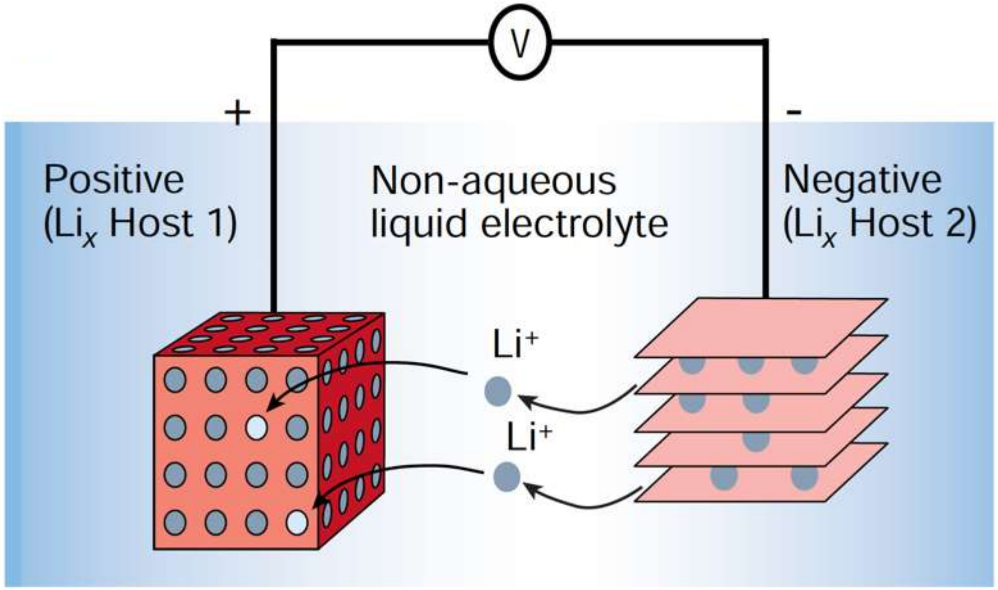
Mixed Ion-Electron-Solvent Transfer in Radical-containing Polymers

Jodie L. Lutkenhaus, Daniel Tabor, Emily Pentzer

Texas A&M University

Today's Li-ion batteries



Cathode

$LiCoO_2$ (LCO)

$LiNi_xMn_yCo_zO_2$ (NMC)

$LiFePO_4$ (LFP)

Anode

Graphite

Key elements: Li, Co, Ni

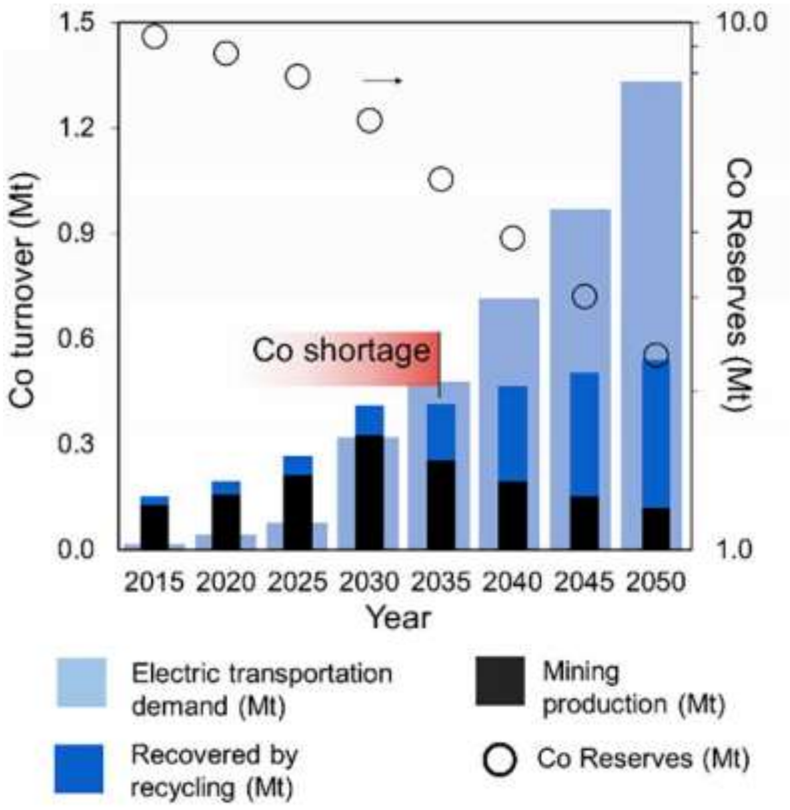
Electrolyte

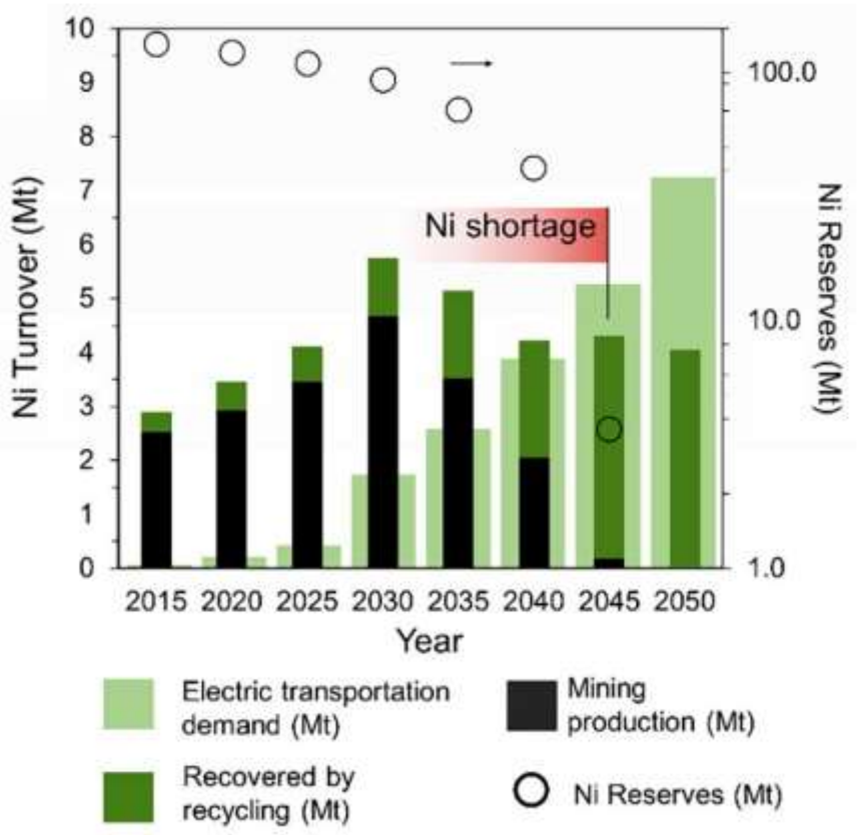
$LiPF_6$

Cyclic and linear carbonates

Tarascon and Armand. Nature 2001, 414, 359-367

Cobalt and Nickel Shortages are Predicted by 2035 and 2045, Respectively





"…the long-term LIB price will be dominated by cost of the cathode materials."

Yushin *et al. Materials Today* 2021, *42*, *57-72*

Human Rights Abuses and Political Friction Over Cobalt


Carmakers Race to Control Next-Generation Battery Technology

The prize: batteries that would be cheaper, faster to charge and less vulnerable to raw material shortages. Whoever gets there first will have a major advantage.

“Many automakers are eager to reduce their reliance on cobalt in part because it mostly comes from the Democratic Republic of Congo, where it is mined by Chinese-financed companies or by freelancers who sometimes employ children.

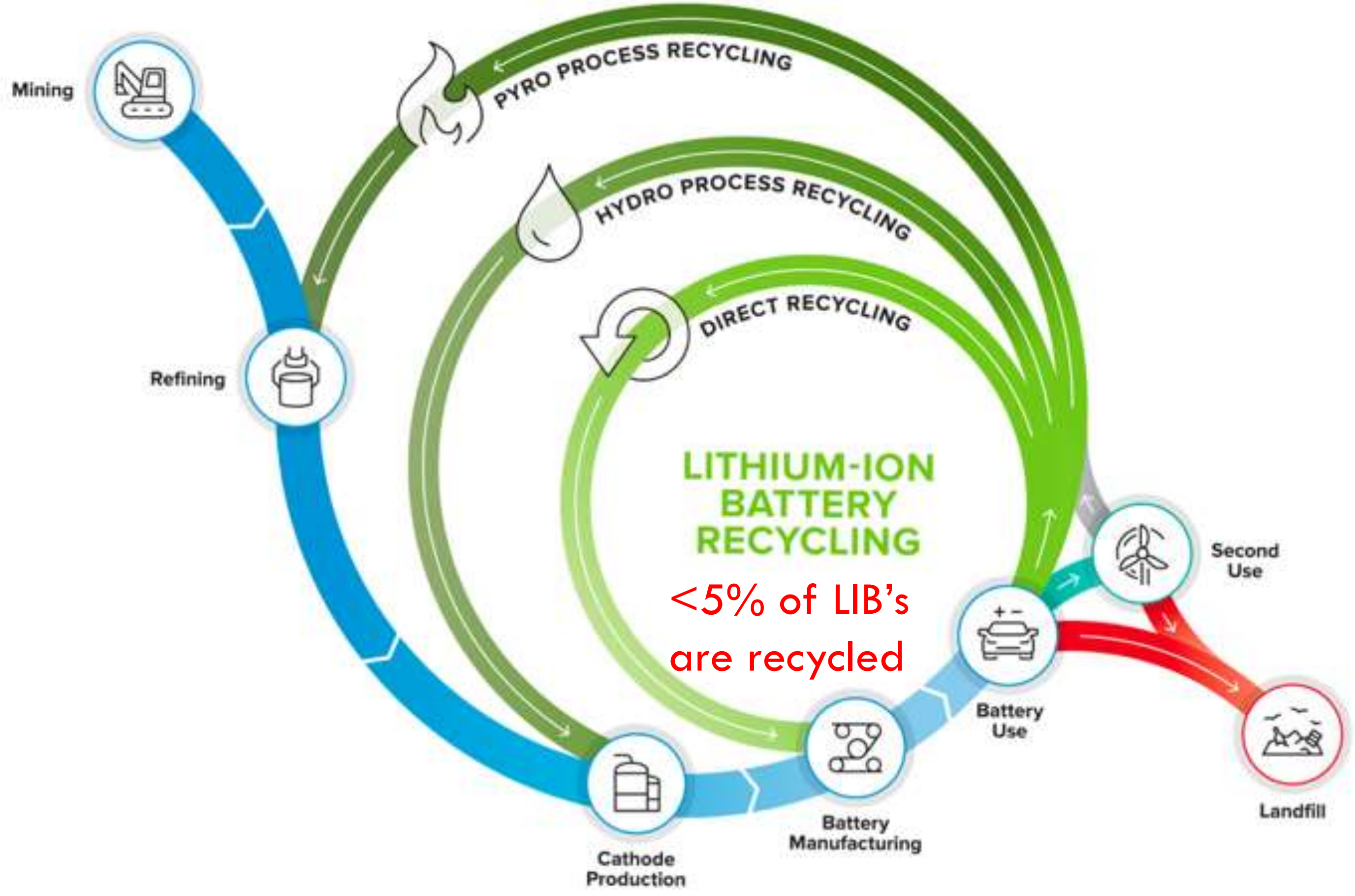
The New York Times (March 7, 2022)

Li-ion Battery Recycling

- Recycling promises to recover valuable critical materials

- But at what cost?
  - High energy requirements
  - Harsh chemicals

- Is lithium-ion battery recycling better or worse for the environment?

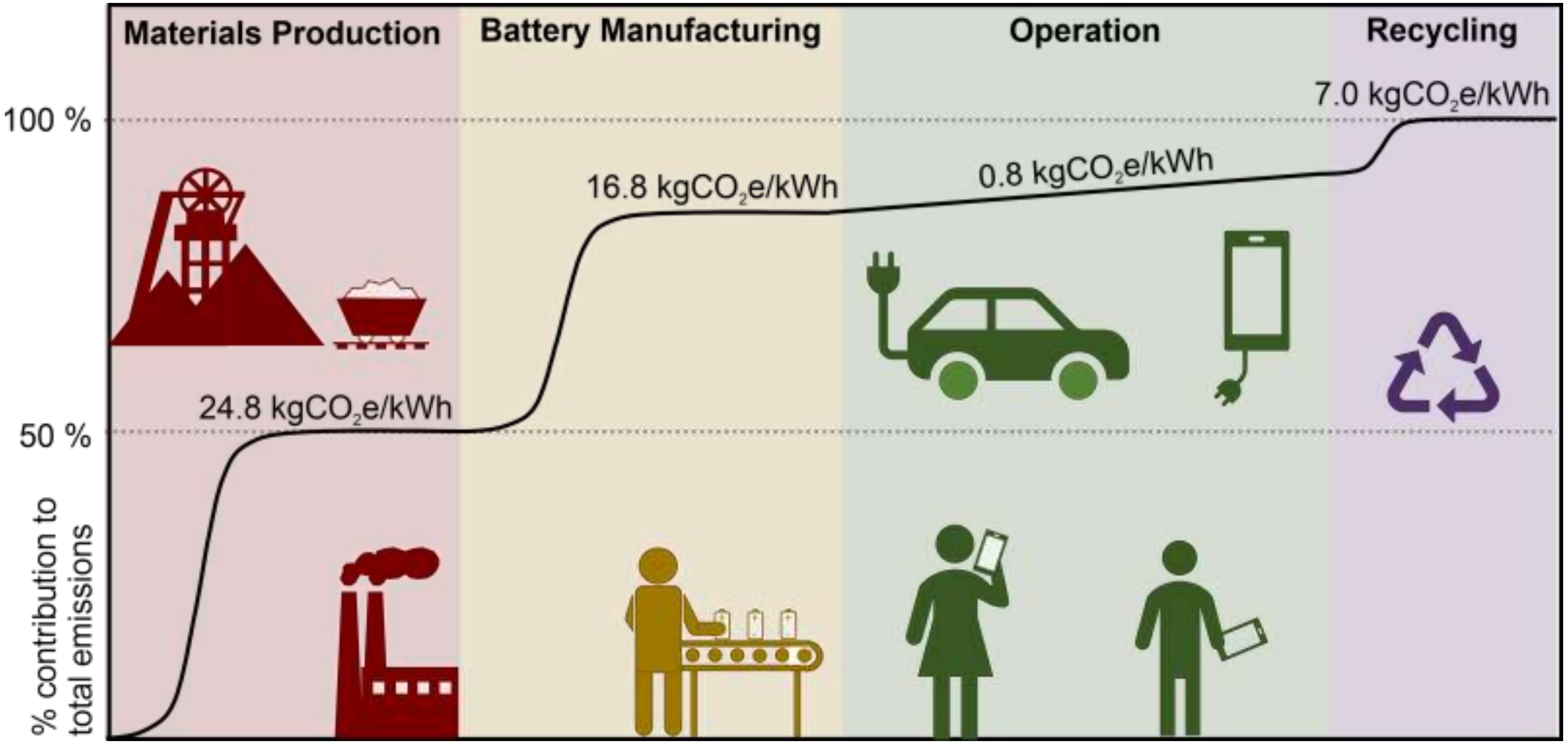


<5% of LIB's are recycled

Bai *et al. Materials Today* 2020, 40, 304-315

https://www.anl.gov/article/doe-launches-its-first-lithiumion-battery-recycling-rd-center-recell

Mining and Manufacturing for Li-Ion Batteries Generates CO_2



Easley, A. D.; Ma, T.; Lutkenhaus, J. L., *Joule* **2022**, *6* (8), 1743-1749.

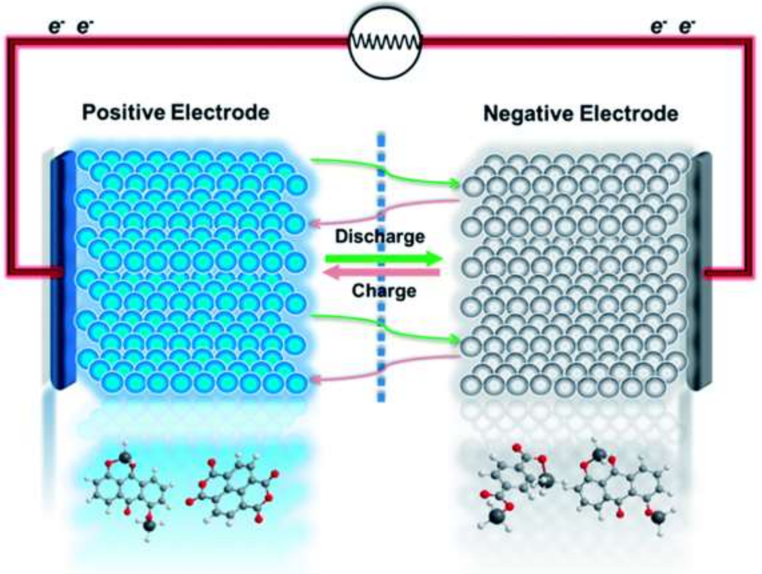
The Battery of the Future Will:

- Contain materials that are easily (domestically) sourced with low CO_2 emission
- Be manufactured and recycled in the same location
- Perform the same or better than today's status quo
- Enable any country to source, manufacture, and recycle their own batteries, thus democratizing energy storage

Organic Batteries

Organic batteries employ redox-active small molecules or polymers as the active material in the electrode

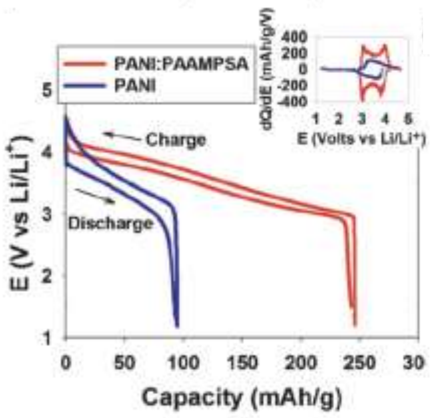
- Going organic frees us from lithium, cobalt, and nickel
- Going organic conceptualizes a whole new resource market based on C, H, N, O, and S



Xie, J. & Zhang, Q., *Journal of Materials Chemistry A* 2016, 4, 7091-7106

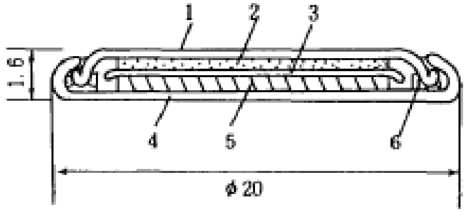
Development of Polyaniline–Lithium Secondary Battery

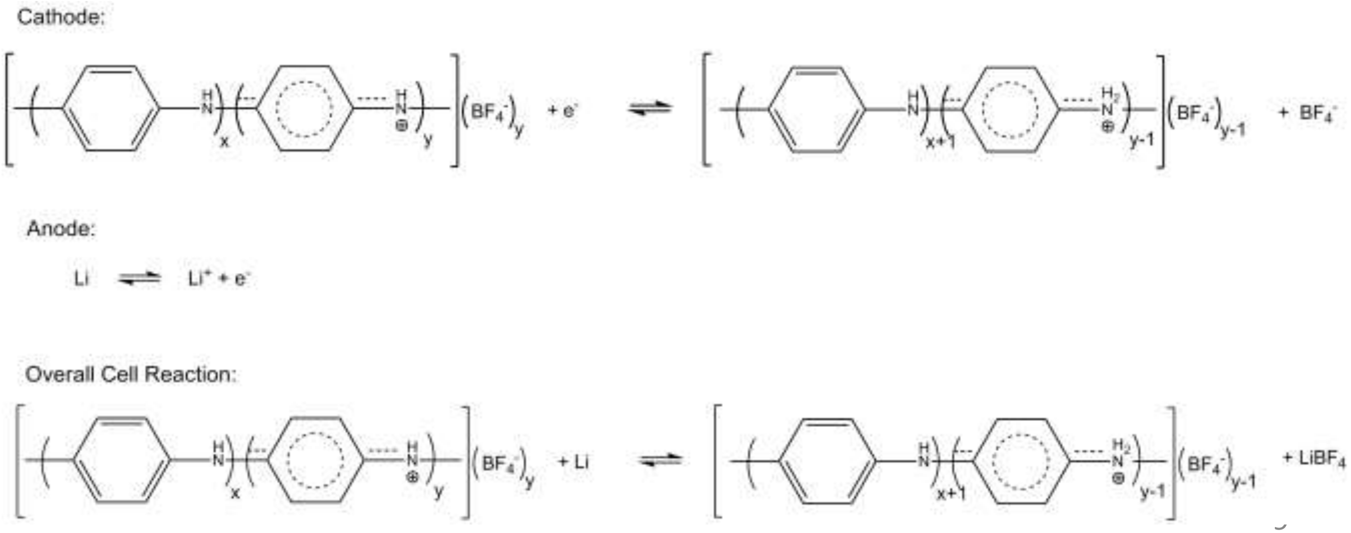
Tsutomu Matsunaga[1], Hideharu Daifuku, Tadashi Nakajima, and Takahiro Kawagoe
Research and Development Division, Bridgestone Corporation, 3-1-1. Ogawahigashi-Cho, Kodaira-Shi, Tokyo 187, Japan
Received May 1, 1989



Lutkenhaus et al. *PCCP*, 2013.

- First commercialized by Bridgestone-Seiko in 1987
  - Great cycle life (>1000), Theoretical capacity of 148 mAh/g
  - Low power density (11 mW/g) – limited to low-demand applications
  - 3 V cell voltage
- Discontinued 5 years later





27 June 2002

ELSEVIER

Chemical Physics Letters 359 (2002) 351–354

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Rechargeable batteries with organic radical cathodes

K. Nakahara *, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa

Functional Materials Research Laboratories, NEC Corporation, Miyazaki, Miyamae-ku, Kawasaki, Kanagawa 216-8555, Japan

Received 19 November 2001

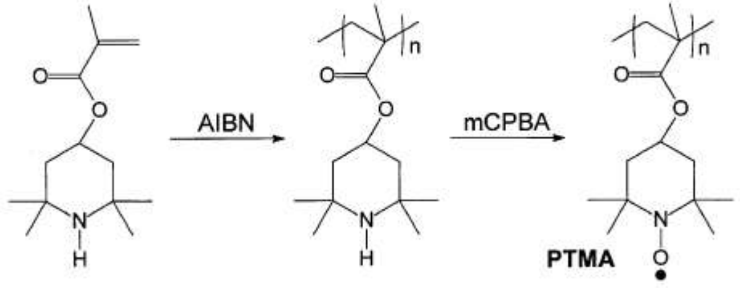
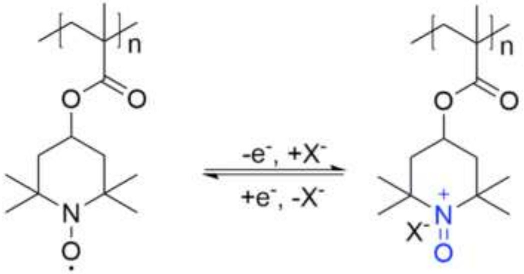
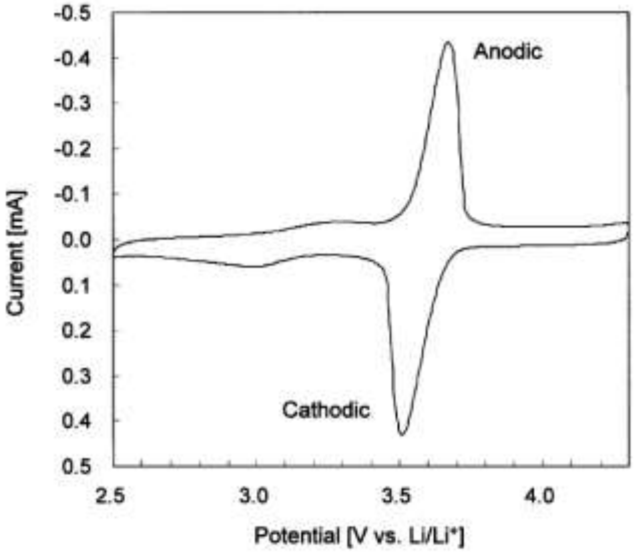
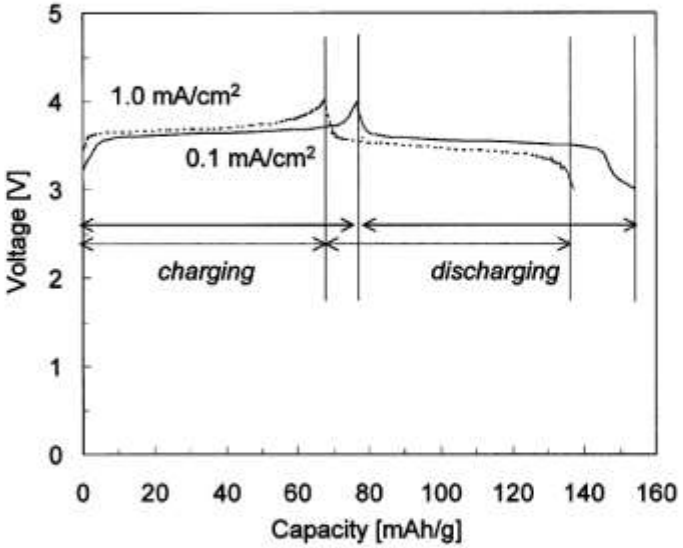


Fig. 1. Synthesis procedure of PTMA.



- $E_{1/2}$ = 3.5-3.6 V vs Li/Li^+
- Theoretical capacity 111 mAh/g
- Coulombic efficiency 95-100%
- Rate capability 5-20 C
- Cycle life 500-2000



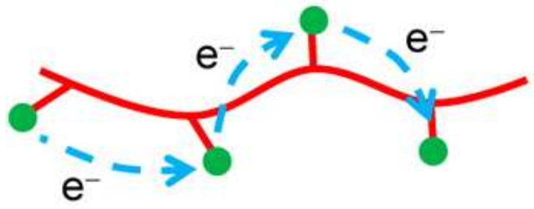


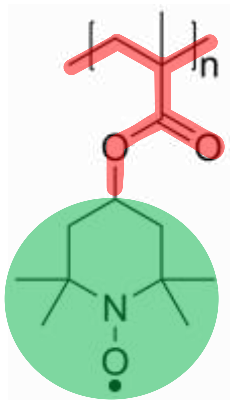
Non-conjugated Redox Active Polymers

- Redox site is usually group pendant to a non-conjugated backbone

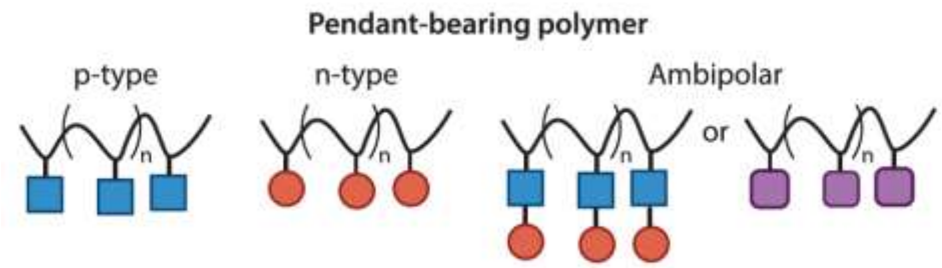
- Insulating, but exceptions exist

- Polymer exchanges cations, anions or both during the redox reaction



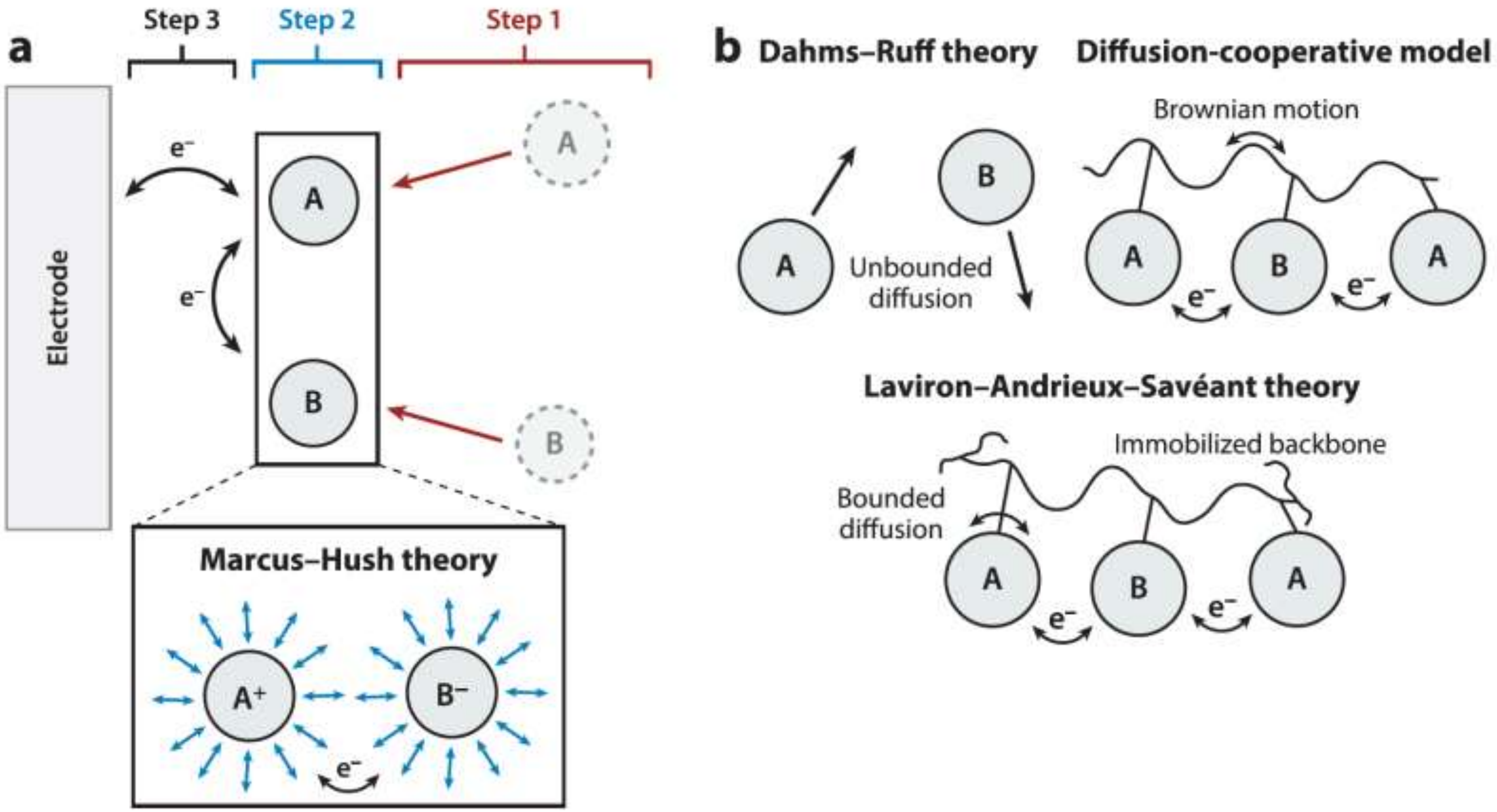


PTMA: Poly(TEMPO methacrylate)



- Ma, T.; Easley, A. D.; Thakur, R. M.; Mohanty, K. T.; Wang, C.; Lutkenhaus, J. L. *Annual Review of Chemical and Biomolecular Engineering* 2023**,** *14* (1), 187-216.
- **Y. Liang, Y. Yao, *et al.* *J. Am. Chem. Soc.* 2015, *137* (15), 4956 – 4959**

Electron transfer theory for non-conjugated redox active polymers



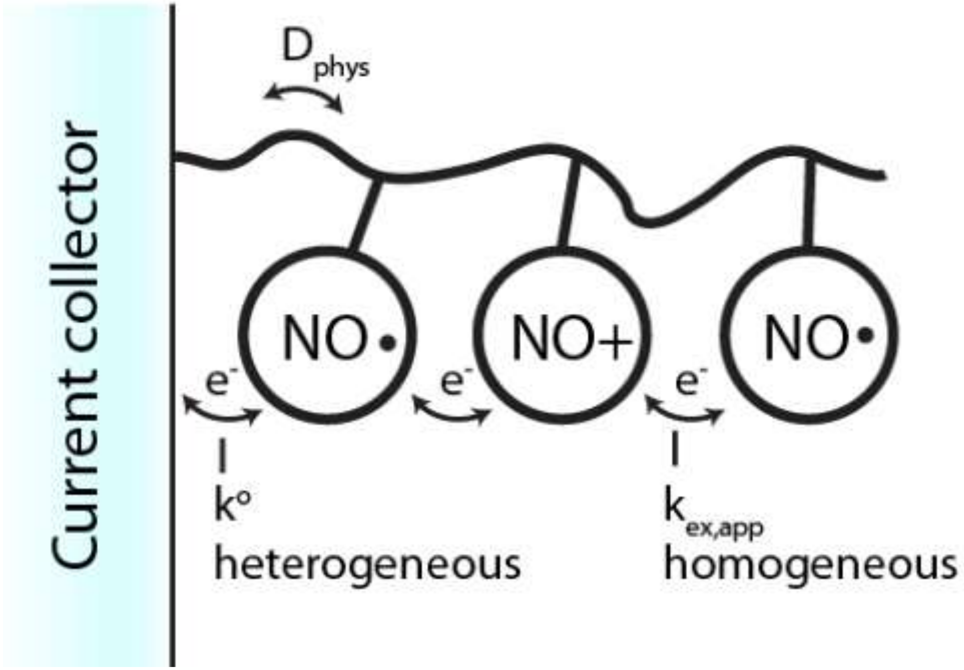
Ma, T.; Easley, A. D.; Thakur, R. M.; Mohanty, K. T.; Wang, C.; Lutkenhaus, J. L. *Annual Review of Chemical and Biomolecular Engineering* 2023, *14* (1), 187-216.

Understanding the mechanism of redox activity in nitroxide radical polymers

- Electrons hop from site-to-site, following Marcus-Hush type kinetics

- Polymer chain diffusion and relaxation can add in the process

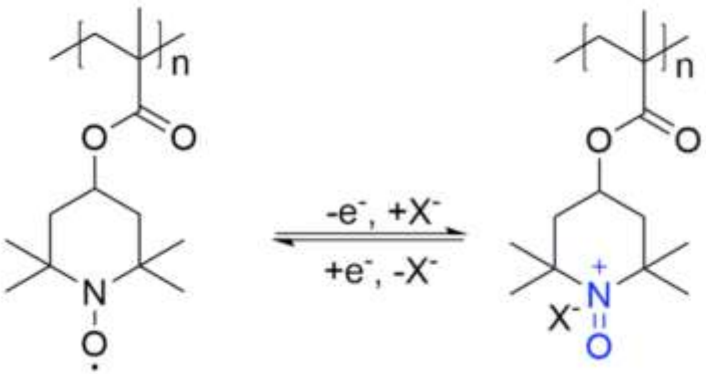
- Mixed electron-ion-solvent transport occurs



How do we “know” what is transporting in a nitroxide radical polymer?

Quartz crystal microbalance with dissipation monitoring (QCMD)

- Estimates real-time changes in mass and thickness of thin polymer film

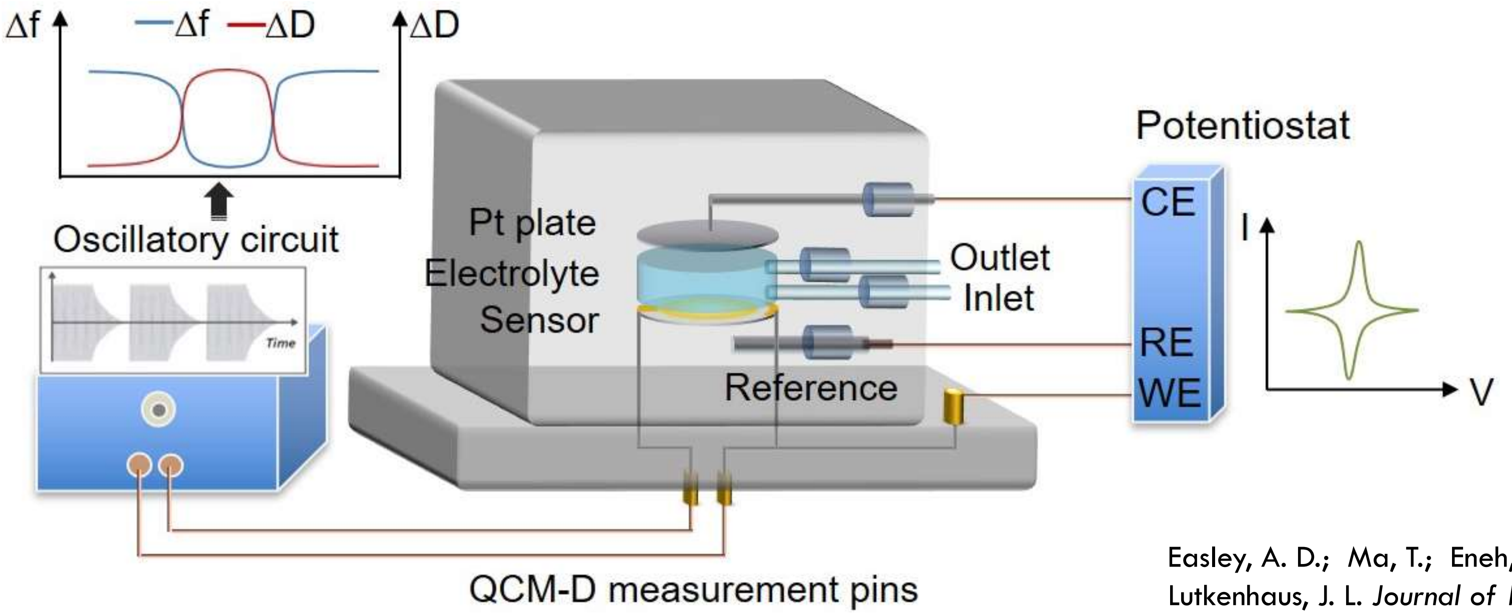


Theoretical $\Delta m/Q$ = 1.54 mg/C
For PTMA and $CF_3SO_3^-$

- We estimate the change in mass per electron to decouple anion, cation, and solvent transport

Electrochemical QCMD Set-up

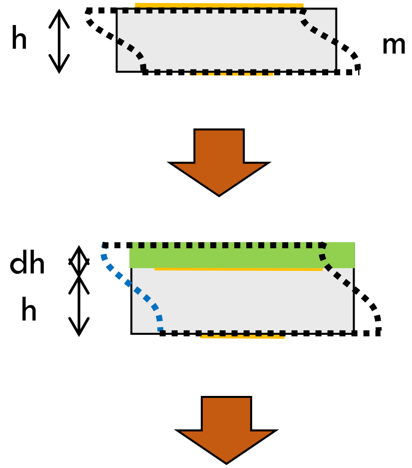
- To monitor mixed ion-electron transfer, a potentiostat is interfaced with the QCMD electrochemistry module
- The QCMD and potentiostat instruments operate simultaneously
- Potentiostat input: cyclic voltammogram, constant current charge/discharge, impedance spectroscopy



Easley, A. D.; Ma, T.; Eneh, C. I.; Yun, J.; Thakur, R. M.; Lutkenhaus, J. L. *Journal of Polymer Science* 2022, *60*, 1090-1107

EQCM-D Response Modeling

(i) Sauerbrey Model
Thin, rigid film

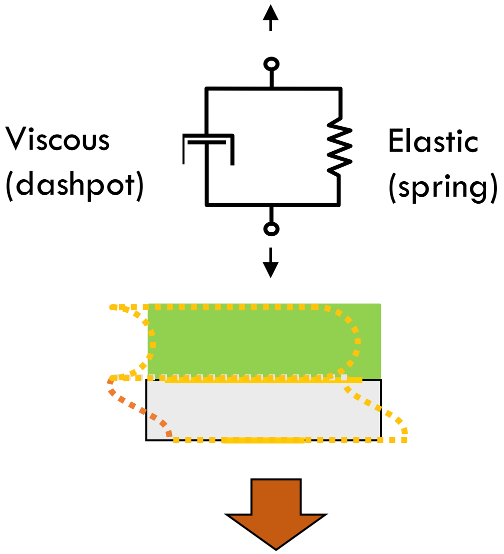


$$\Delta m = -C\frac{1}{n}\Delta f$$

C = 17.7 ng cm^{-2} s^{-1}

n – overtone

(ii) Voigt Model
Thicker, and/or soft film



QTools Fitting

$$D = \frac{E_{dissipated}}{2pE_{stored}}$$

In summary

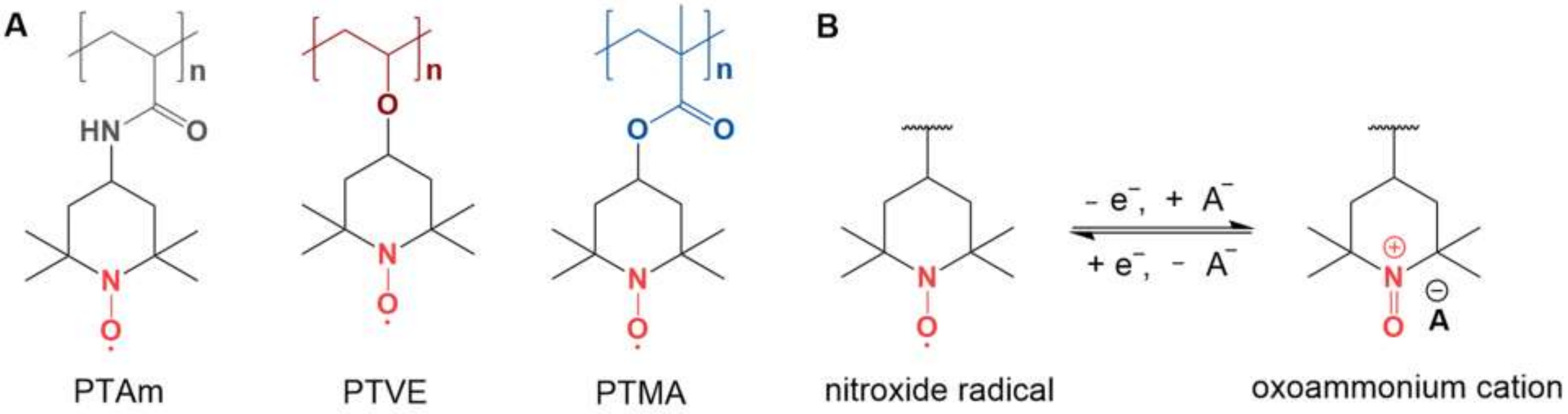
- Δf ➡ coupled mass
- ΔD ➡ viscoelastic properties

frequency decrease ⟷ mass increase

dissipation increase ⟷ softening

Introduction to data analysis, Q-sense basic training, Biolin Scientific

Which macromolecular radical is best and why?



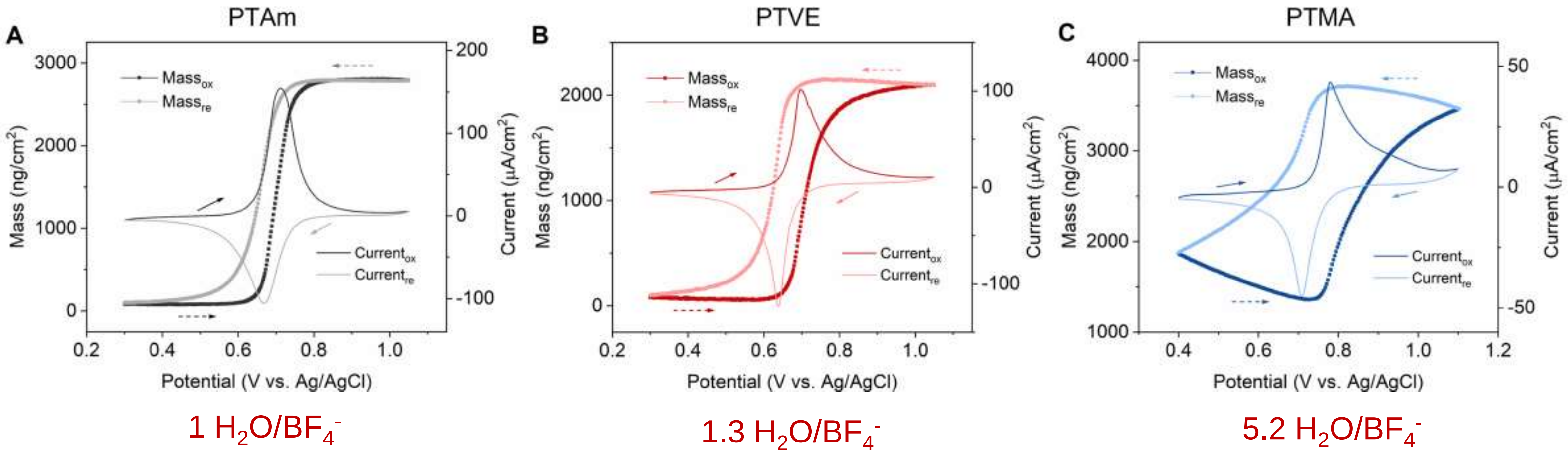
PTAm = poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide)
PTVE = poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether)
PTMA = poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl)

Organic salt = tetraethylammonium tetrafluoroborate aqueous solution ($TEABF_4$)

Ma and Lutkenhaus, *et al*. *Cell Reports Physical Science* 2021, 2, 100414

EQCM-D reveals the role of coupled ion-water transfer in the kinetics

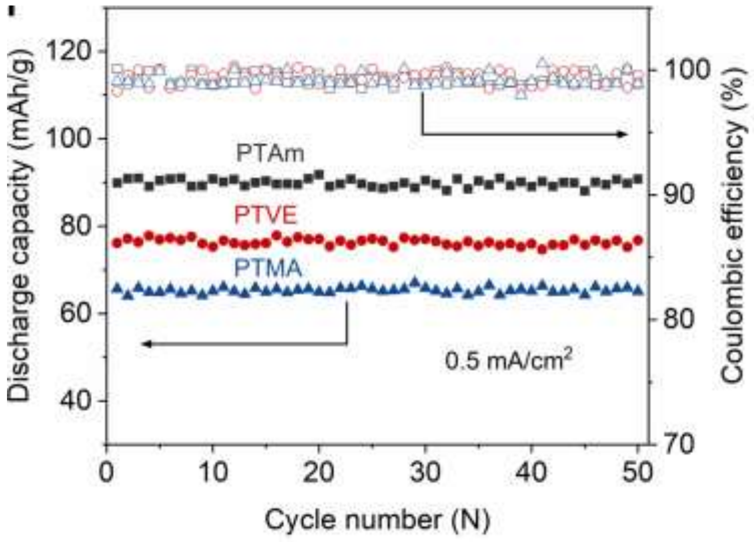
- PTMA has severe mass-hysteresis (least favorable polymer-water interaction)
- PTAm has least mass-hysteresis (most favorable polymer-water interaction)



Ma and Lutkenhaus, *et al. Cell Reports Physical Science* 2021, 2, 100414

Polymer-water affinity controls the no. of water molecules exchanged

- Water-polymer interactions from most to least favorable are:
    - PTAm > PTVE > PTMA
- Number of water molecules exchanged from least to most:
    - PTAm>PTVE>PTMA



Favorable polymer-water interactions are essential for metal-free aqueous batteries

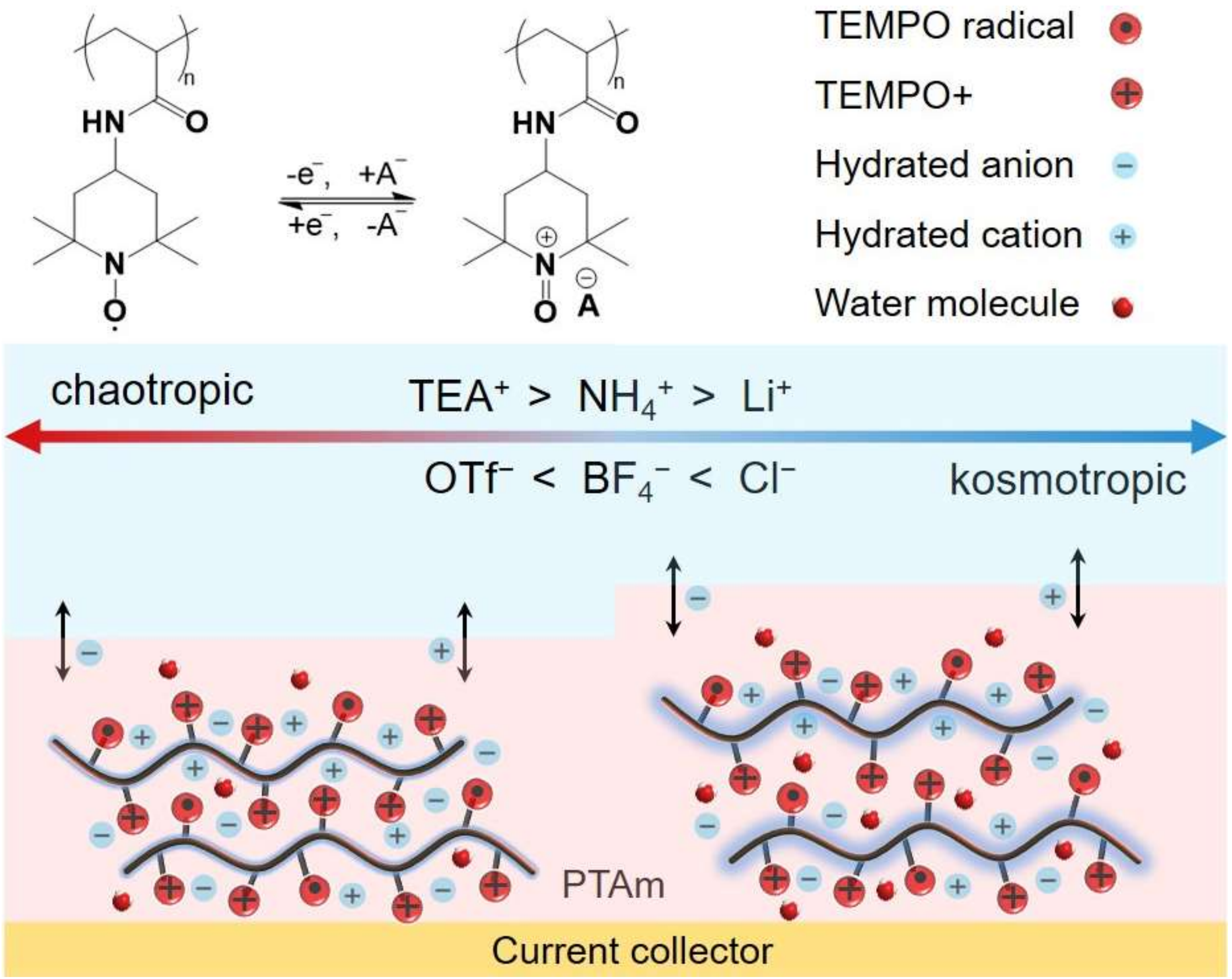
- Enhanced kinetics
- Reduced overall mass of the transporting species (less water transfer)
- Improved capacity

Ma and Lutkenhaus, *et al. Cell Reports Physical Science* 2021, 2, 100414

Aqueous Electrolytes for Organic Radical Batteries

- PTAm performs well in aqueous electrolyte, but only $TEABF_4$ was examined

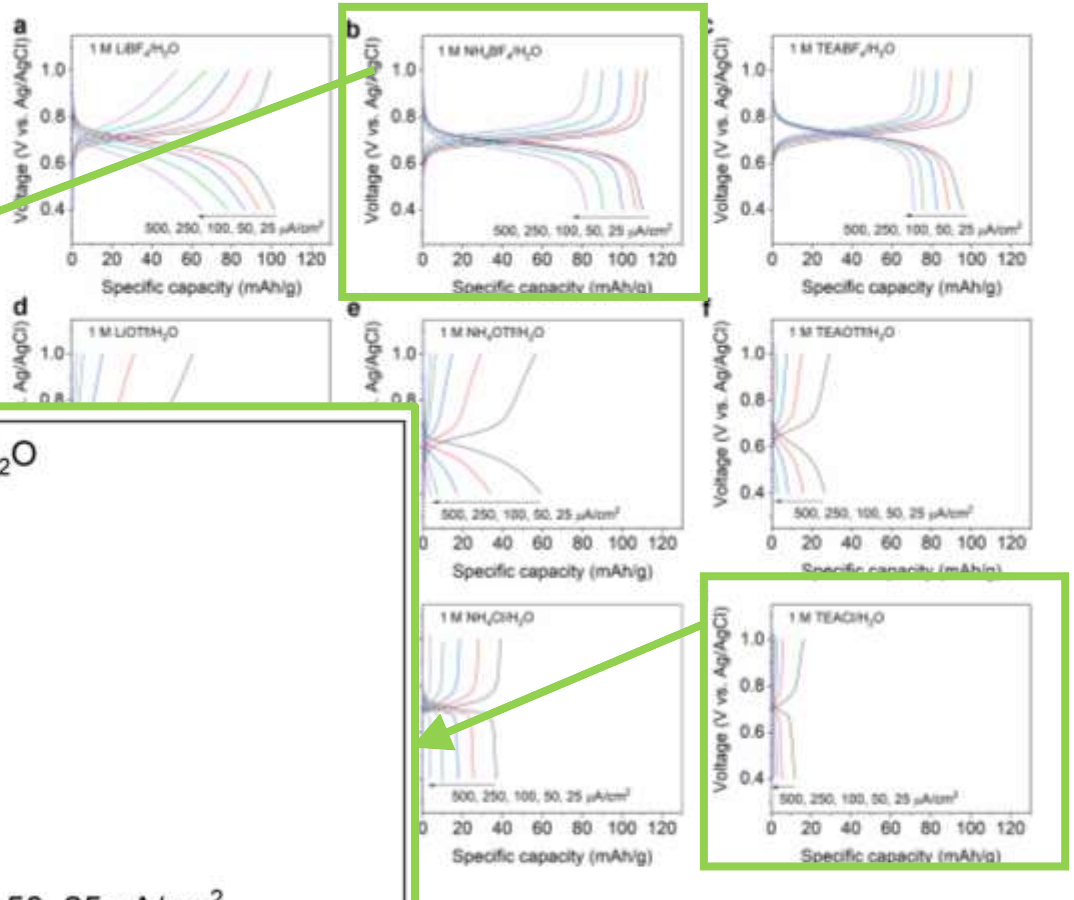
- Is there a better aqueous electrolyte and why so?

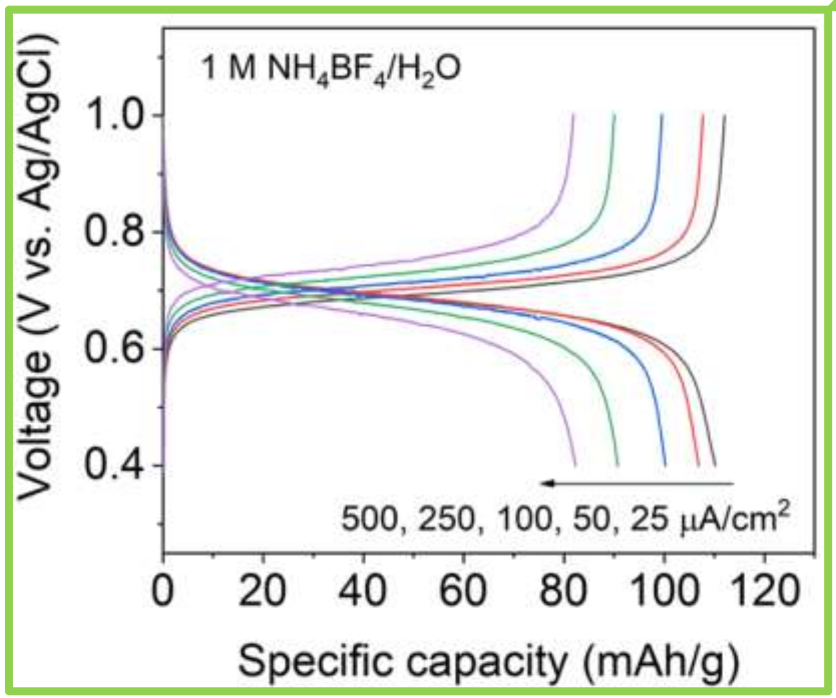


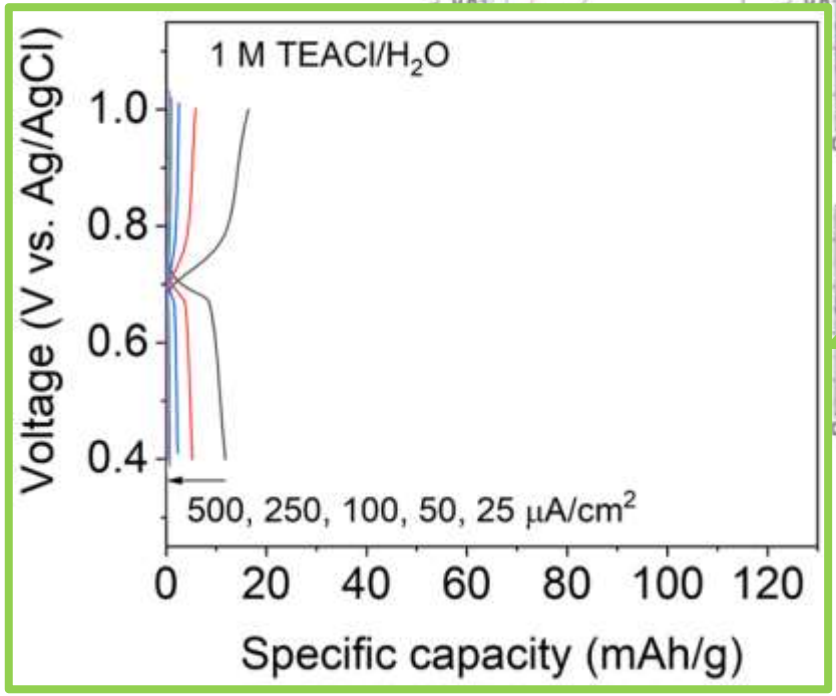
Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Nine Electrolytes – Totally Different Performance!

- Capacity varies by as much as 1000%!
- Cl^- electrolytes are the worst



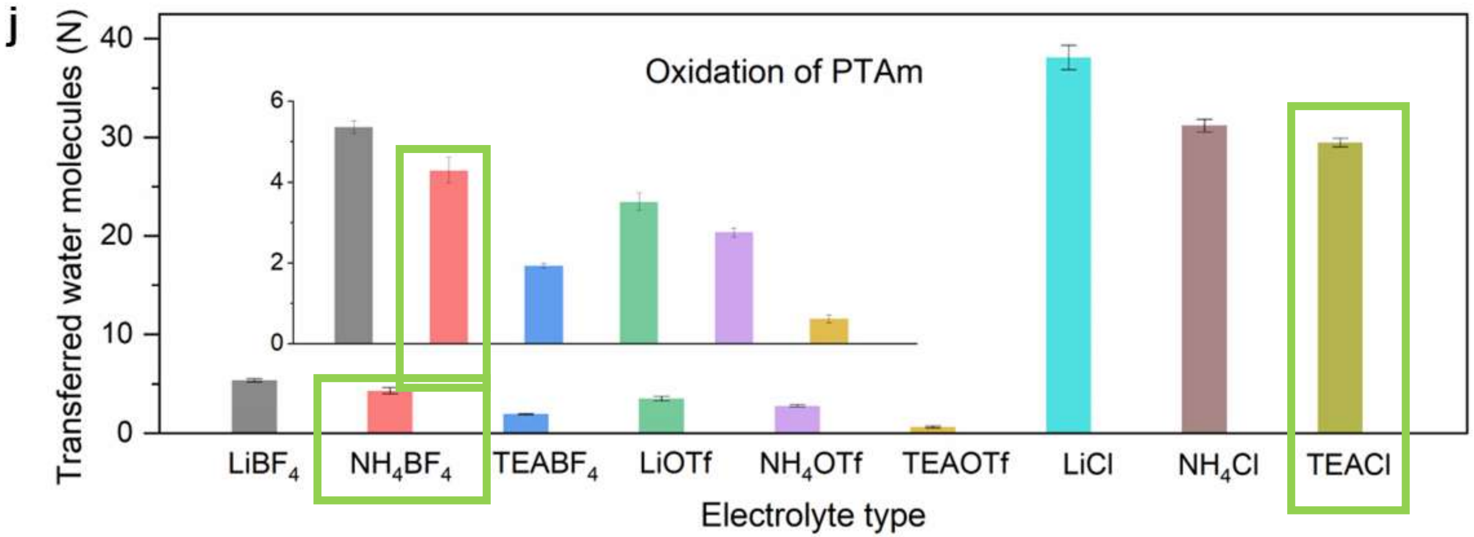




Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Explaining 10x Changes in Capacity

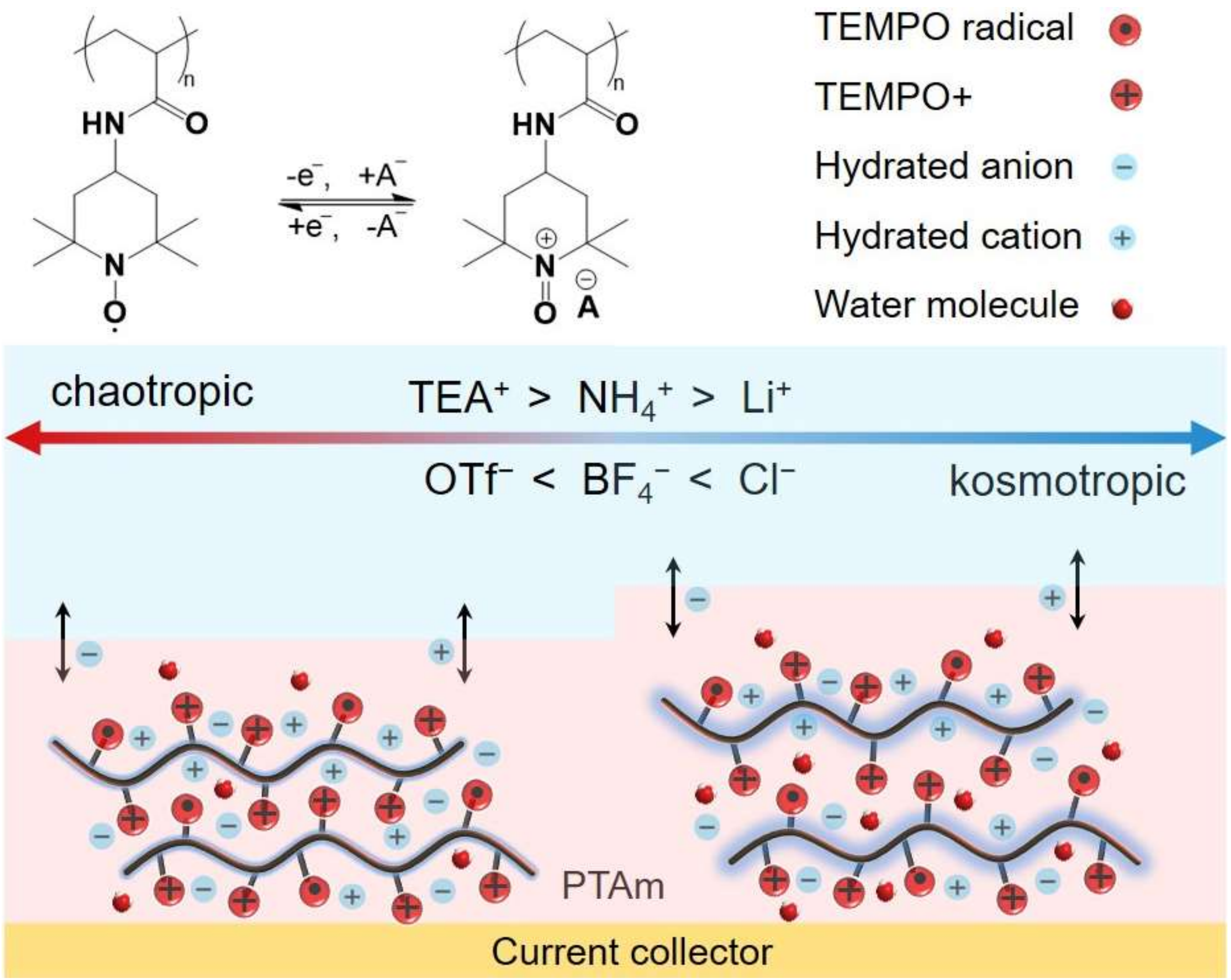
- The Cl^- counterion causes huge amounts of swelling and dimensional changes during cycling
  - As indicated by the number of transferred water molecules via electrochemical QCMD
- The BF_4^- counterion has significantly less



Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Kosmotropic/Chaotropic Considerations for Aqueous Electrolytes

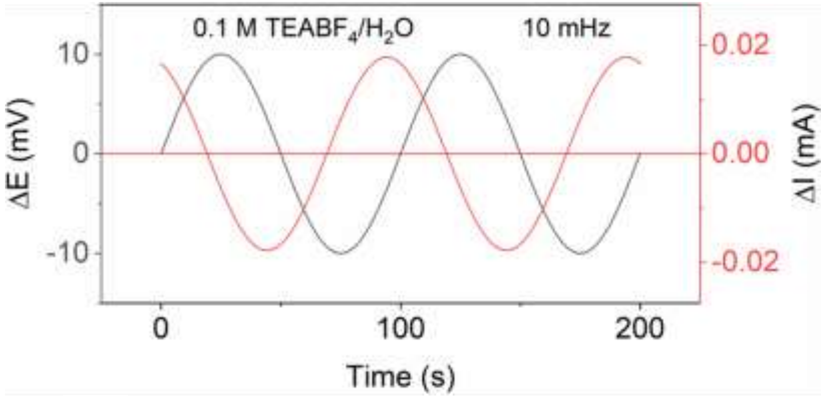
- Cl^- ions are more kosmotropic (order-making with water) than BF_4^- ions
- BF_4^- ions are more chaotropic (disorder making with water) than Cl^- ions
- i.e., Cl^- ions have a stronger solvation shell such that the ions drag around more water

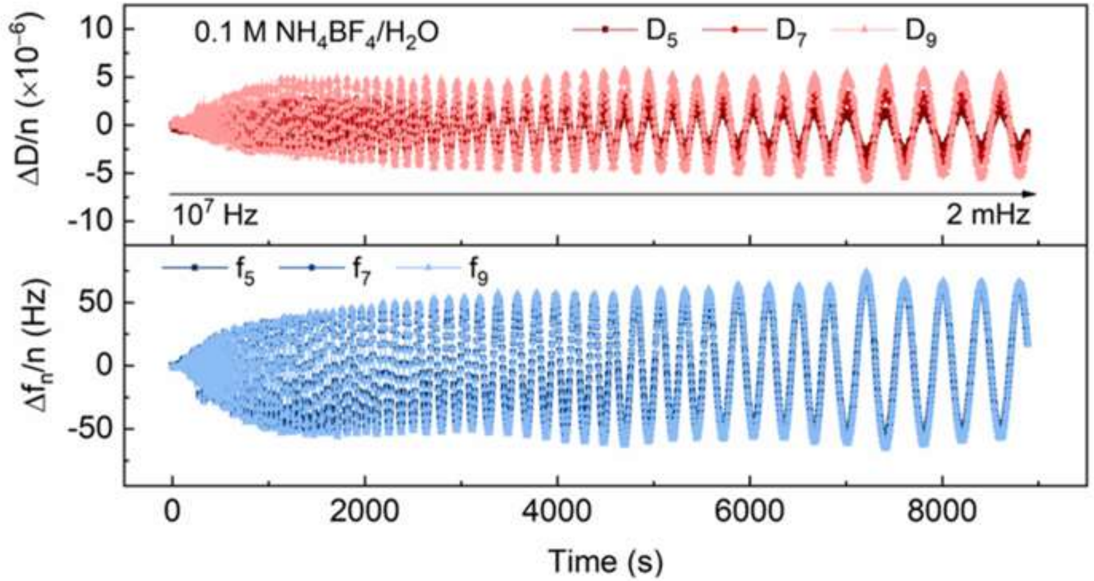


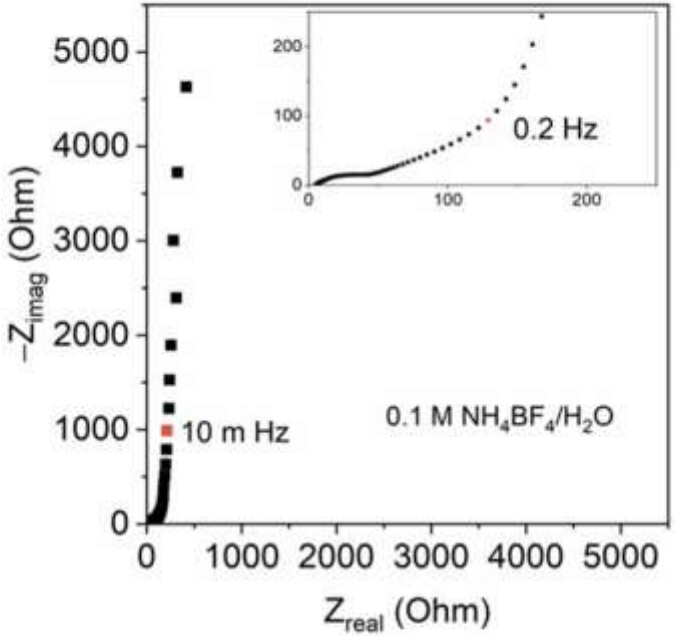
Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials.* **2023**; 22(4):495-502.

In Situ Electrochemical Impedance Spectroscopy (EIS) - QCMD

- Yields relative time-scale of mass transport
- In electrochemical impedance spectroscopy (EIS):
  - Sinusoidal voltage is applied, current is measured
  - EIS Frequency is swept

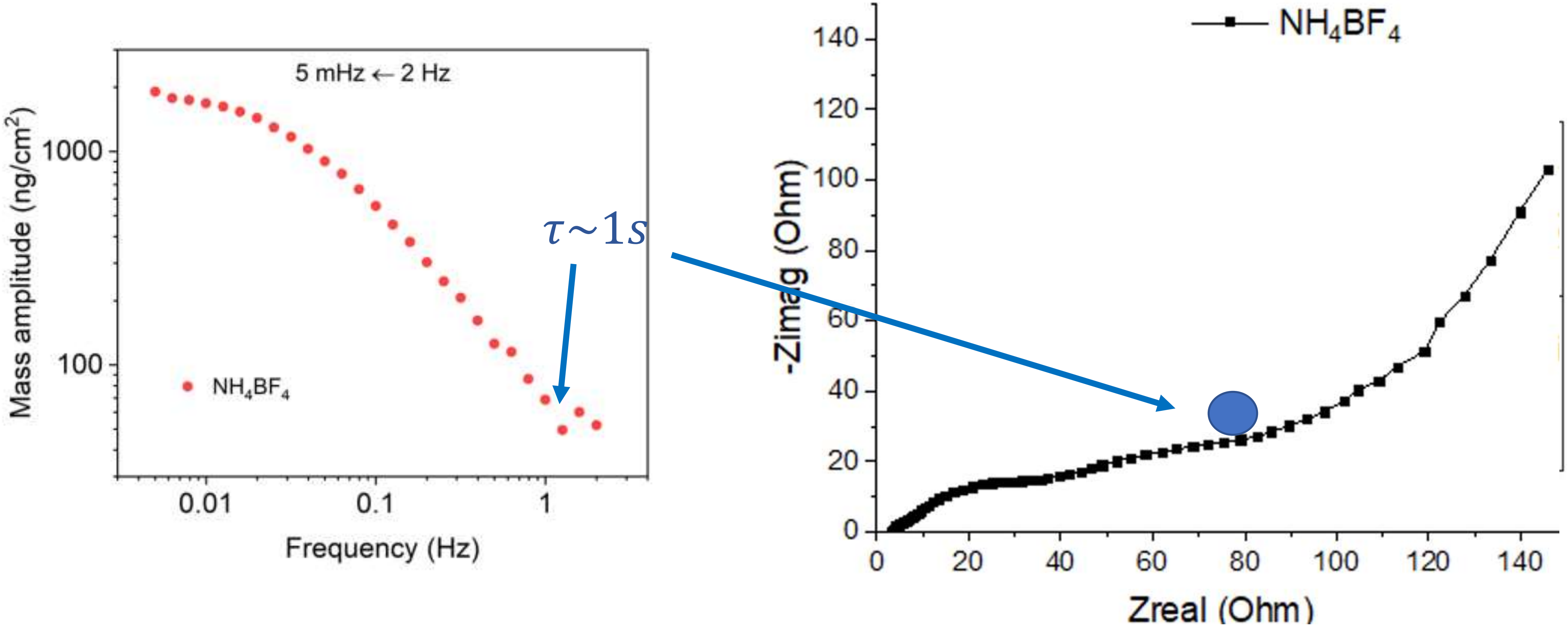






Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Time scale of reaction-diffusion from EIS-QCMD

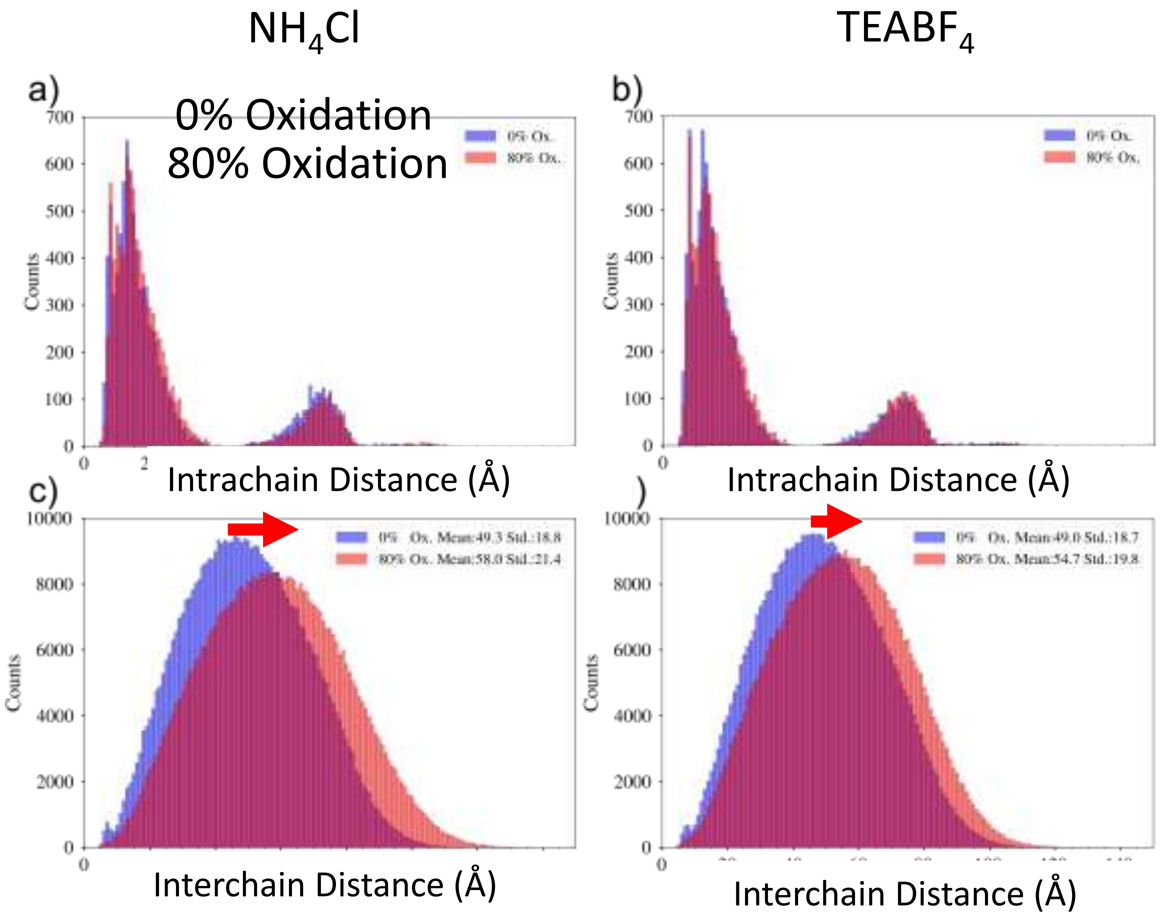


The onset frequency of mass transport corresponds to the beginning of the low-frequency diffusion tail

Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Excessive Swelling Diminishes Interchain Electron Transport

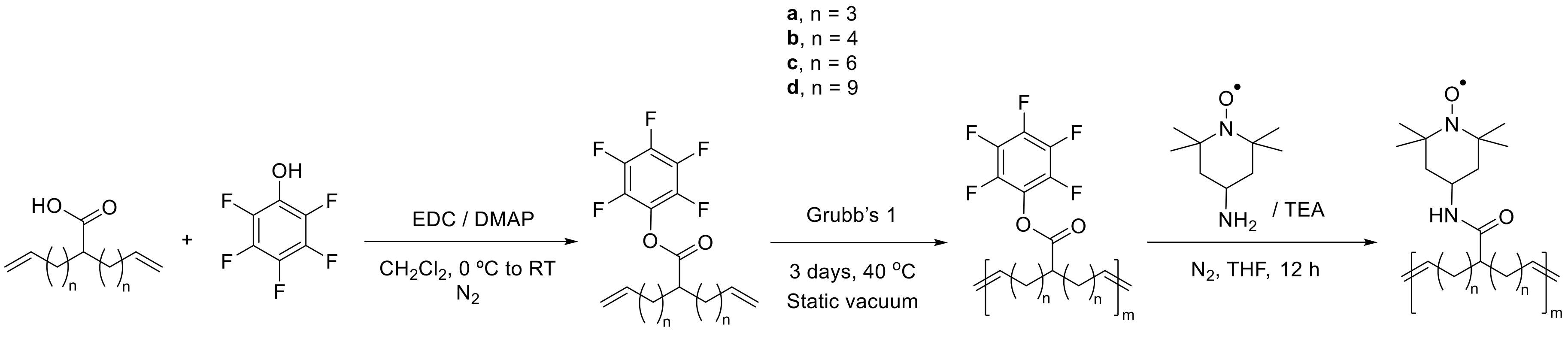
- MD simulations of a PTAm film
- Intrachain distance does not change much with oxidation or electrolyte
- Interchain distance increased more for NH_4Cl with PTAm oxidation
  - Electron transport becomes hindered, resulting in large losses in capacity



Ma T, Li C-H, Thakur RM, Tabor DP, Lutkenhaus JL. *Nature Materials*. **2023**; 22(4):495-502.

Spatially defined radical-containing polymers

- How does intrachain radical spacing affect the redox kinetics?
- Spatially defined radical-containing polymers synthesized via ADMET
- Each nitroxide radical unit is separated by 9, 11, 15, or 21 carbons



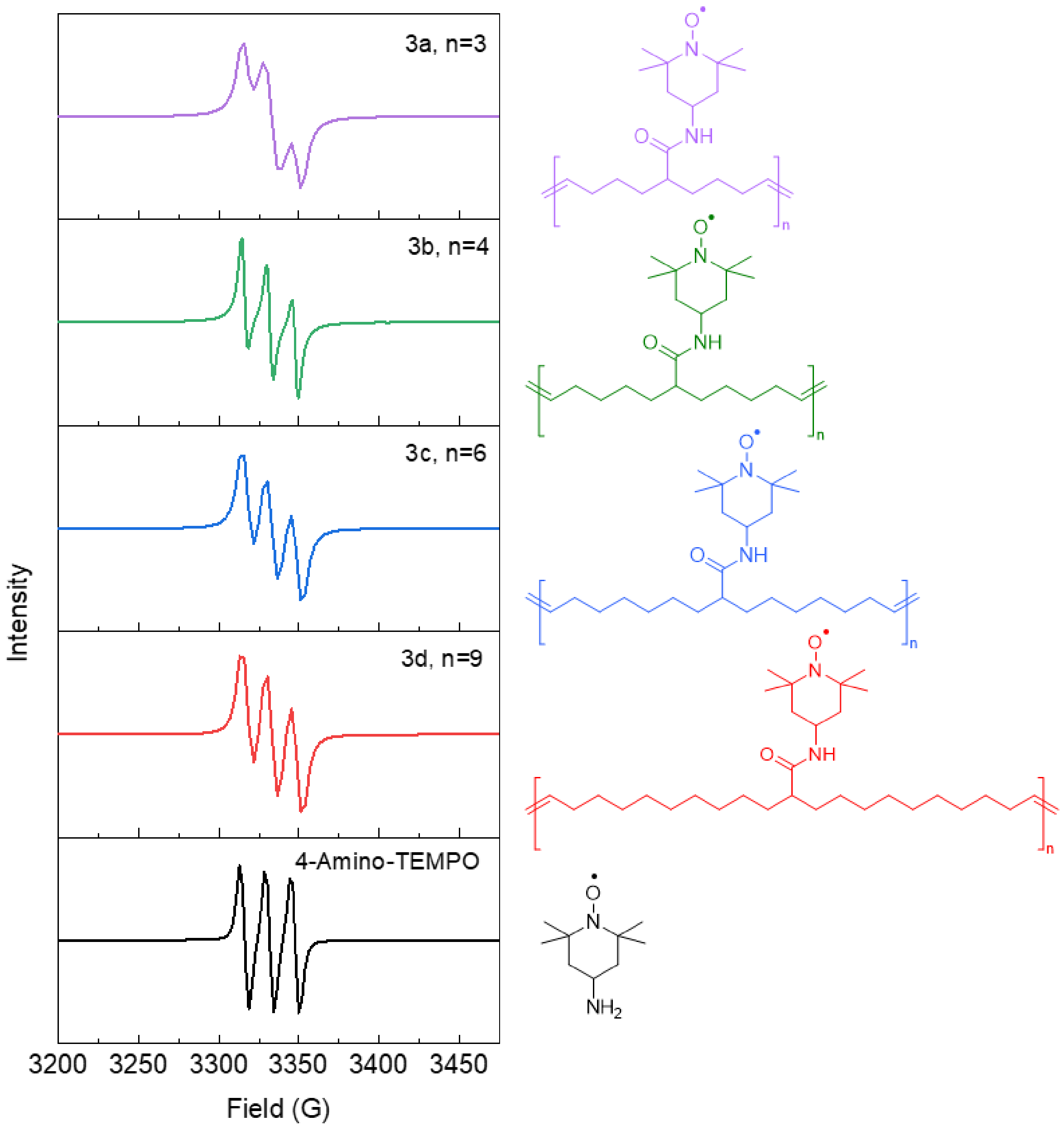
1 **2** **3**

Polymer	T_g (°C)
3a, n=3	47.6
3b, n=4	26.6
3c, n=6	−13.8
3d, n=9	36.5
PTAm	~150

Pentzer EB, Lutkenhaus JL, *et al. Chemistry of Materials, ASAP.*

Spacing Affects Spin-spin Coupling

- As spacing increases, spin-spin coupling decreases
- Individual nitroxide radicals are less influenced by their neighbor for larger *n*

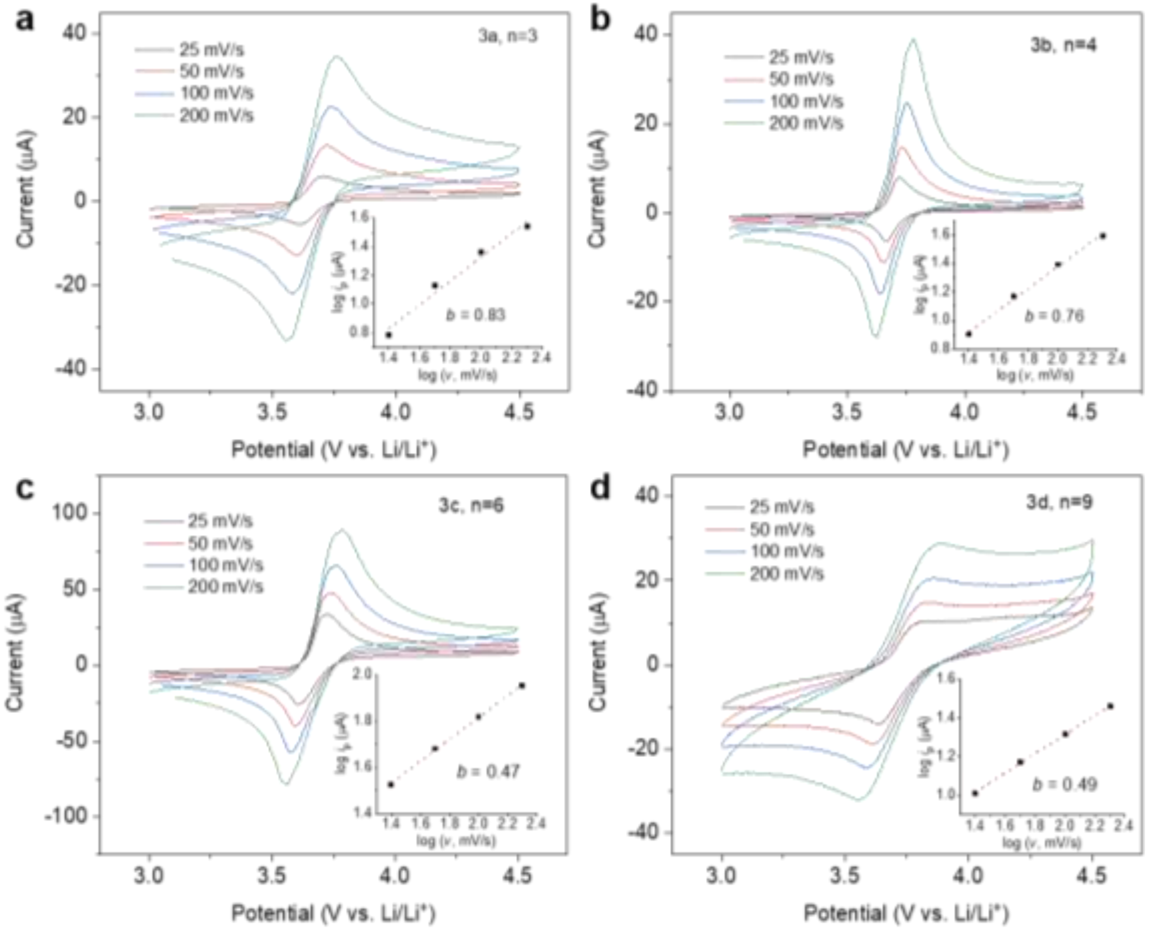


EPR spectroscopy

Pentzer EB, Lutkenhaus JL, *et al.* *Chemistry of Materials, ASAP*.

Spacing Affects the Redox Behavior

- The b-value shifts from 0.83 to 0.49 as *n* increases
  - Shift from reaction to diffusion control
- The voltammogram for *n*=9 is especially distorted
  - Indicates sluggish reaction

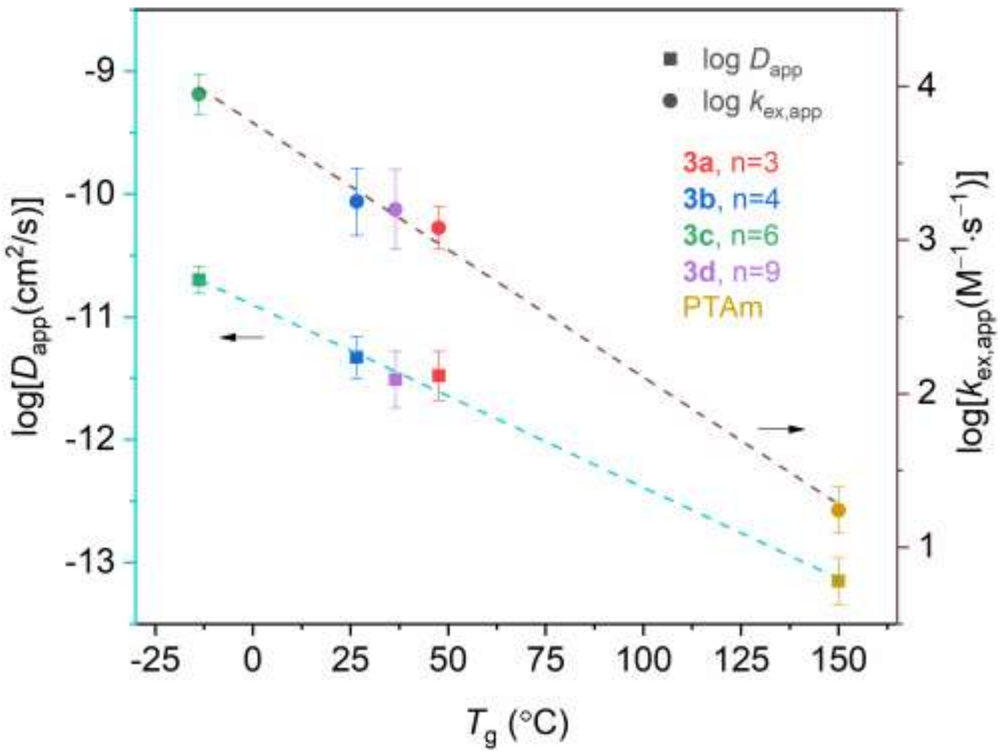


Pentzer EB, Lutkenhaus JL, *et al. Chemistry of Materials, ASAP*.

Three-electrode cell
WE: Polymer on glassy carbon (1.0-1.3 mg cm^{-2})
RE and CE: Lithium metal
Electrolyte: 0.5 M lithium triflate in propylene carbonate

This Doesn't Make Sense, Or Does It?

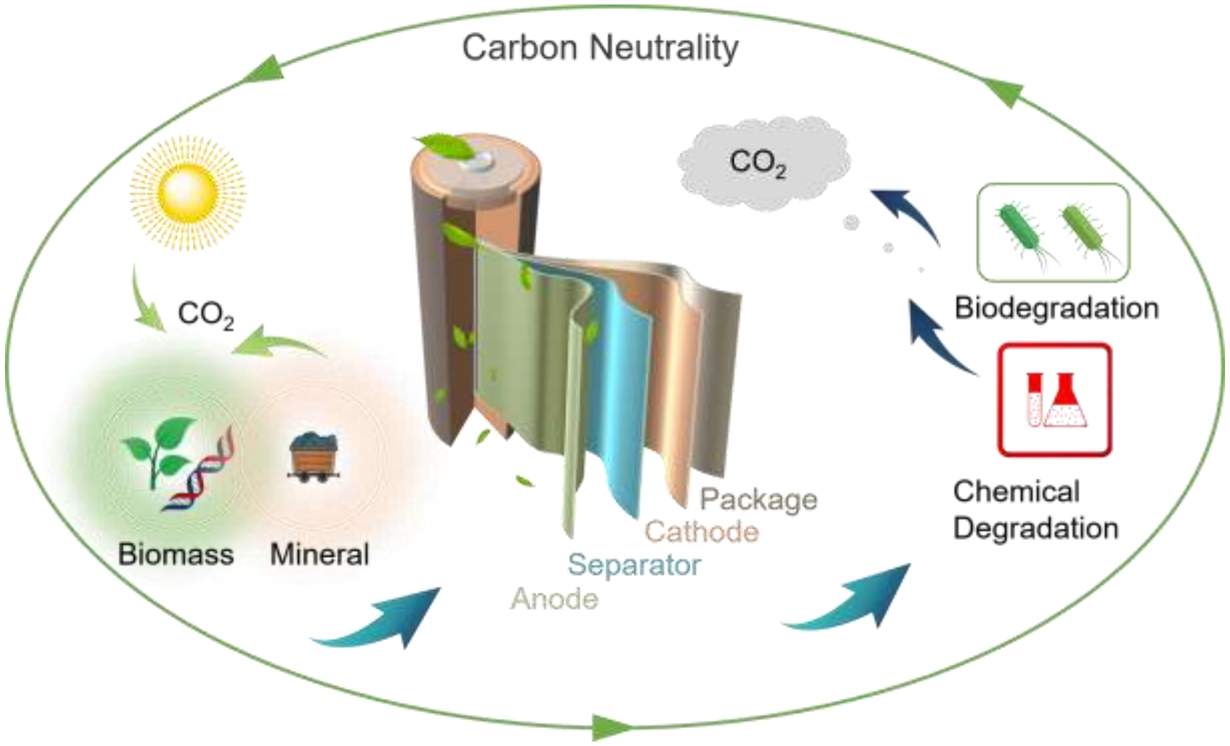
- These T_g's are above and below room temperature, and the measurements were taken at room temperature
- The polymer is plasticized with electrolyte in the electrochemical environment
  - True T_g is unknown, but it is likely well below RT
- Need to explore same polymer chemistry, vary molecular weight



Pentzer EB, Lutkenhaus JL, *et al. Chemistry of Materials, ASAP.*

Parting Thoughts

- Redox-active polymers are promising materials for metal-free batteries
- Their mixed conduction behavior and swelling can explain differences in energy storage performance
- Organic batteries can address global materials sourcing challenges for batteries



Easley, A. D.; Ma, T.; Lutkenhaus, J. L., *Joule* **2022,** *6* (8), 1743-1749.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Acknowledgements

Collaborators

Daniel Tabor and Emily Pentzer (TAMU)

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Kasturi Sarang
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Suyash Oka
Ting Ma
Junyeong Yun
Miao Qi