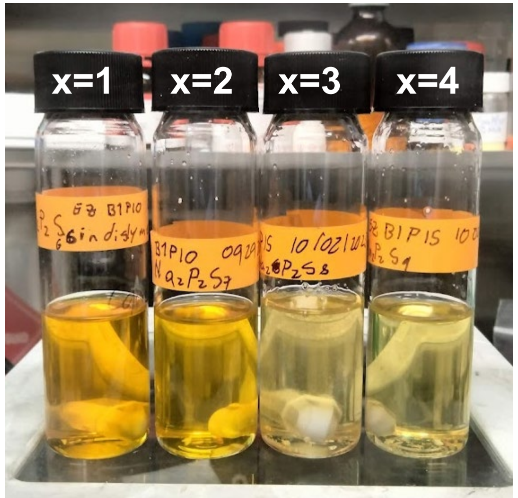
Recap: Complexing Na_2S_x with P greatly increases solubility. Ternary phase space is ripe for materials discovery.

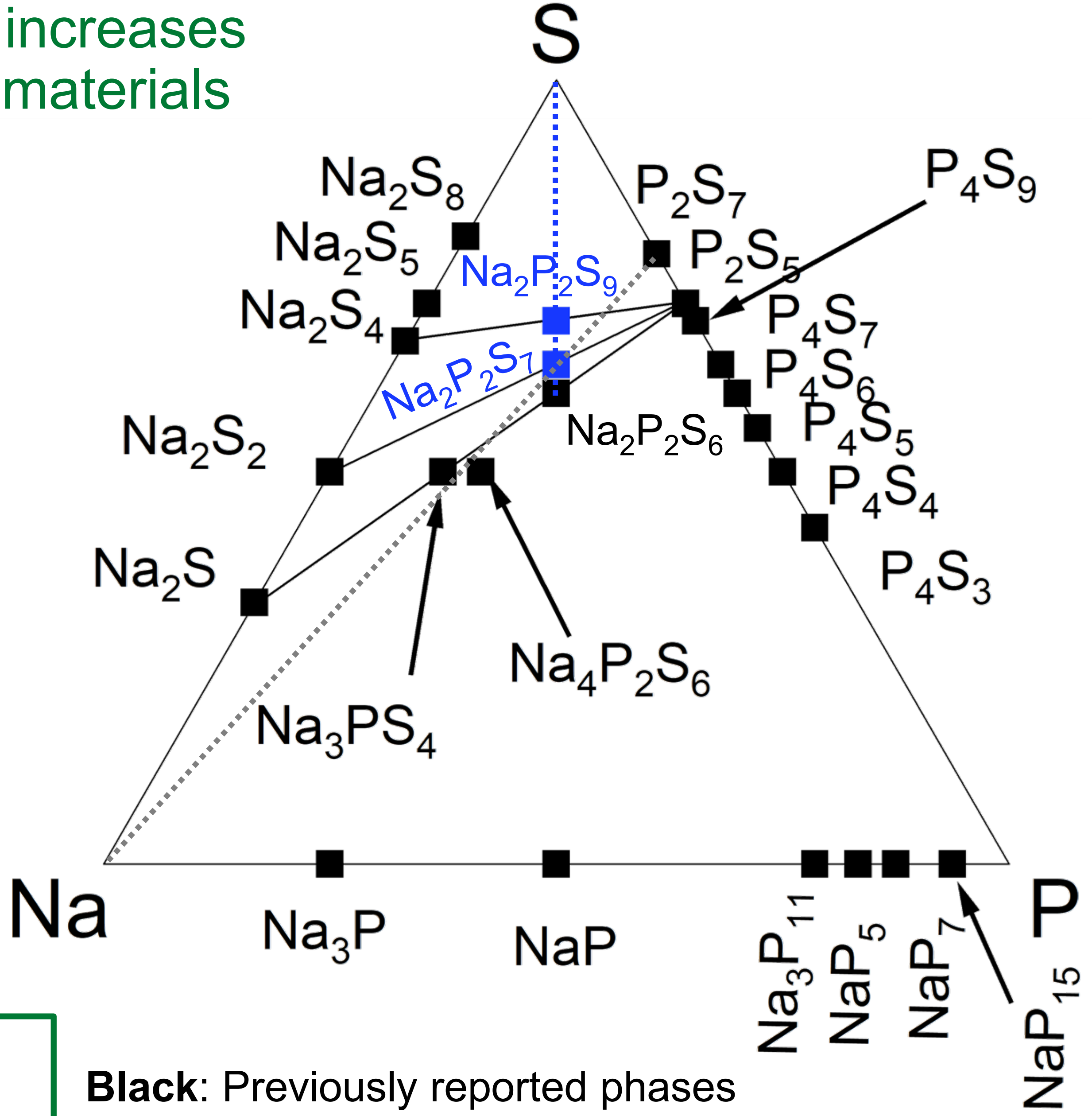
$$Na_2S_x + P_2S_5 \xrightarrow{\text{Diglyme}} Na_2P_2S_{5+x}$$

Insoluble ($Na_2S_x + P_2S_5$)

High-capacity solvated complex ($Na_2P_2S_{5+x}$)

0.7m $Na_2P_2S_{5+x}$ in Diglyme





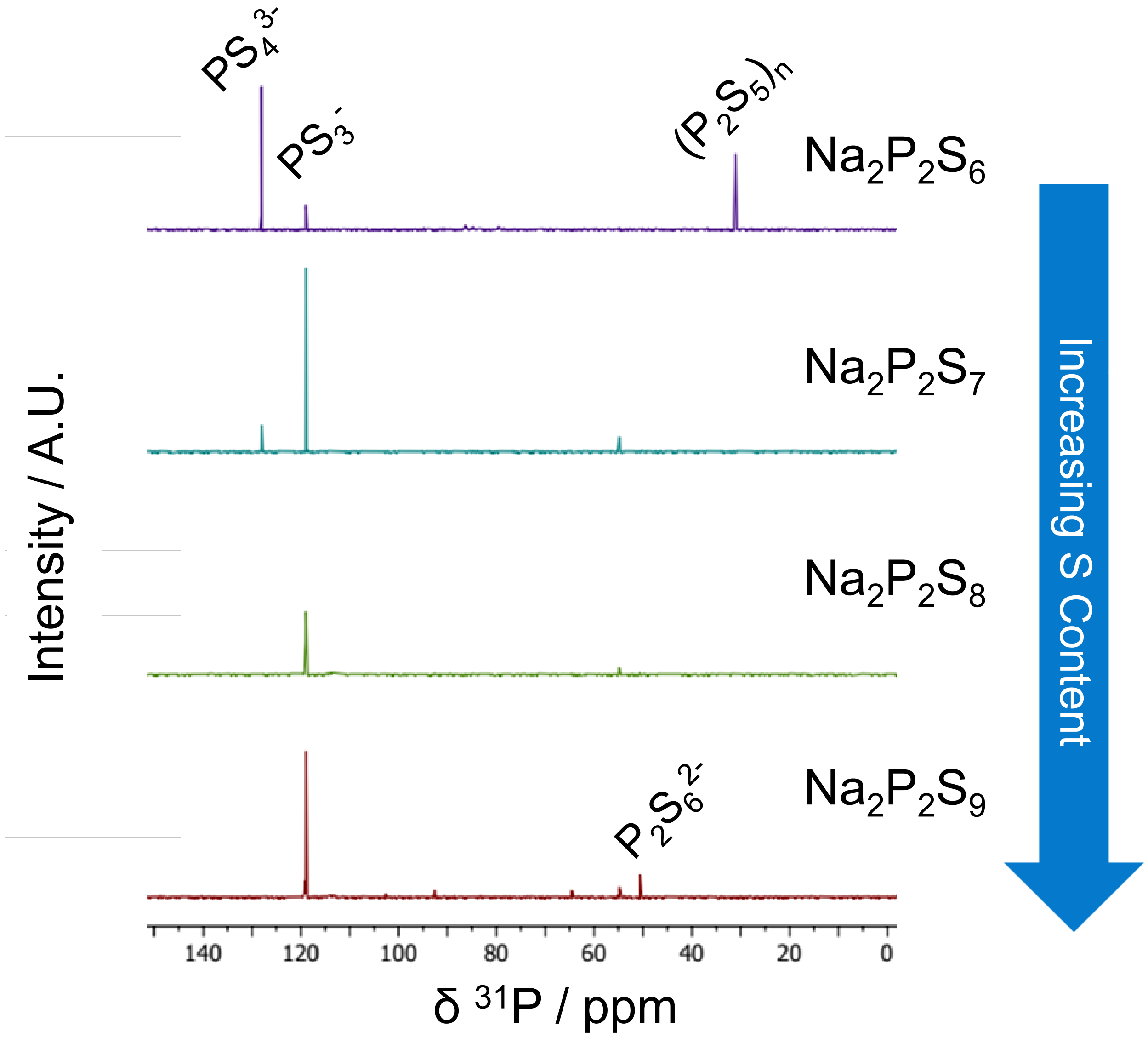
Black: Previously reported phases
Blue: New Na-P-S ternary compositions

Lehmann, Zuleta Suarez, Self et al. 2023 (Unpublished)

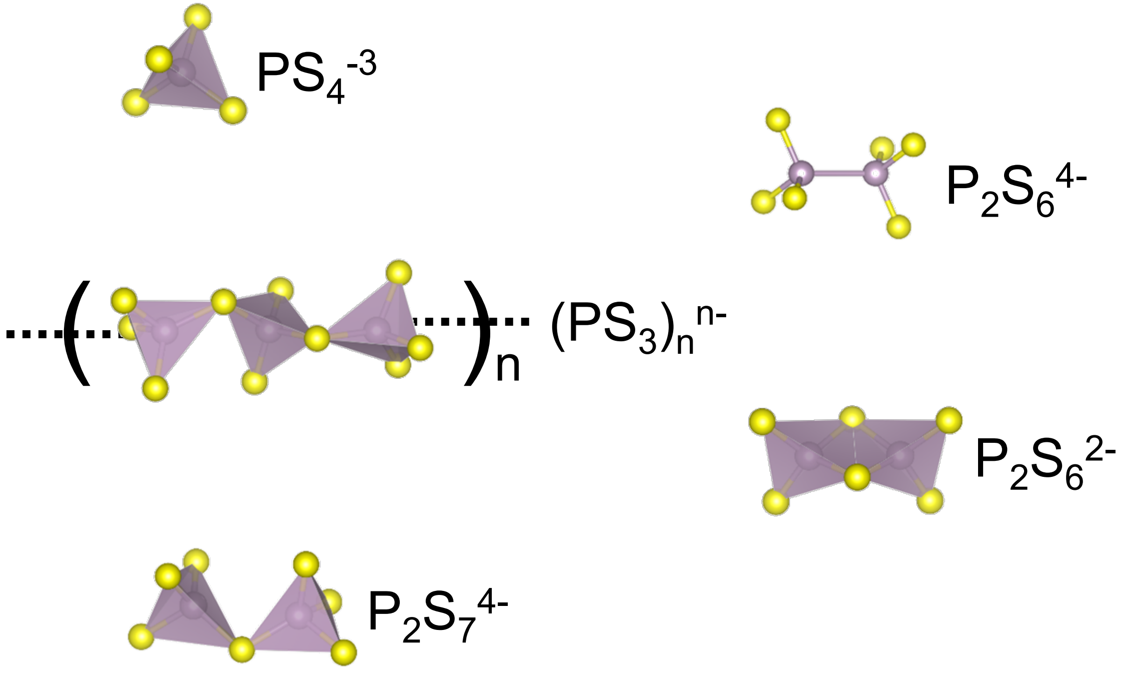
Overarching Science Questions

1. How does P coordination impact structure and electrochemistry of Na-P-S catholytes?
2. How does structure evolve upon Na insertion/extraction?

^{31}P NMR measurements indicate major differences in polyanionic structure across $Na_2P_2S_x$ phase space.



Common Thiophosphate Polyanions



Key Findings

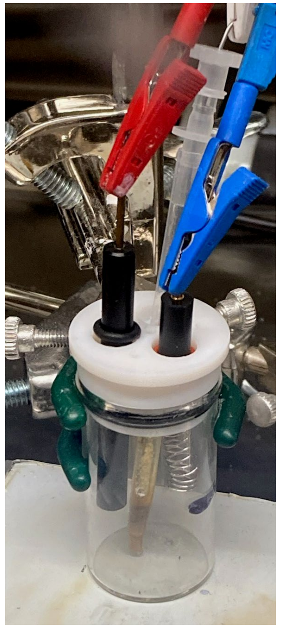
1. P^{5+} is tetrahedrally coordinated in all structures
2. Na-P-S compounds have common PS_3^- moiety
3. Quantitative analysis of polyanion distribution beyond the scope of this work

^{31}P peak assignments from *PNAS* **2021,** 118, e2116184118

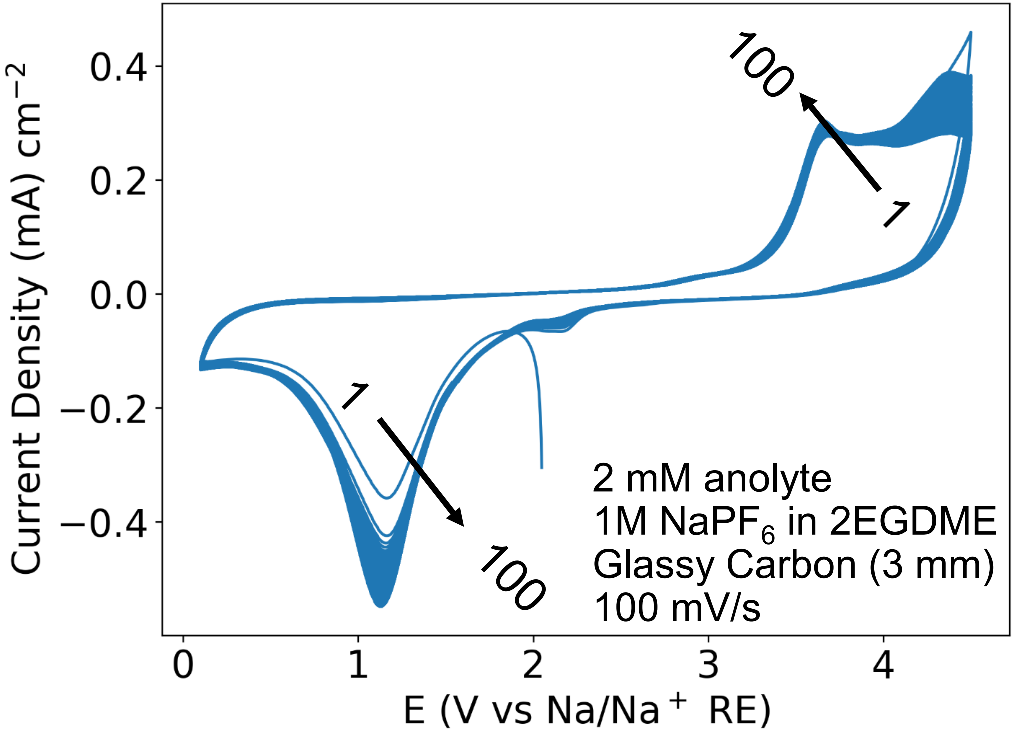
Zuleta Suarez, Lehmann, Self, et al. (2023, Unpublished)

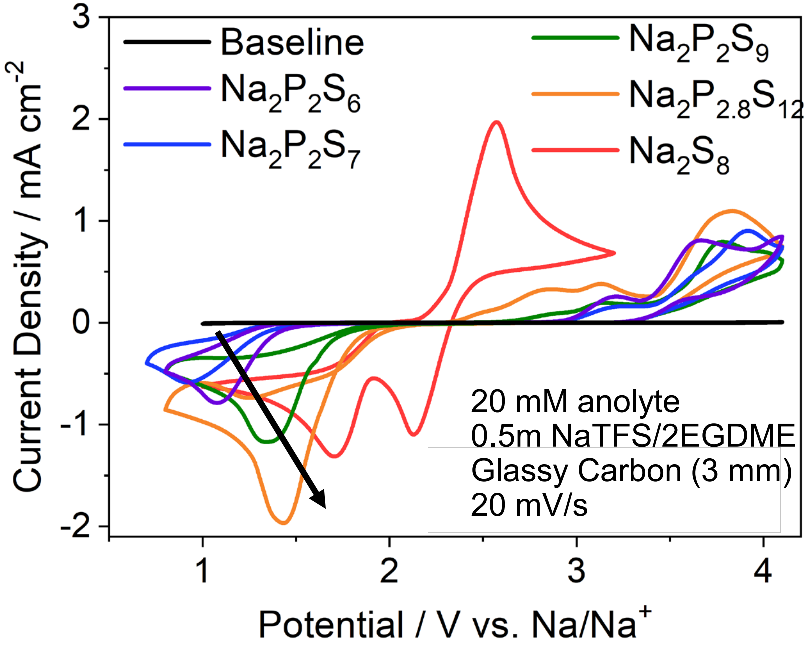
Electrochemical properties of Na-(P)-S are strongly influenced by structure and stoichiometry.

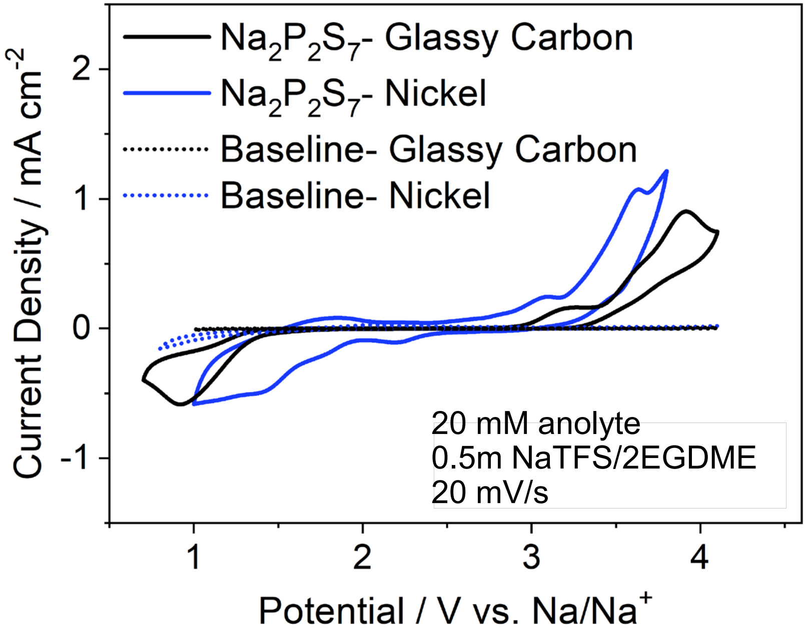
Voltammetry Cell



$Na_2P_2S_8$



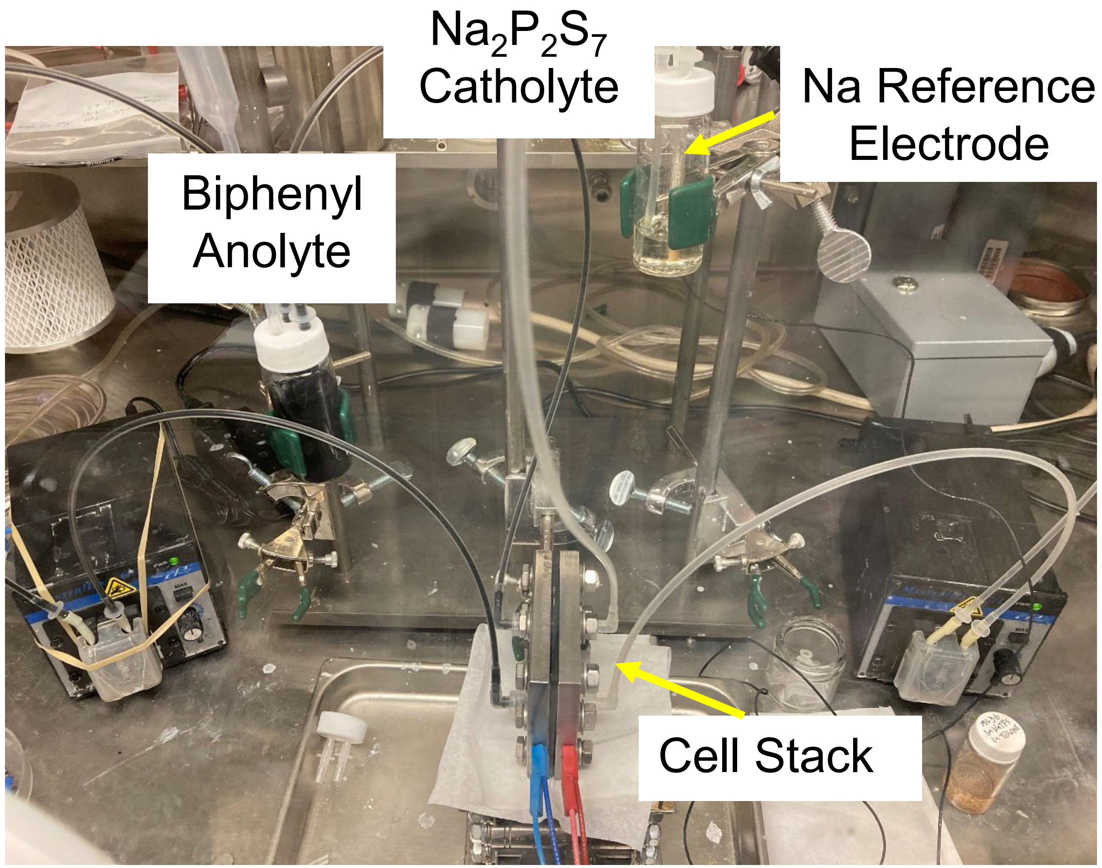




Key Findings

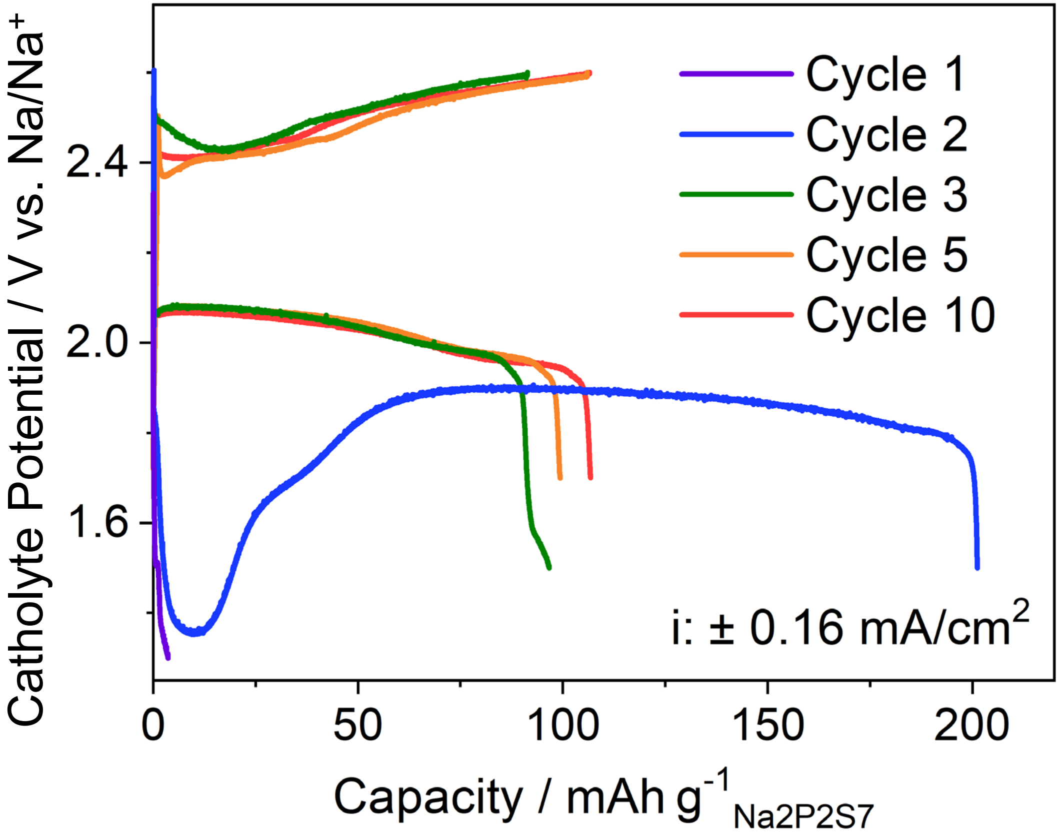
1. Na-P-S catholytes are stable upon repeated cycling
2. Large voltage hysteresis (>1V) for Na-P-S. Sluggish kinetics?
3. Open-circuit voltage ~2V vs. Na/Na^+ suggests charge compensation through sulfur redox center

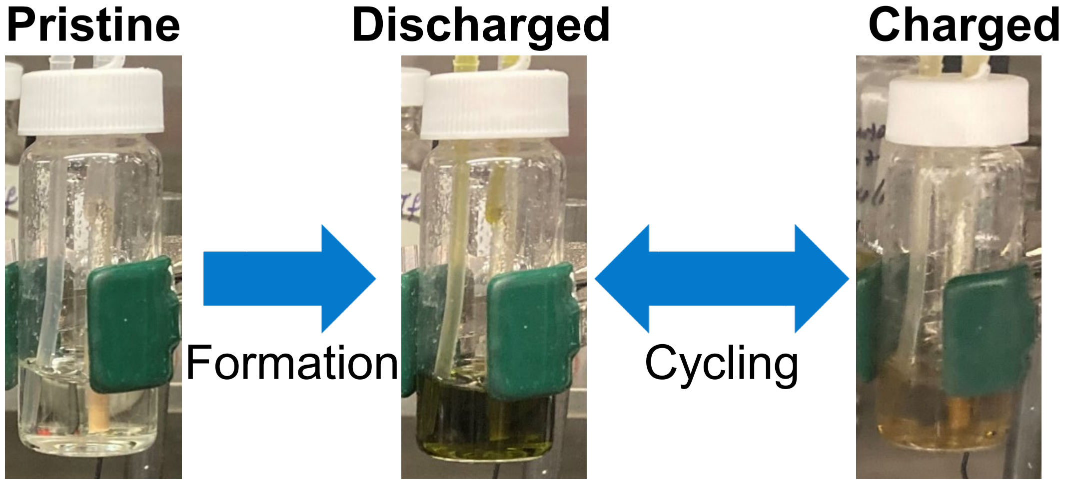
Flow cells with $Na_2P_2S_7$ catholyte exhibit reversible voltage profiles after formation step with deep discharge.



$Na_2P_2S_7 + nNa^+ + ne^- \longleftrightarrow Na_{2+n}P_2S_7$

$Q = 81*n\ mAh/g_{Na2P2S7}$





FY23 Research Focus Areas

I: Structure and Electrochemistry of Na-(P)-S Cathoytes

II: AC Impedance Method Development (Battery Diagnostics)

In FY23, team developed AC impedance model to augment experimental tools for RFB diagnostics.

Method Overview (Technique Developed at ORNL[1-4])

- Z is a differential quantity describing **local**, linear response.
- For nonlinear systems, measure Z under different steady-state biases to recover **global** polarization.

$$Z(\omega, i_{ss}) = \left.\frac{d\tilde{\eta}_s}{d\tilde{\iota}_s}\right|_{s=j\omega} = R + Xj \quad \Rightarrow \quad \eta_k = \int_0^{i_{ss}} \lim_{\omega\to 0}[R_k(i'_{ss})]\, di'_{ss}$$

Faradaic Reaction: (time domain) A → B + e⁻

$$i_t = i_o\left\{\frac{[A]_t^*}{[A]^b} e^{\left(\frac{ßF}{RT}\eta_t\right)} - \frac{[B]_t^*}{[B]^b} e^{\left(-\frac{\alpha F}{RT}\eta_t\right)}\right\}$$

1. Separate quantities into steady-state and sinusoidal components
2. Laplace transform and math details

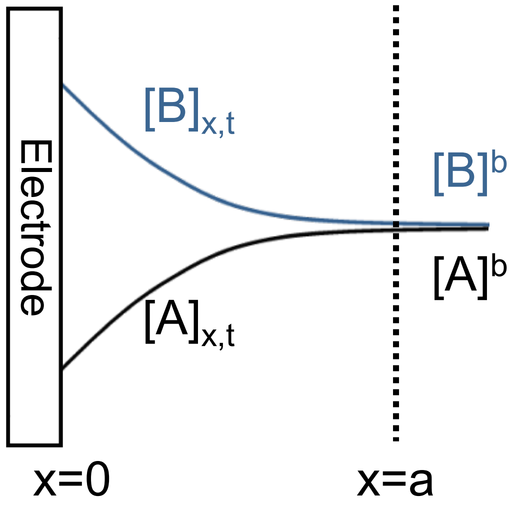
$$Z_{far} = \left.\frac{d\tilde{\eta}_s}{d\tilde{\iota}_s}\right|_{s=j\omega} = \frac{1}{N} - \frac{i_0 e^{\left(\frac{ßF}{RT}\eta_{ss}\right)}}{N[A]^b}\left.\frac{d\widetilde{[A]}_s^*}{d\tilde{\iota}_s}\right|_{s=j\omega} + \frac{i_0 e^{\left(-\frac{\alpha F}{RT}\eta_{ss}\right)}}{N[B]^b}\left.\frac{d\widetilde{[B]}_s^*}{d\tilde{\iota}_s}\right|_{s=j\omega}$$

Faradaic Impedance (frequency domain) — Charge Transfer Resistance — Diffusional Impedance

$$N = \frac{i_0 ßF[A]_{ss}^*}{RT[A]^b} e^{\left(\frac{ßF}{RT}\eta_{ss}\right)} + \frac{i_0 \alpha F[B]_{ss}^*}{RT[B]^b} e^{\left(-\frac{\alpha F}{RT}\eta_{ss}\right)}$$

[1] *ECS Electrochem. Lett.* **2013,** *2* (5), A43-A45.
[2] *J. Electrochem. Soc.* **2014,** *161* (6), A981-A988.
[3] *Electrochim. Acta* **2017,** *229*, 261-270.
[4] *J. Electrochem. Soc.* **2021,** *168*, 080540.

$Z_{Diffusion}$ Depends on Geometry and Boundary Conditions



Fick's 2nd Law $$\frac{\partial [A]_{x,t}}{\partial t} = D_A \frac{\partial^2 [A]_{x,t}}{\partial x^2}$$

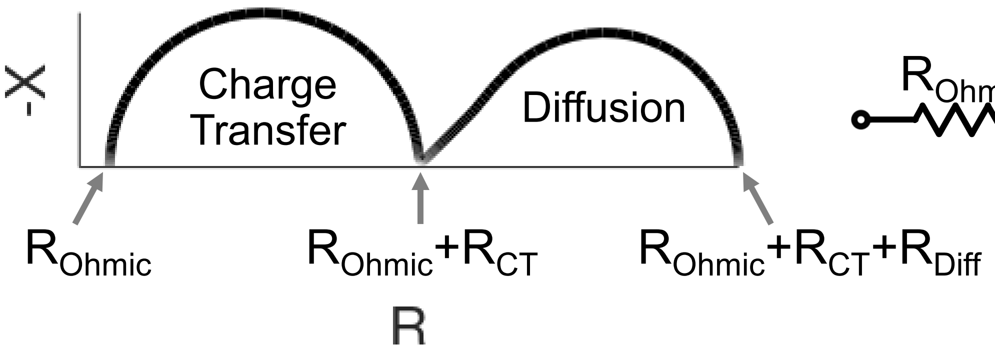
IC $$[A]_{x,t}\big|_{t=0} = [A]^b$$

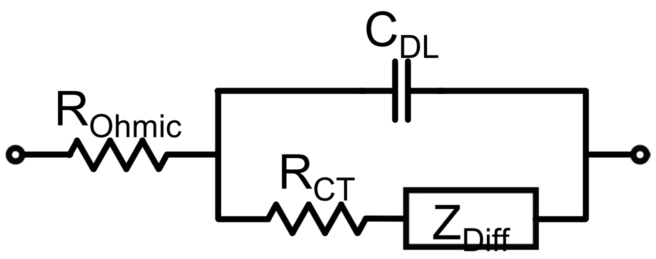
BC1 $$\left.\frac{\partial [A]_{x,t}}{\partial x}\right|_{x=0} = \frac{i_t}{FD_A}$$

BC2 $$[A]_{x,t}\big|_{x=a} = [A]^b$$

E. C. Self et al. 2023 (To Be Submitted Early FY24)

Methodology allows one to quantify how component selection affects various overvoltages.

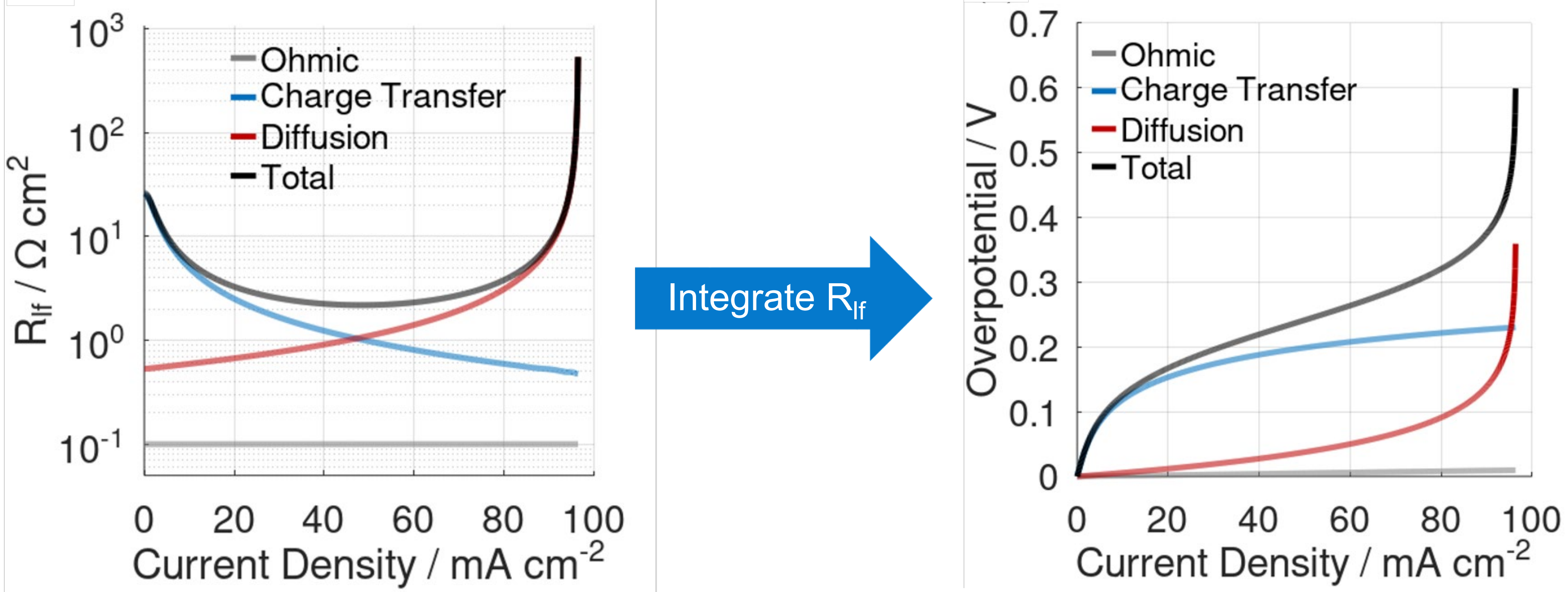




Component Design Influences:

1. Transport Phenomena
   - Electrode porosity/thickness
   - Flow field design
   - Membrane chemistry
2. Reaction Kinetics
   - Catholyte composition
   - Electrode surface chemistry
   - Addition of electrocatalysts

- Most experimental work only measures Z around open-circuit
- Charge transfer and diffusional impedance change with steady-state bias!



Ongoing and Future Work

Continue development of RFBs containing Na-P-S catholytes

- Effect of supporting electrolyte on material solubility and electrochemistry
- Evaluate rate limiting processes using AC impedance
- Compare how component selection impacts performance
  - Ceramic vs. polymer membranes (coordination with program led by G. Yang, ORNL)
  - Na metal anode vs. liquid anolyte (e.g., biphenyl)

Complementary structural and material property investigations for Na-P-S compositions

- Solvated state (NMR and Raman spectroscopy) vs. dried state (XRD)
- Potential new phases of matter which may be valuable ionic conductors, active materials for Na-ion batteries, etc.

Deep eutectic solvent (DES) mixtures to solvate low order polysulfides

- If successful, will greatly enhance S utilization in Na_2S_x catholytes
- Assess how H-bonding donor/acceptor affect solvation properties

FY23 Manuscripts and Presentations

[1] J. L. Tyler, R. L. Sacci, M. L. Lehmann, G. Yang, T. A. Zawodzinski, J. Nanda "Nafion inhibits polysulfide crossover in hybrid nonaqueous redox flow batteries" *J. Phys. Chem. C* **2022**, *126*, 21188.

[2] M. L. Lehmann, E. C. Self, T. Saito, G. Yang "Composite Membrane for Sodium Polysulfide Hybrid Redox Flow Batteries" *Membranes* **2023**, 13, 700.

[3] E. C. Self, F. M. Delnick, R. L. Sacci, J. Nanda "Using AC Impedance Spectroscopy to Assess Nonlinear Polarization in Electrochemical Cells" **2023** (In Preparation, Expect to Submit Early FY24)

[4] E. C. Self, M. Lehmann, G. Yang, "Nonaqueous Flow Batteries Containing Sulfide and Thiophosphate Catholytes" 243rd Meeting of the Electrochemical Society, Boston, MA (May 30, 2023)

[5] E. C. Self, M. Lehmann, G. Yang, "Nonaqueous Sodium-Based Catholytes for Redox Flow Batteries" TechConnect World Innovation Conference & Expo, National Harbor, MD (June 19, 2023)

FY23 Intellectual Property

[1] E. C. Self, M. Lehmann, G. Yang, J. Nanda, "Na-P-S Catholytes for Nonaqueous Flow Batteries" ORNL Invention Disclosure ID#81939560 (elected for provisional patent coverage)

Questions?

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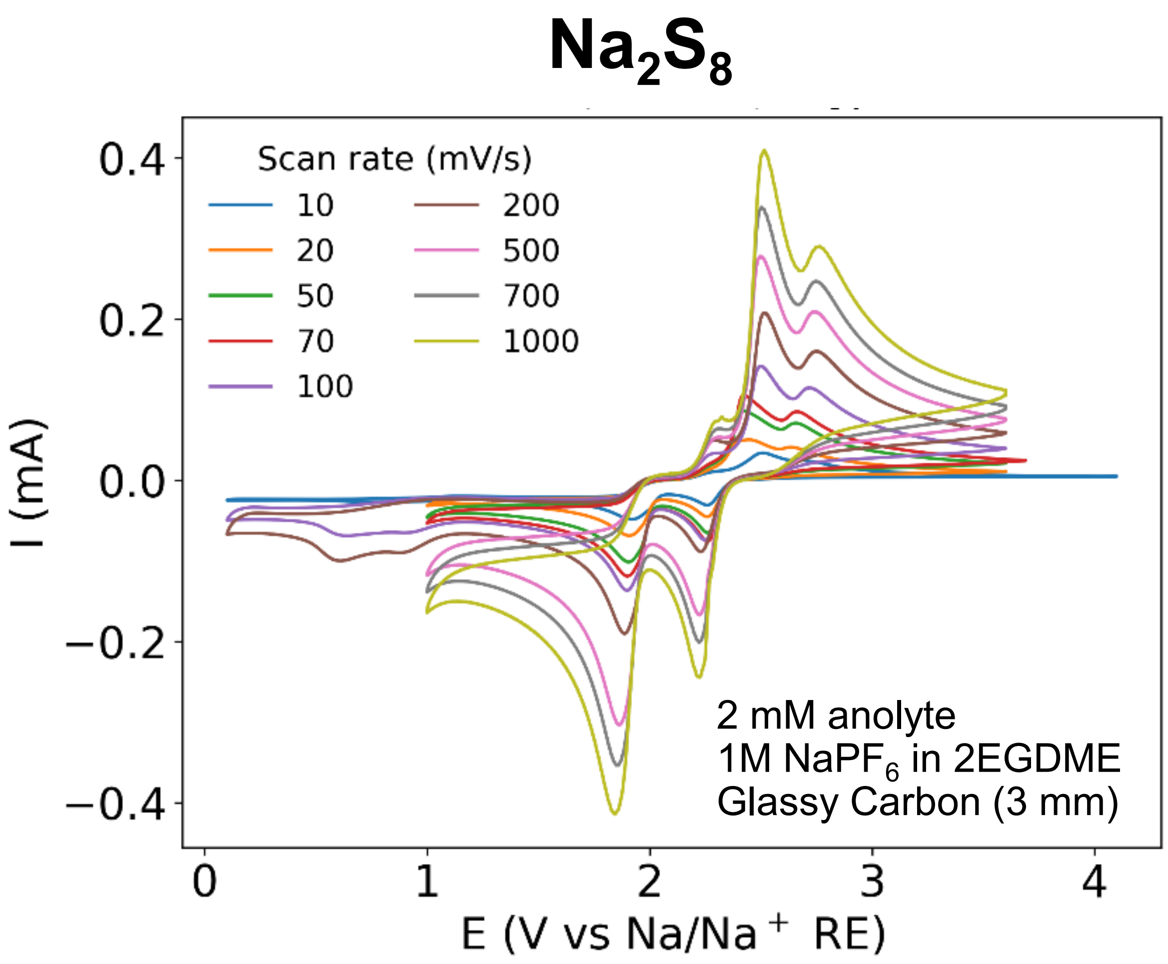
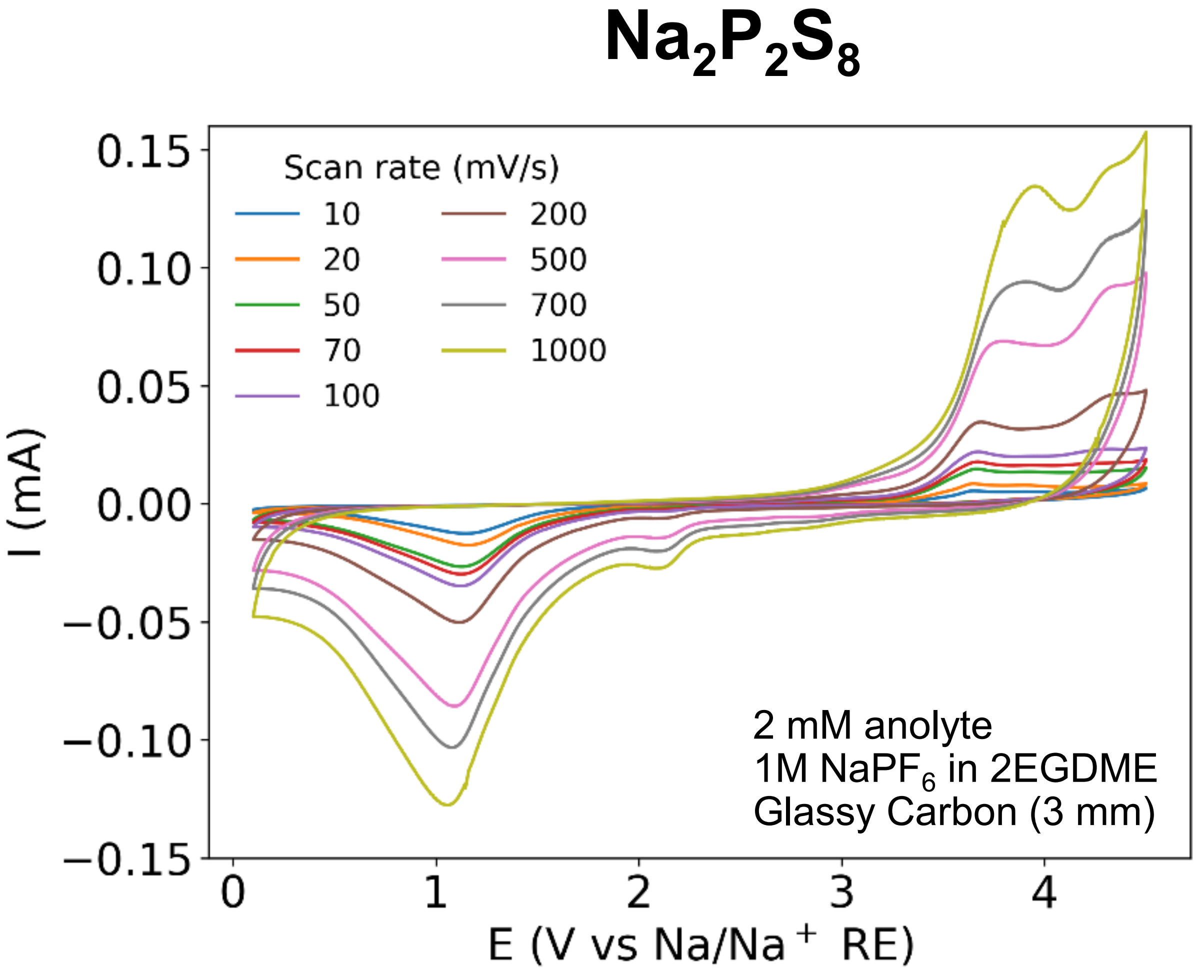
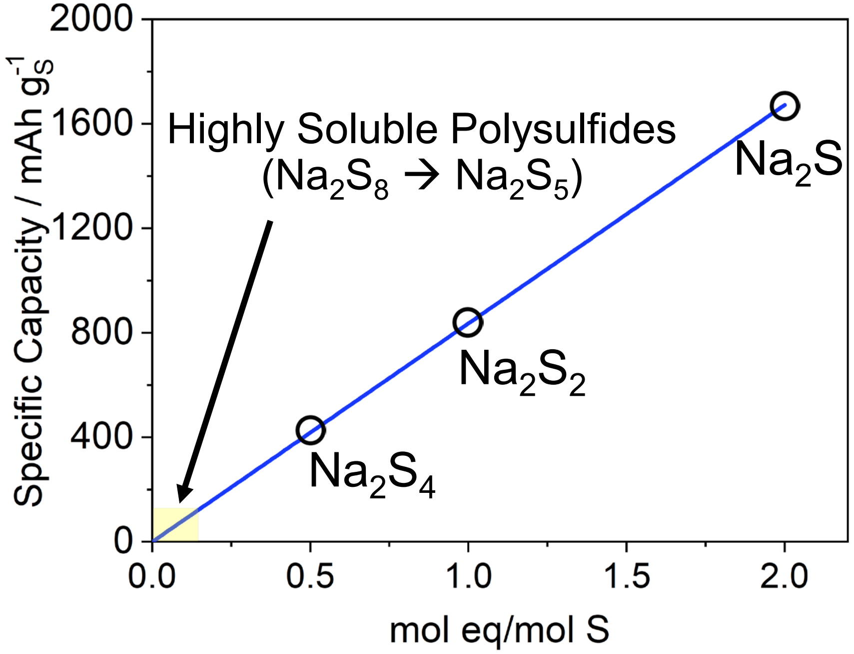
Supplemental Slides

Additional voltammograms of Na_2S_8 and $Na_2P_2S_8$ catholytes.





FY24 Task: Increase sulfur utilization by designing deep eutectic solvent (DES) blends to solvate low order sodium polysulfides (Na_2S_x, x≤4).



Traditional Electrolytes (e.g., Ethers)

DES

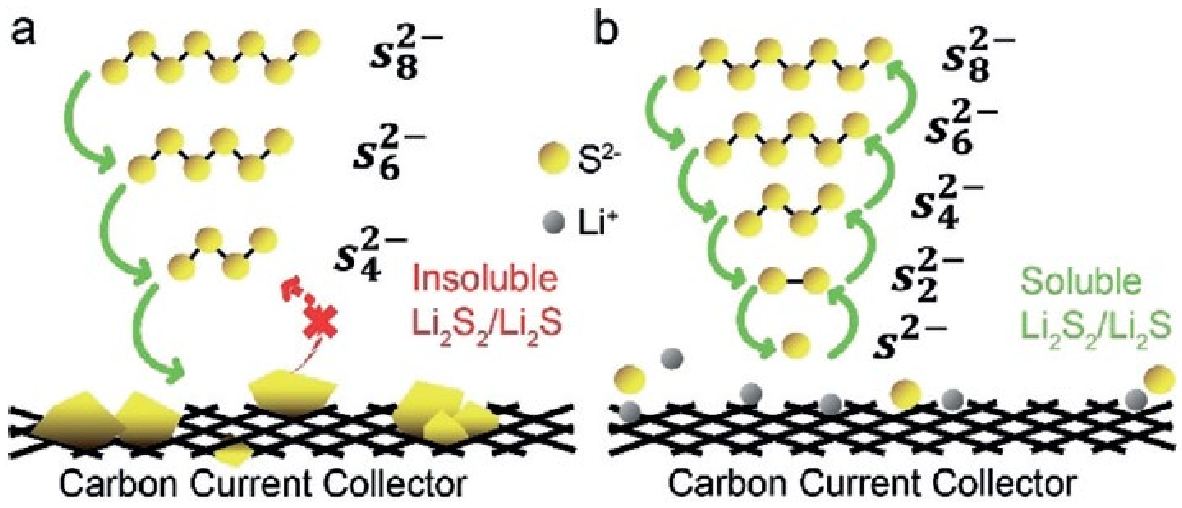


Image adapted from [1]: Q. Cheng et al., *Angew. Chem. Int. Ed.* **2019**, 58, 5557.

Na_2S in DES

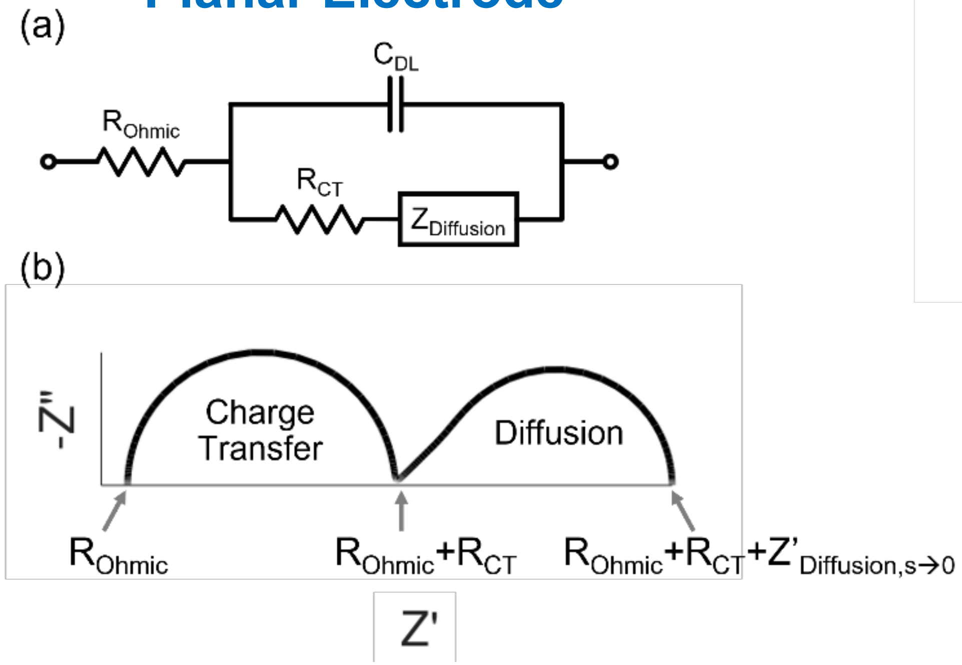
Composition A

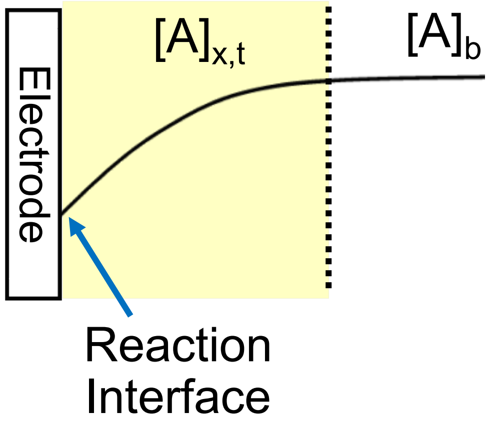
Composition B

- Previous work[1] has shown DES mixtures dissolve wide range of <u>lithium sulfides/polysulfides</u>.
- FY24 will explore DES possibilities for Na_2S_x catholytes
  - Various hydrogen-bonding donors/acceptors
  - Electrolyte blends (e.g., DES + ether blends)

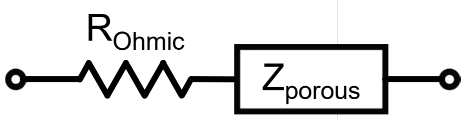
Analogous relationships apply for model electrode symmetries and porous electrodes used in real-world devices.

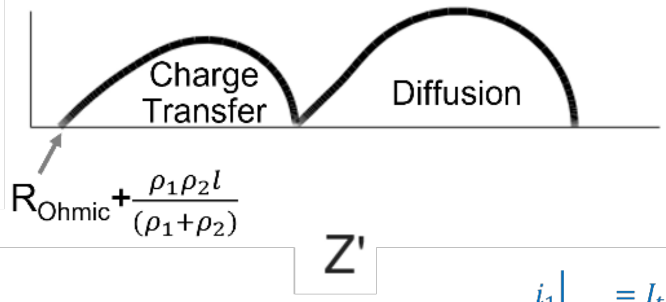
Planar Electrode

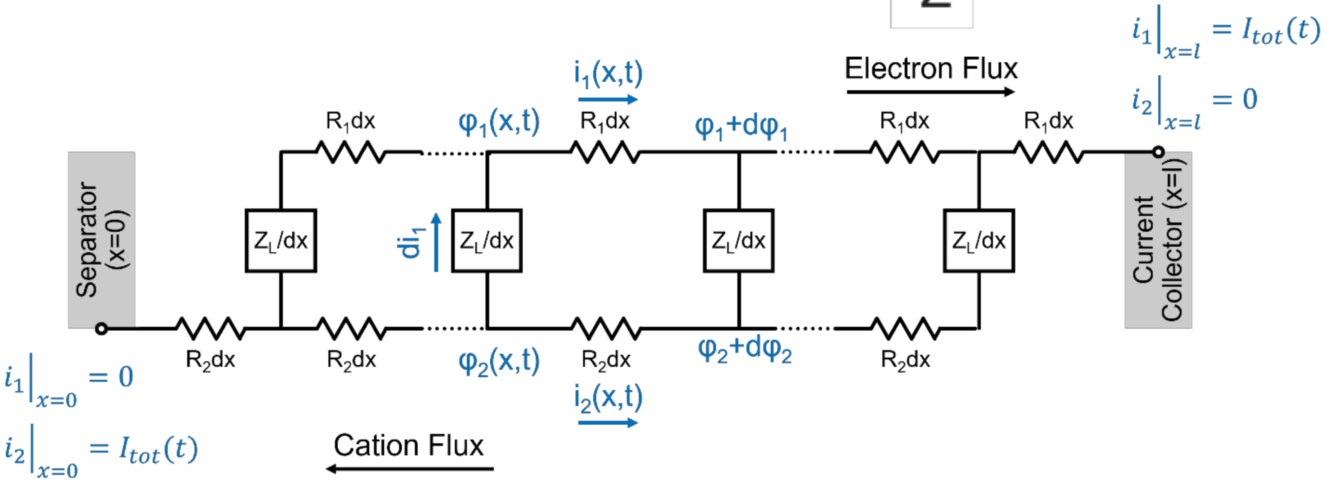




Porous Electrodes







$$Z_{porous} = \frac{(\rho_1^2+\rho_2^2)\coth Ql}{Q(\rho_1+\rho_2)} + \frac{2\rho_1\rho_2}{Q(\rho_1+\rho_2)\sinh Ql} + \frac{\rho_1\rho_2 l}{(\rho_1+\rho_2)}$$

High frequency $Z_{porous} = \frac{(\rho_1^2+\rho_2^2)}{(\rho_1+\rho_2)^{\frac{3}{2}}}\sqrt{\frac{A_g l}{A_t} Z_{planar}} + \frac{\rho_1\rho_2 l}{(\rho_1+\rho_2)}$

Low frequency $Z_{porous} = \frac{A_g}{A_t} Z_{planar} + \frac{(\rho_1+\rho_2)l}{3}$