Molecular Redox Carriers:

Lessons Learned in Route to New Strategies

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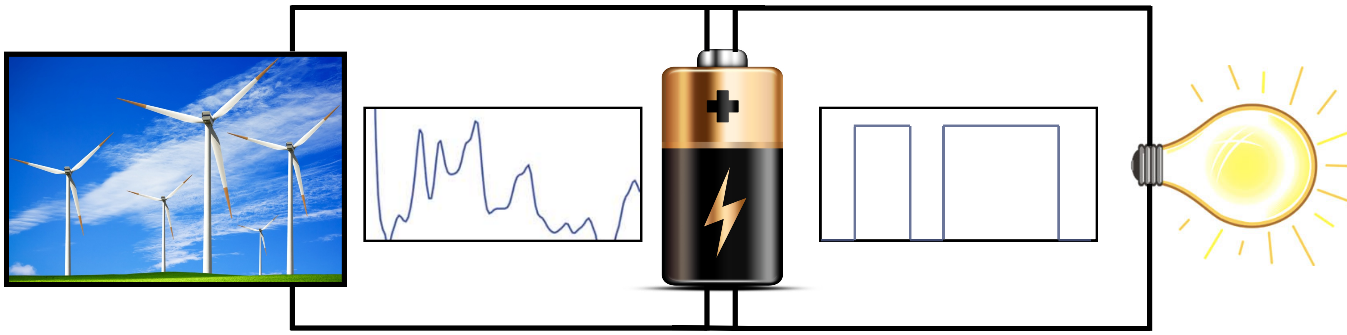
The Ohio State University

30 January, 2019
Workshop on Non-Aqueous Flow Batteries

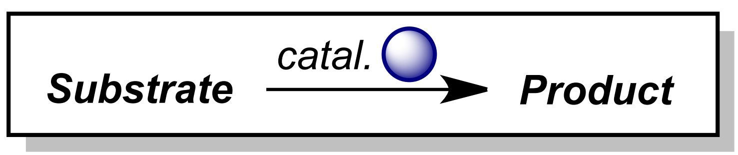
APPROACH TO ENERGY STORAGE



Batteries are required to store the collected energy, and discharge upon demand.

Unconventional Battery – Unconventional Approach

Develop battery materials by utilizing principles from
physical and synthetic organic chemistry.

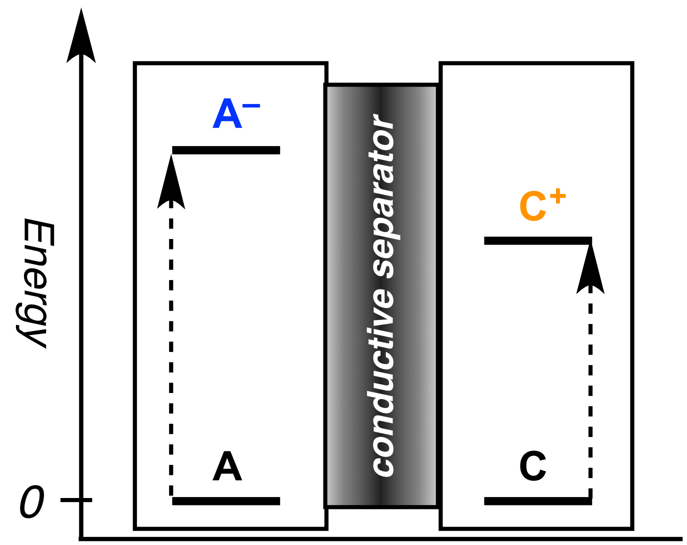


Electrochemical Energy Storage

A physical chemist's perspective

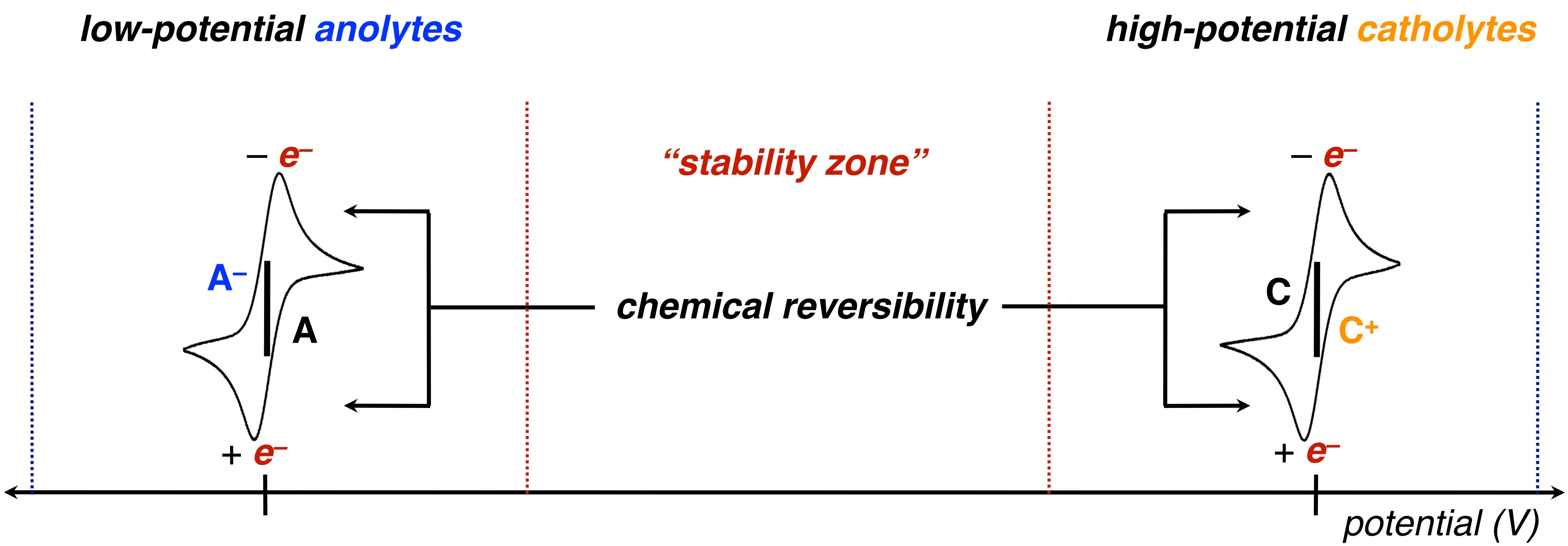
$$\mathbf{A} + \mathbf{C} \rightleftharpoons \mathbf{A^-} + \mathbf{C^+}$$

$\Delta G° > 0$



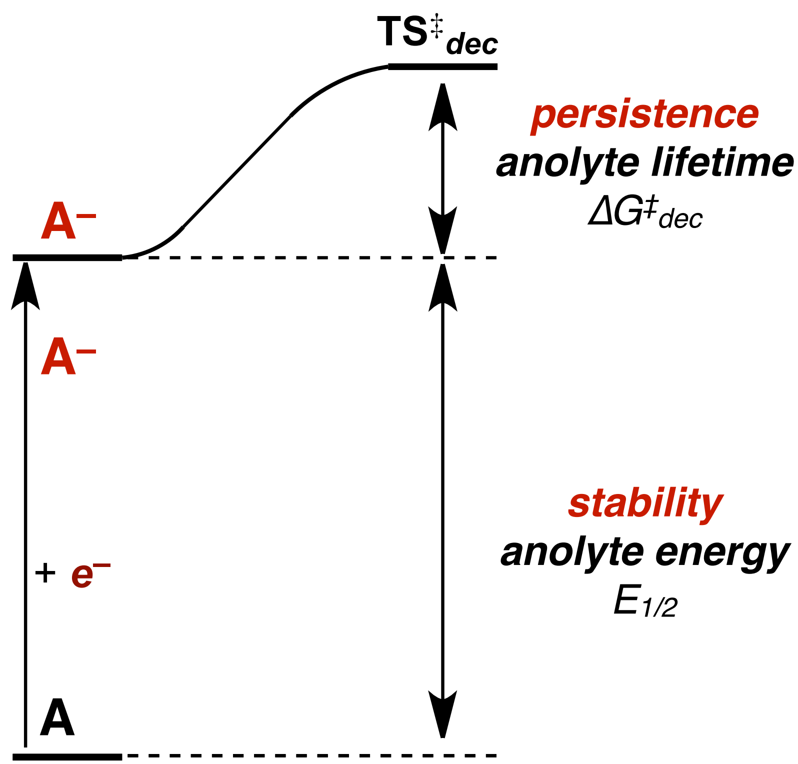
RFB ELECTROLYTES

Energy Density ∝ ***Cell Voltage*** *x* ***Solubility*** *x* ***#e⁻ Transferred***



Electrolytes must be persistent at all redox states!

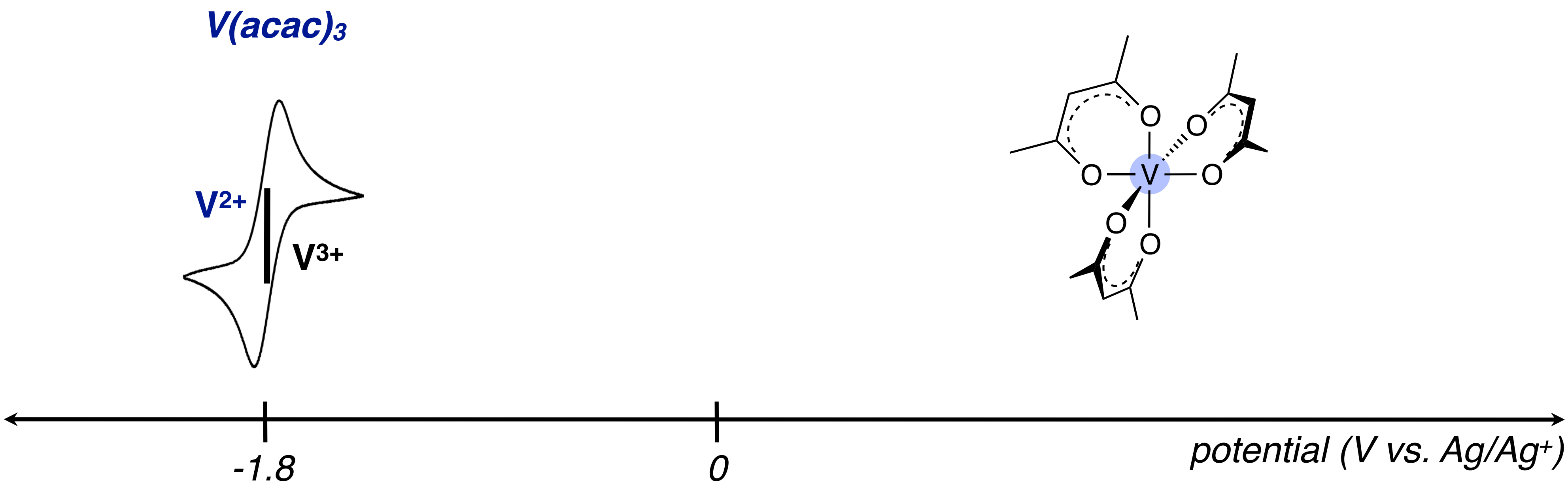
ELECTROLYTE STABILITY VS PERSISTENCE



Chemist's Goal: Maximize $E_{1/2}$ and $\Delta G^{‡}$.

A LOOK BACK: 1ST-GEN METAL COMPLEXES

Energy Density $\propto$ ***Cell Voltage*** x ***Solubility*** x ***#e⁻ Transferred***

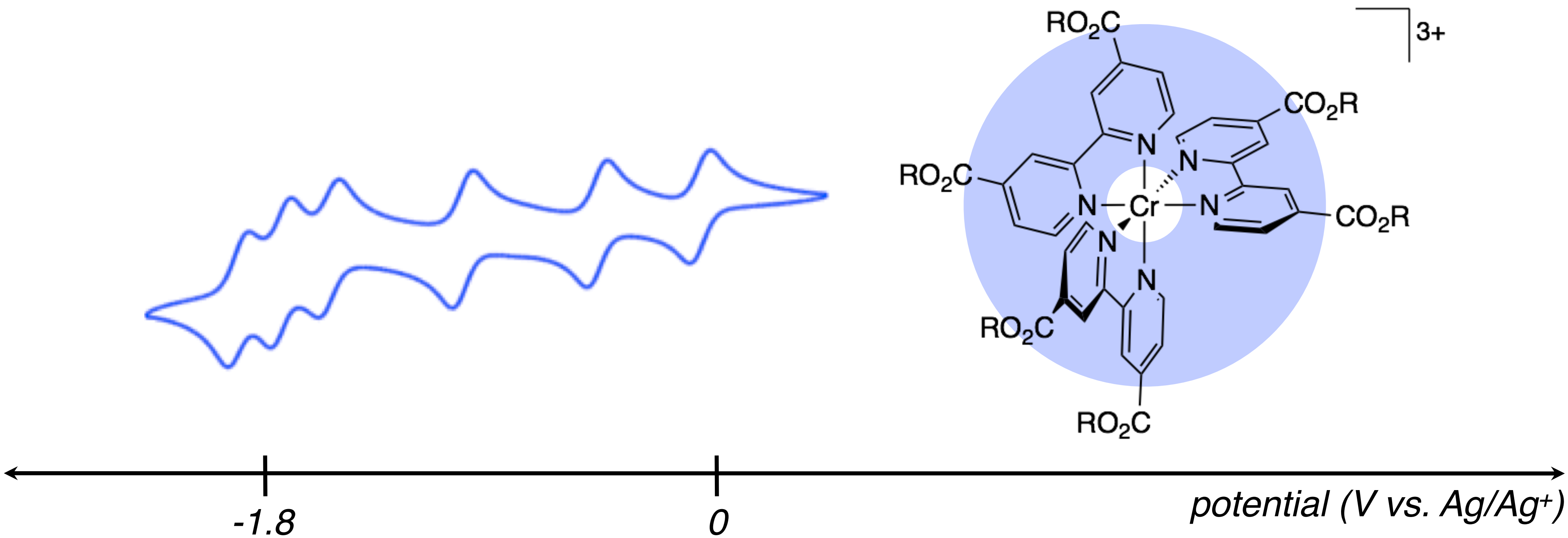


Liu, Q.; Sleightholme, A. E. S.; Shinkle, A. A.; Li, Y.; Thompson, L. T. *Electrochem. Commun.* **2009**, *11*, 2312

A LOOK BACK: REDOX-ACTIVE LIGANDS

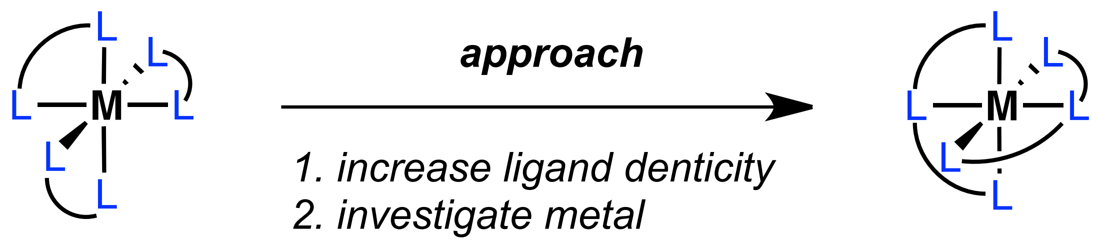
Energy Density* ∝ *Cell Voltage* x *Solubility* x *#e⁻ Transferred

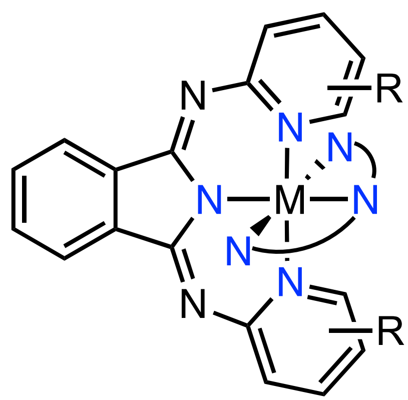
These complexes, and most others, decompose during bulk cycling.



Cabrera, P. J.; Yang, X.; Suttil, J. A.; Hawthorne, K. L.; Brooner, R. E. M.; Sanford, M. S.; Thompson, L. T. *J. Phys. Chem. C* **2015**, *119*, 15882.

3RD-GEN COORDINATION COMPLEXES

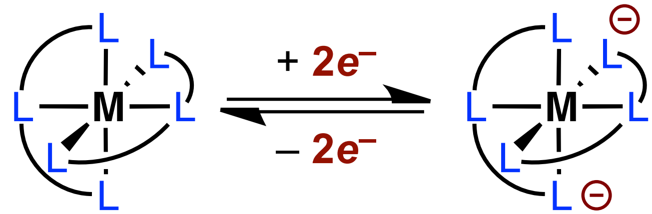




M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

Sevov, C. S.; Fisher, S. L.; Thompson, L. T.; Sanford, M. S. *JACS* **2016**, *138*, 15378.

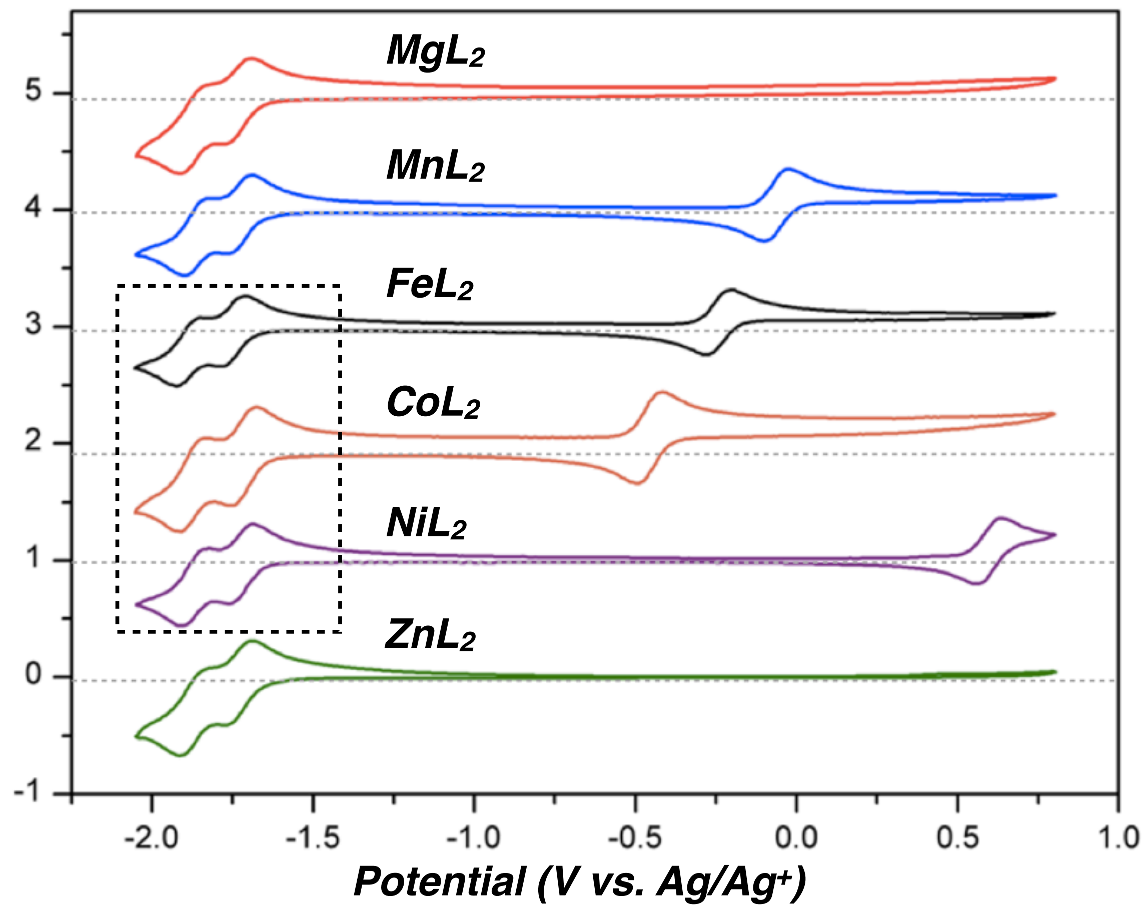
CYCLABLE COMPLEXES - NOT ALL



First examples of stable, multielectron charge-discharge cycling of NRFB electrolytes.

>200 stable cycles through 2e⁻

stable for days in fully-charged state at high concentration

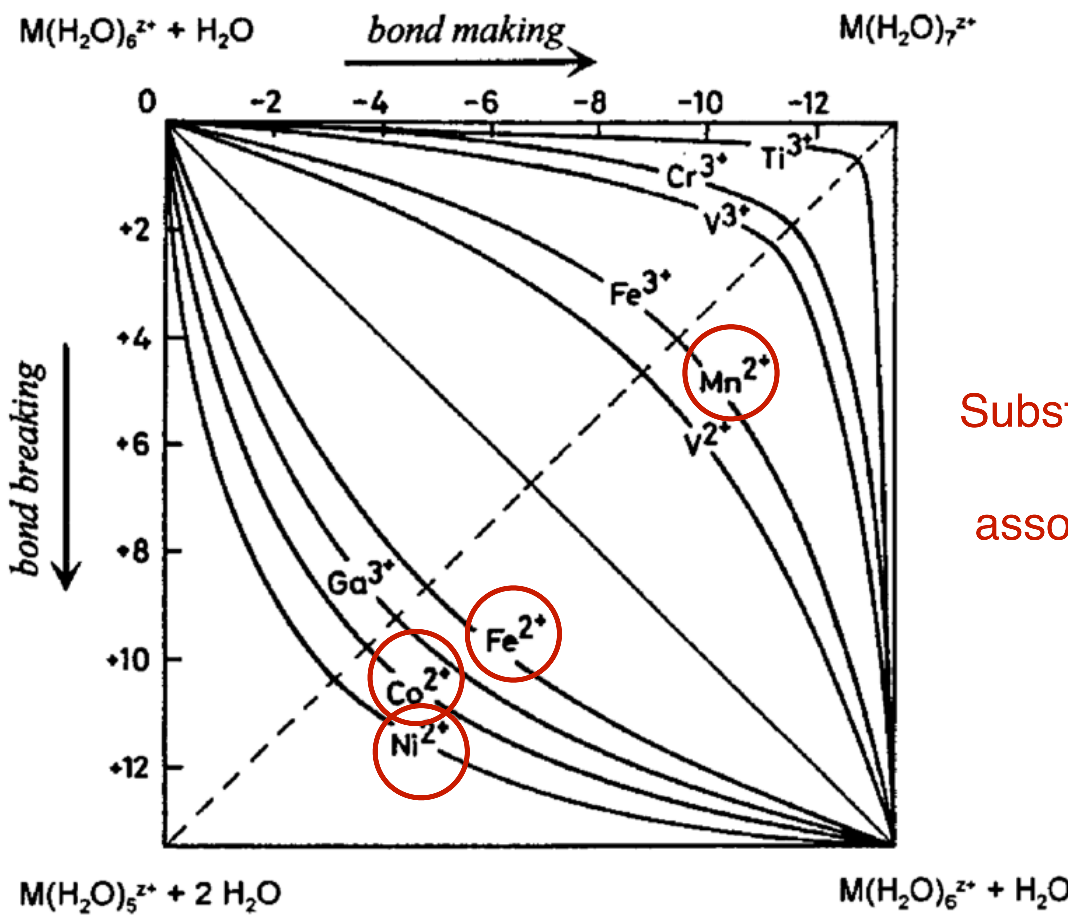


Sevov, C. S.; Fisher, S. L.; Thompson, L. T.; Sanford, M. S. *JACS* **2016**, *138*, 15378.

PERSISTENCE OF M^{2+} COMPLEXES

***Lesson #1*: Ligand shedding and its mechanism should be carefully considered.**

$\mathbf{Ni}(MeCN)_6^{2+}$	$\mathbf{Mn}(MeCN)_6^{2+}$
$k_{\text{rel exchange}} = 1$	$k_{\text{rel exchange}} =$ **10,000**



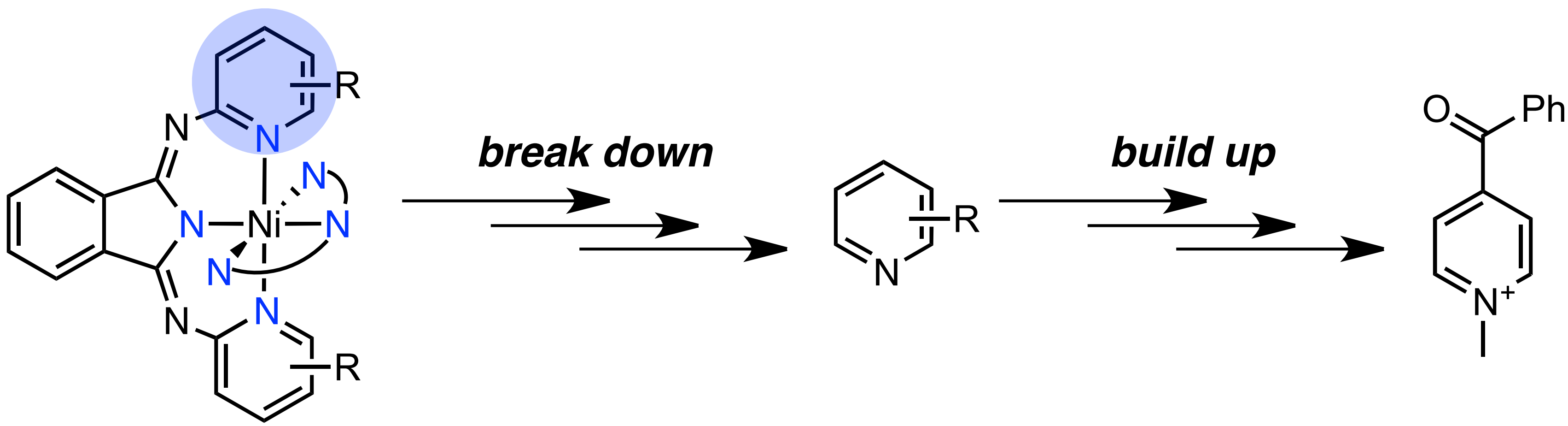
Substitution at octahedral Mn^{2+} is an associative mechanism.

Helm, L.; Merbach, A. E. *Chem. Rev.* **2005**, *105*, 1923.

NON-INNOCENT LIGANDS

***Lesson #2*: Polydentate ligands decrease solubility.**

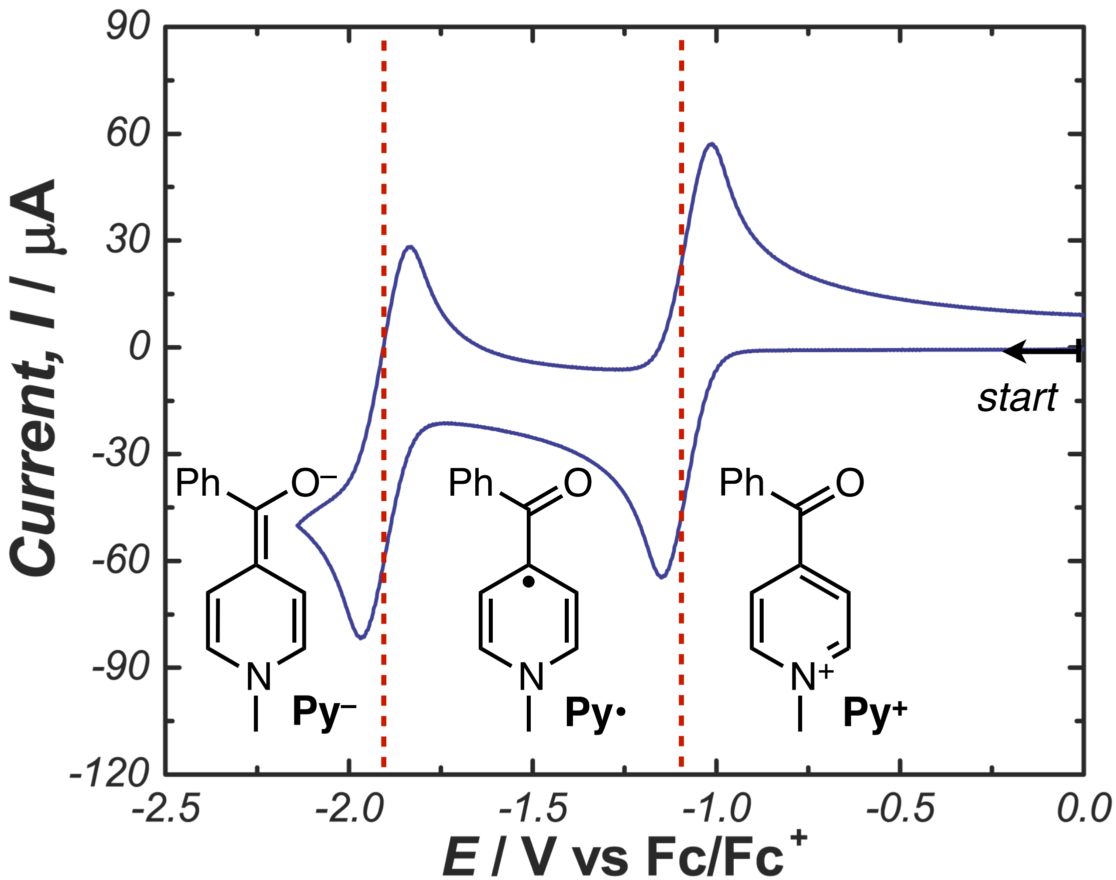
Liquid NiL_2
0.75 M maximum



Sevov, C. S.; Brooner, R. E. M.; Chénard, E.; Assary, R. S.; Moore, J. S.; Rodríguez-López, J.; Sanford, M. S. *JACS* **2015**, *137*, 14465.

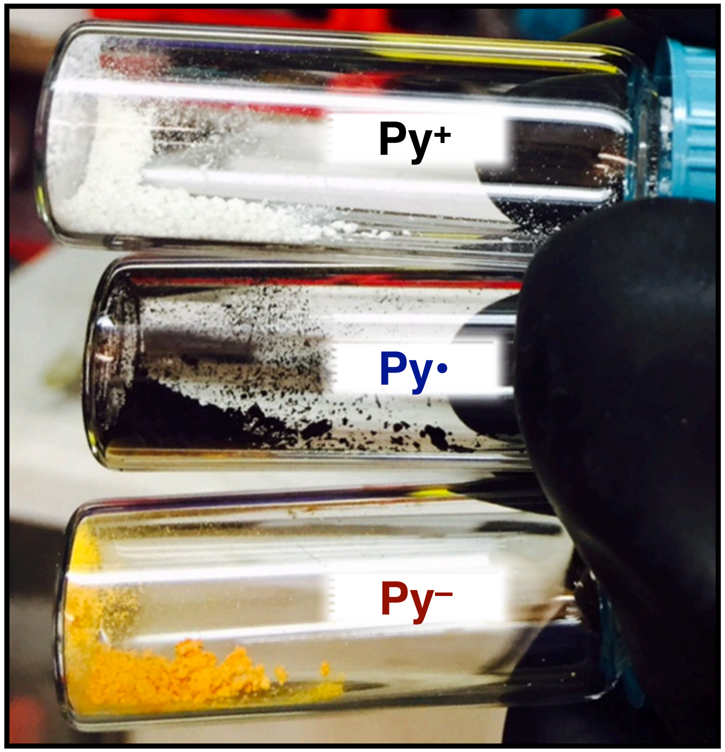
Sevov, C. S.; Hickey, D. P.; Cook, M. E.; Robinson, S. G.; Barnett, S.; Minteer, S. D.; Sigman, M. S.; Sanford, M. S. *JACS* **2017**, *139*, 2924

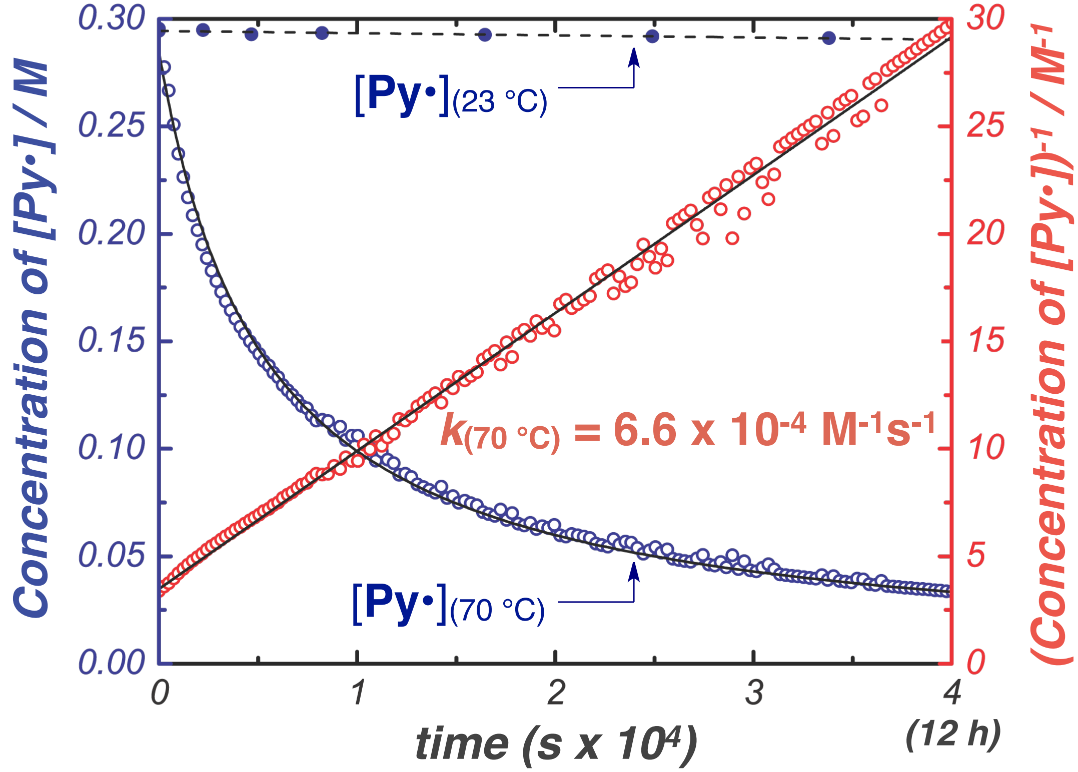
PYRIDINIUM ANOLYTES



Sevov, C. S.; Hickey, D. P.; Cook, M. E.; Robinson, S. G.; Barnett, S.; Minteer, S. D.; Sigman, M. S.; Sanford, M. S. *JACS* **2017**, *139*, 2924

QUANTIFYING ANOLYTE PERSISTENCE (ΔG‡)

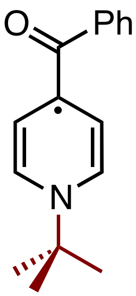


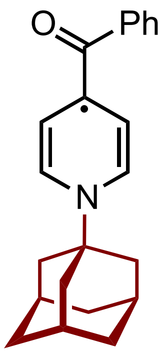


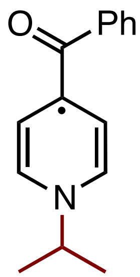
Anolyte can be isolated in all 3 redox states to characterize solubility and persistence.

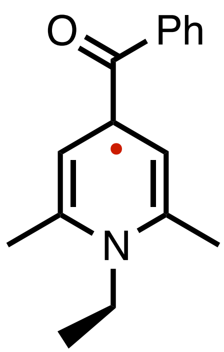
The rate of decomposition fits a second-order plot, consistent with radical dimerization. Persistence (ΔG‡) is the measured rate constant.

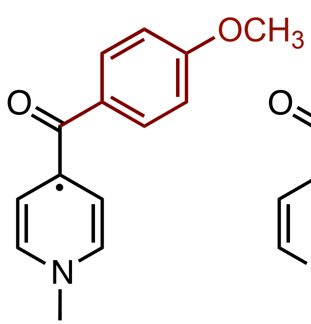
Physical Properties vs. Degradation

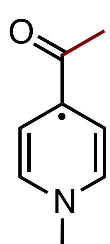


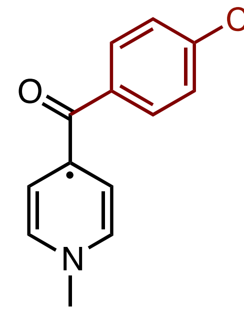


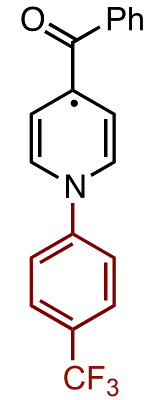


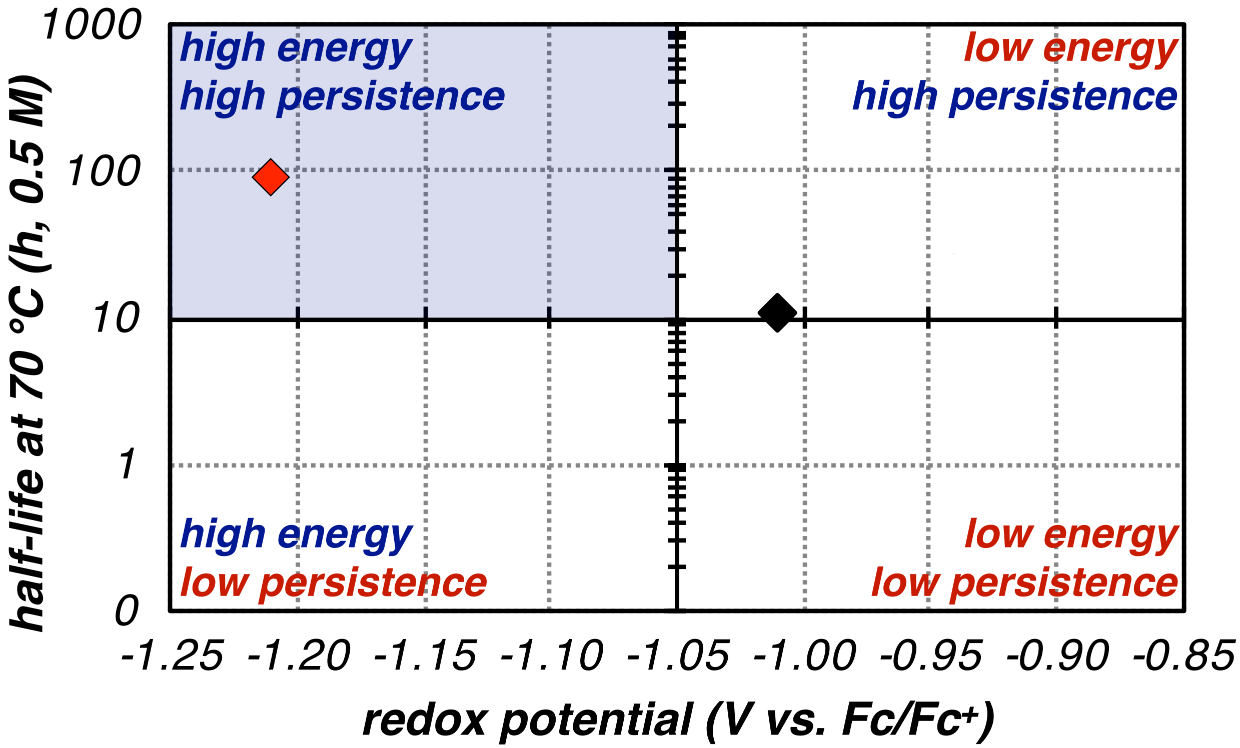










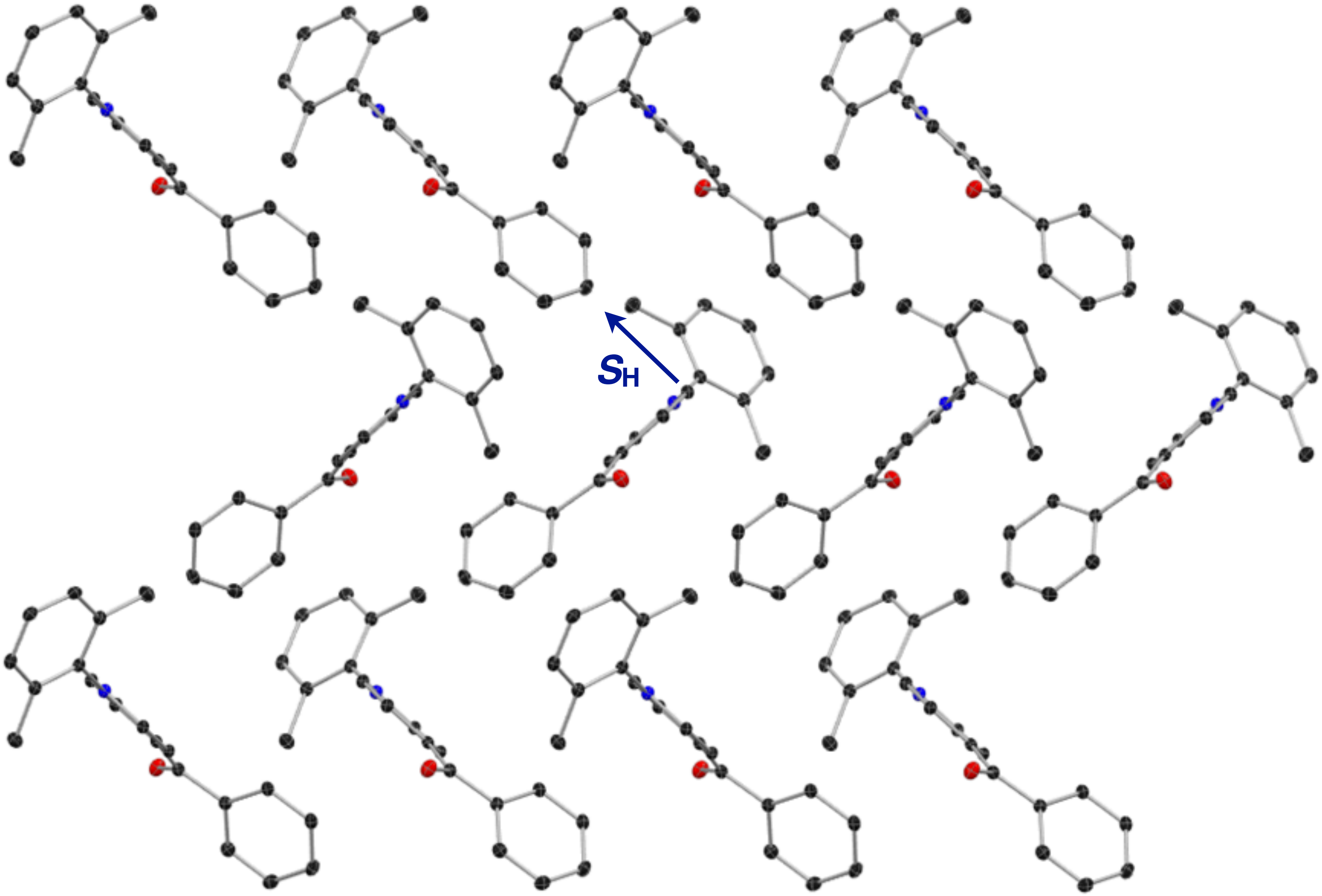


Sevov, C. S.; Hickey, D. P.; Cook, M. E.; Robinson, S. G.; Barnett, S.; Minteer, S. D.; Sigman, M. S.; Sanford, M. S. *JACS* **2017**, *139*, 2924

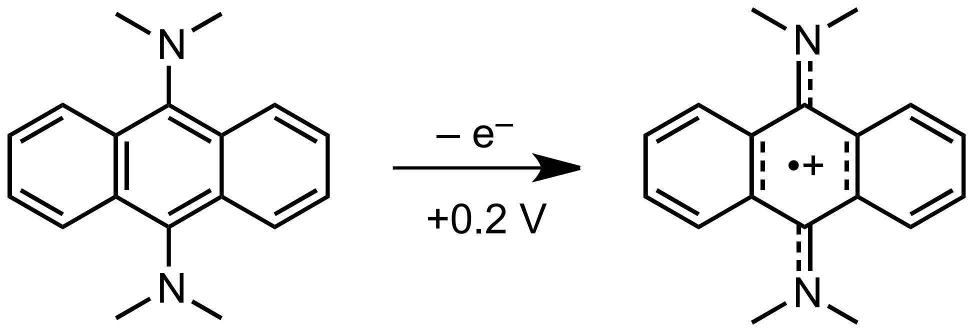
SOLID-STATE ANALYSIS

Lesson #3: Persistence can be controlled independently of $E_{1/2}$ by tuning steric properties.

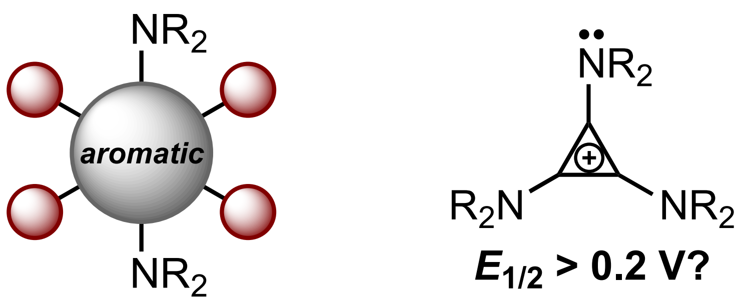
$$0.49E_{1/2} + 1.17S_H + 0.07 = \Delta G^{\ddagger}_{dec}$$



STERIC HINDRANCE - CATHOLYTES

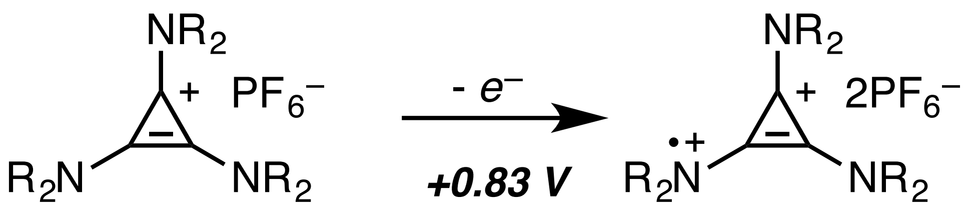


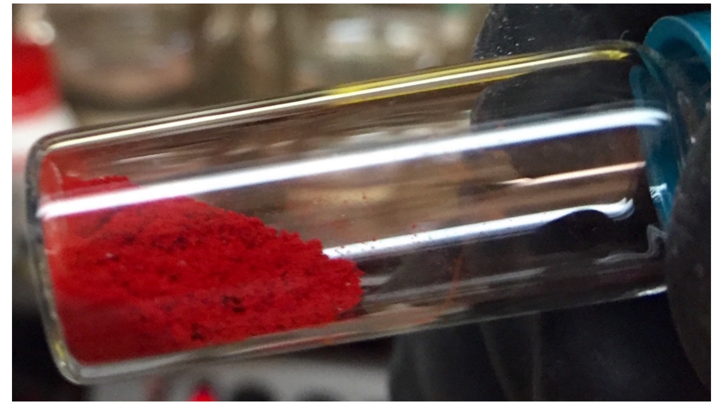
Persistent radical cations: derivatives of Wurster's blue.



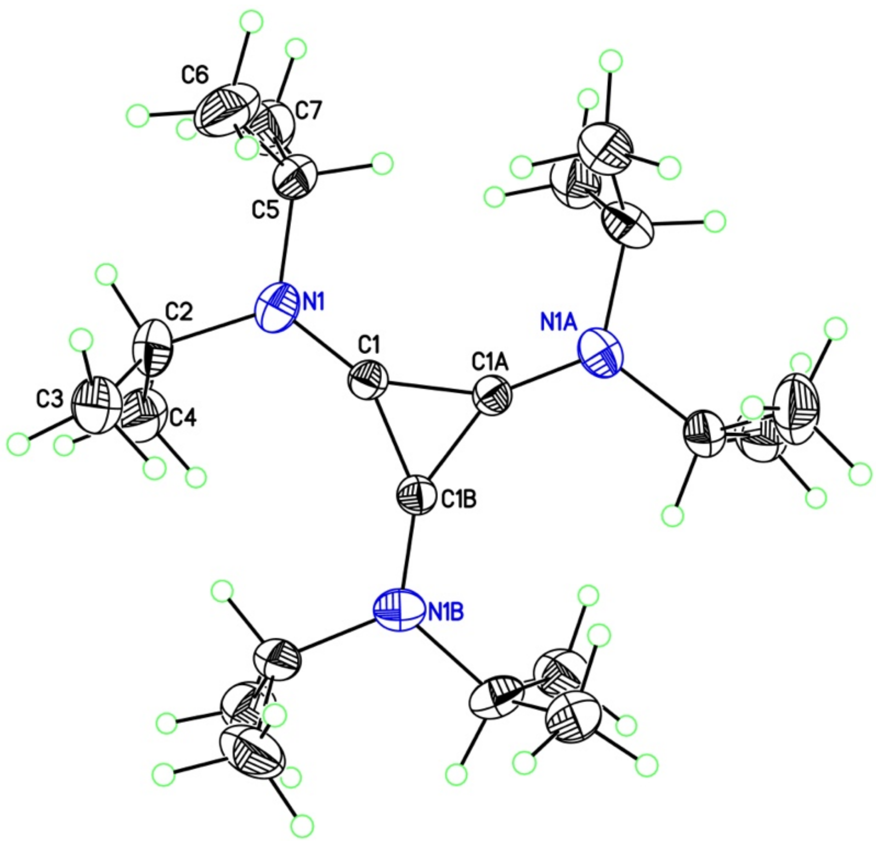
Can this architecture be exploited to identify persistent, high potential catholytes?

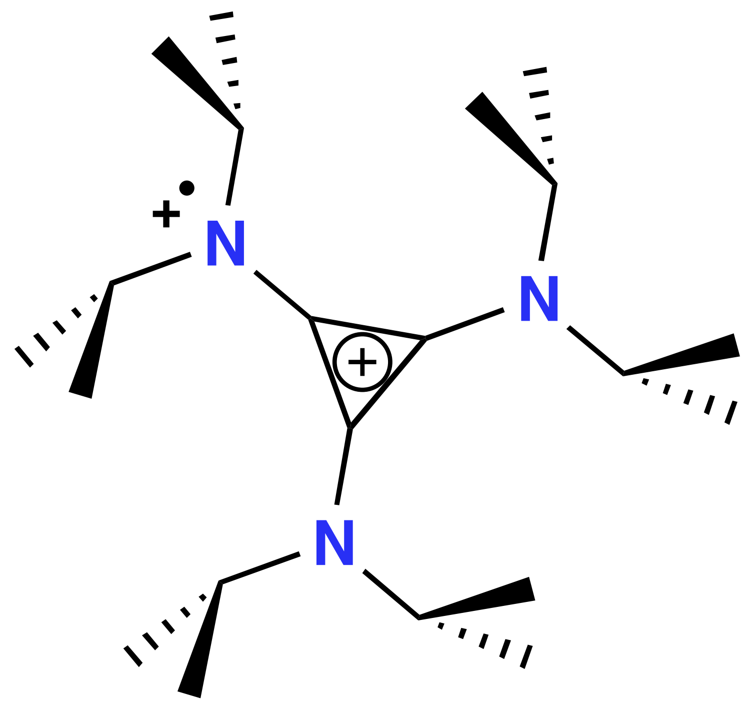
CHARGED, ISOLABLE CYCLOPROPENIUM





The radical dication is isolable as a pure solid.

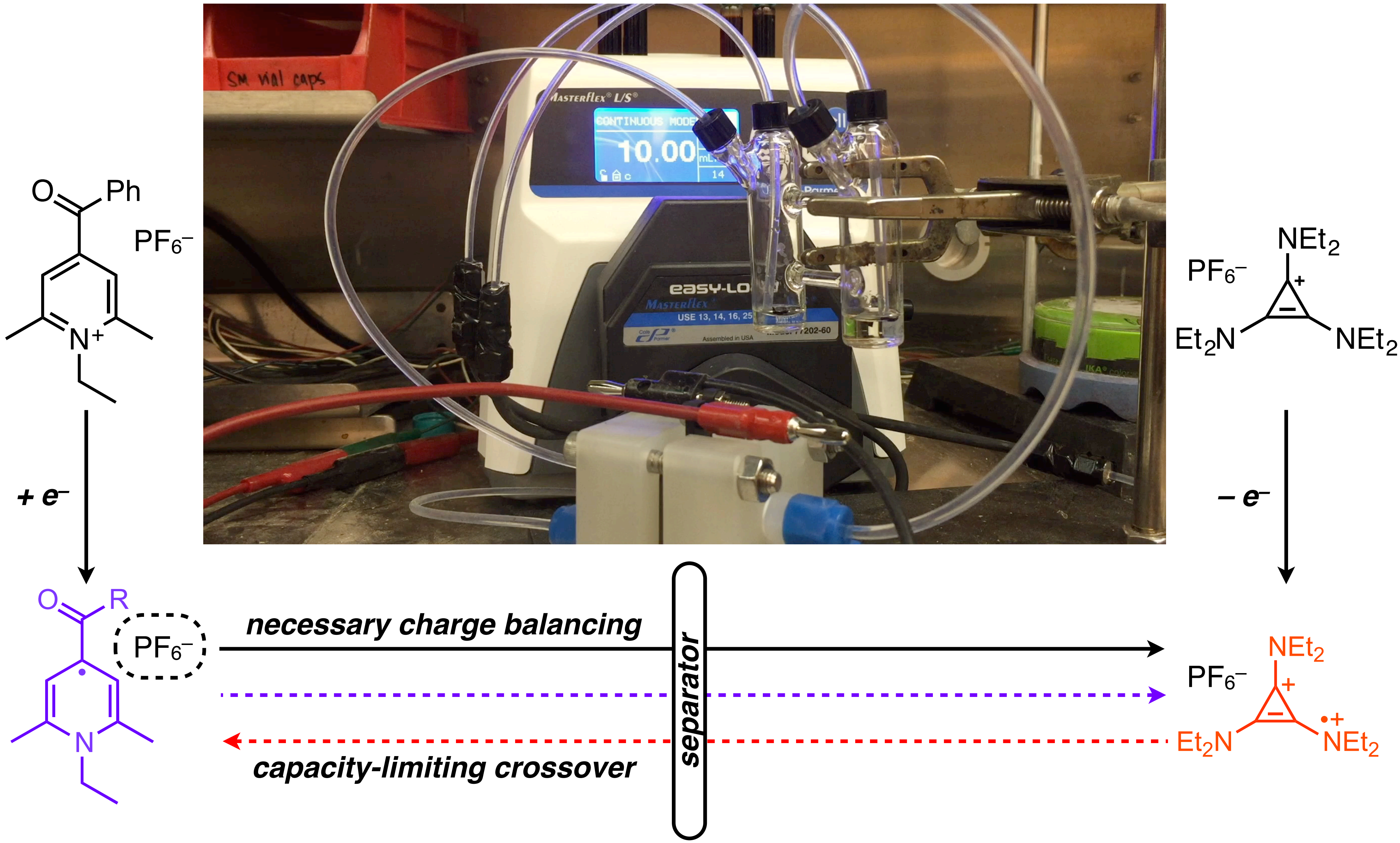




Sevov, C. S.; Samaroo, S. K.; Sanford, M. S. *Adv. Energy Mater.* **2016**, 1602027.

FULL-CELL RFB TESTING

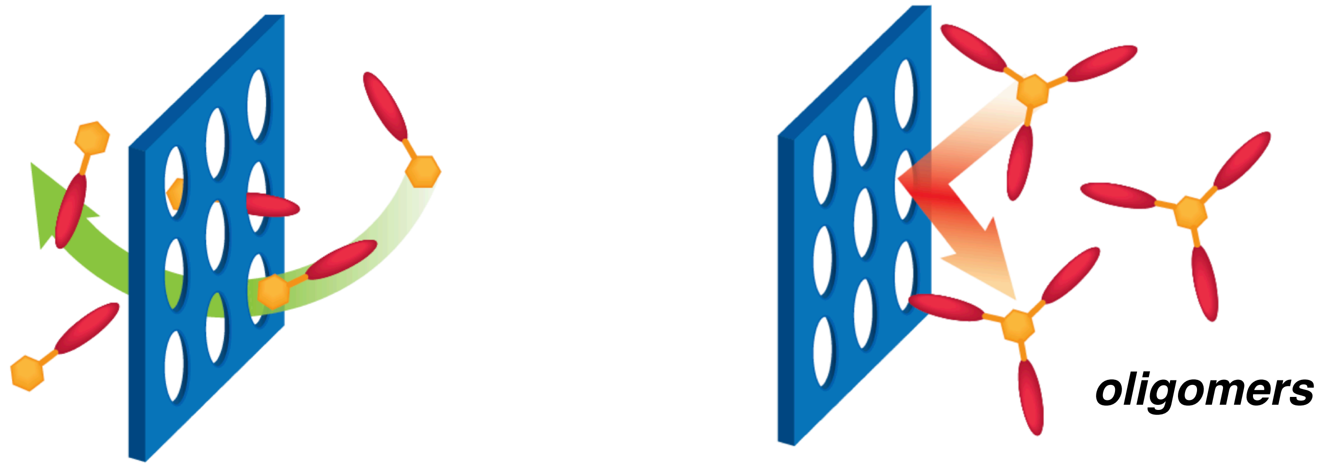
with Dr. Koen Hendriks



Membrane selection in combination with molecular design is key for long-term cycling.

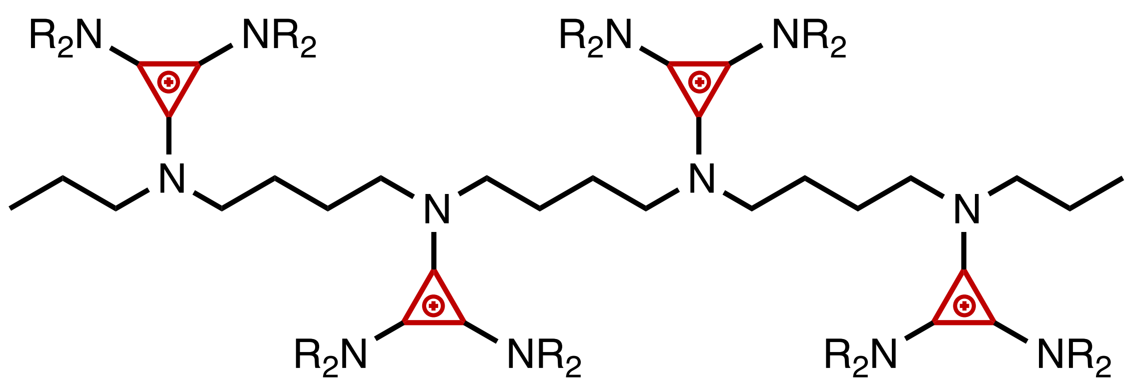
PIM Separators for Oligomeric Analogs

***Lesson #4*: Crossover is a critical limitation, especially at high concentration.**



Doris, S. E.; Ward, A. L.; Baskin, A.; Frischmann, P. D.; Gavvalapalli, N.; Chénard, E.; Sevov, C. S.; Prendergast, D.; Moore, J. S.; Helms, B. A. *ACIE* **2017**, *56*, 1595

Pair a microporous separator with a redox-active oligomer to prevent crossover



Hendriks, K. H.; Robinson, S. G.; Braten, M. N.; Sevov, C. S.; Helms, B. A.; Sigman, M. S.; Minteer, S. D.; Sanford, M. S. *ACS Central Science* **2018**, *4*, 189

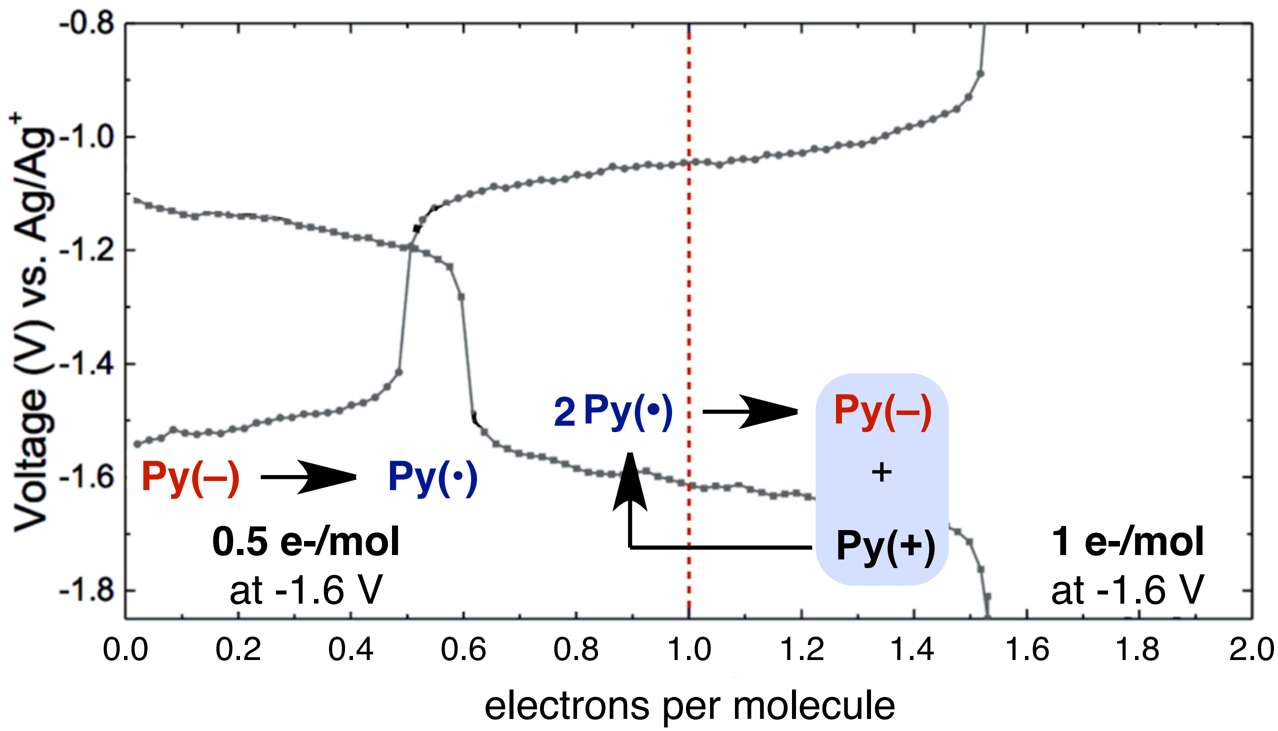
ELECTRON EXCHANGE

***Lesson #5*: Electron transfer between redox states of multielectron species leads to low voltaic efficiency.**

Multielectron electrolytes can reduce MW/e– of electrolytes (target ≤150).

Py(+) → **Py(•)** → **Py(–)**

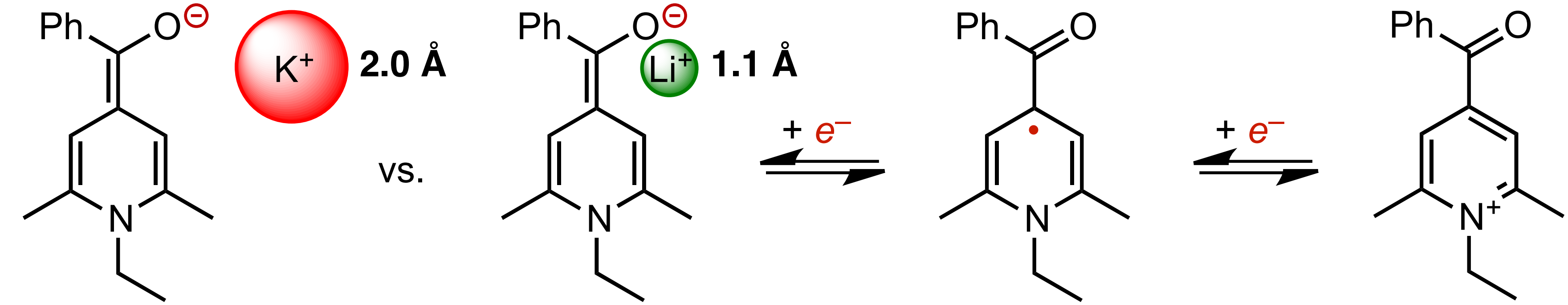
-1.2 V -1.6 V



***Py(–)* is behaving as a <u>redox carrier</u> to charge the Py(+).**

Hendriks, K. H.; Sevov, C. S.; Cook, M. E.; Sanford, M. S. *ACS Energy Letters* **2017**, *2*, 2430

ELECTROLYTE INTERACTIONS

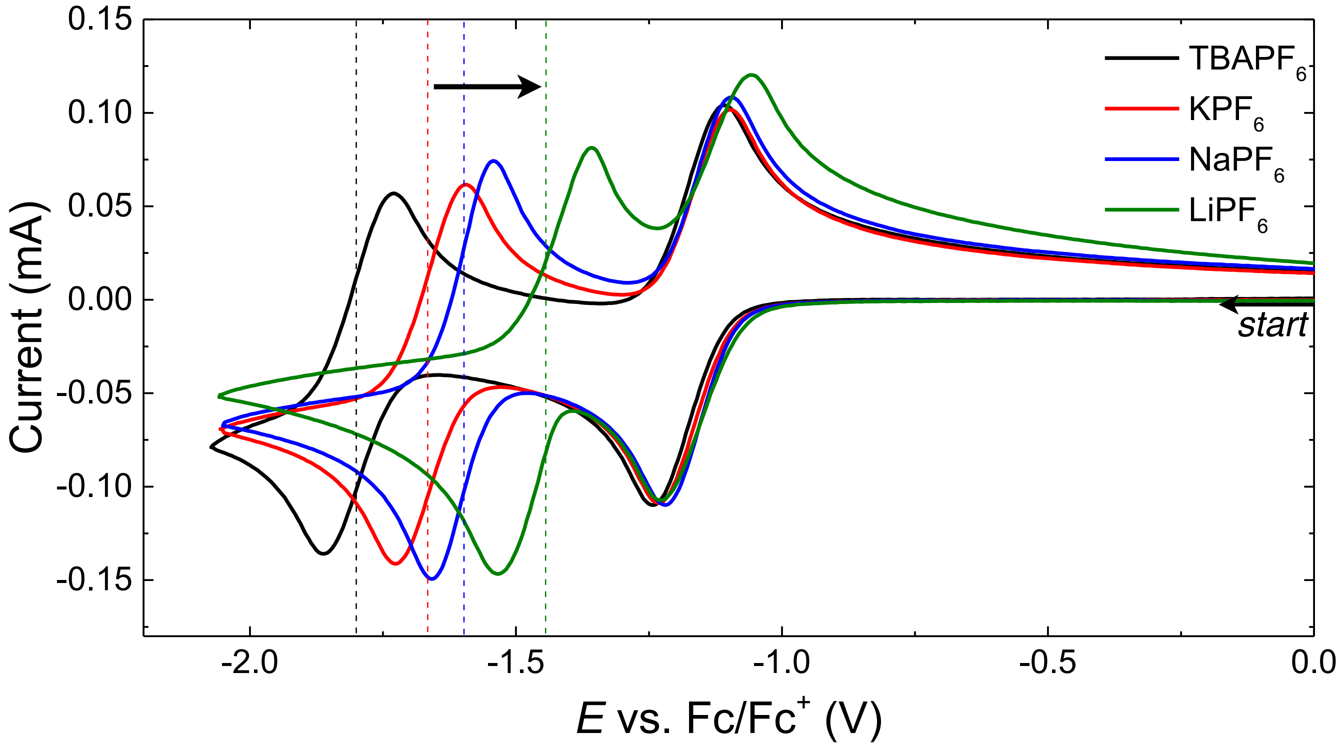


$E^2_{1/2} = -1.66$ V

$E^2_{1/2} = -1.40$ V

undesirable anolyte stabilization

(lose 260 mV = 6 kcal/mol)



Potassium salts support more negative anolyte potentials than lithium salts.

Hendriks, K. H.; Sevov, C. S.; Cook, M. E.; Sanford, M. S. *ACS Energy Letters* **2017**, *2*, 2430

LESSONS IN ELECTROLYTE DESIGN

1. Ligand shedding and its mechanism should be carefully considered.
The metal, its oxidation state, and the ligands should be carefully considered.

2. Polydentate ligands generally decrease solubility.
Breaking symmetry and polar functional groups increase solubility in polar aprotic solvents.

3. Persistence can be controlled independently of $E_{1/2}$ by tuning steric properties.
Electronic tuning increases lifetime, but generally reduces cell voltage.
Tuning of steric parameters decouples these two features.

4. Crossover is a critical limitation, especially at high concentration.
Macromolecules or oligomers paired with inexpensive separators are potential solutions.

5. Multielectron electrolytes often suffer from comproportionation events that reduce voltaic efficiency.
Simultaneous multielectron transfer is preferred over two, single-electron transfer events.

6. The electrolyte can dramatically impact redox potentials because stabilizing interactions.
Potassium salts are preferable over lithium salts for anolyte chemistries.