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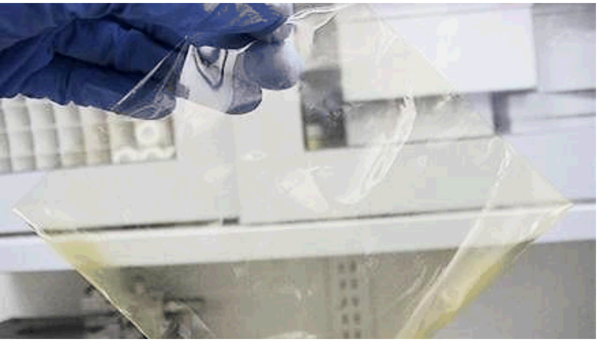

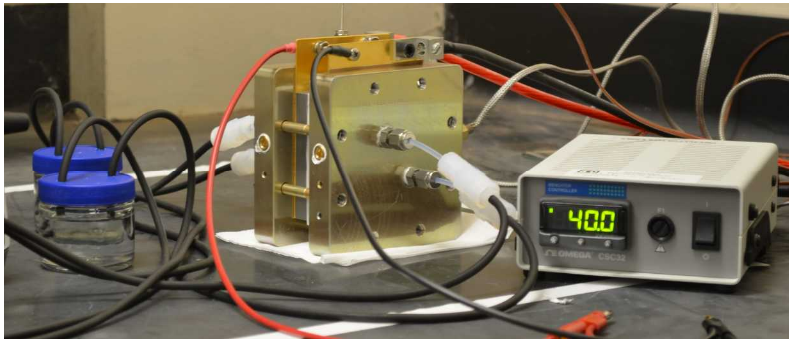

Redox Non-Innocence: Enhancing the Stability and Performance of Flow Battery Electrolytes

Dr. Mitchell R. Anstey

Sandia National Laboratories, Livermore, CA

June 3rd, 2014

SunEdison simplifying solar

OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Energy R&D at Sandia

Fuel Cell Development
(Mobile Light Project)

Concentrated
Solar Power

The Photovoltaic Systems
Evaluation Laboratory (PSEL)

Battery Research
(Na-Sulfur Battery
System)

Energy R&D at Sandia

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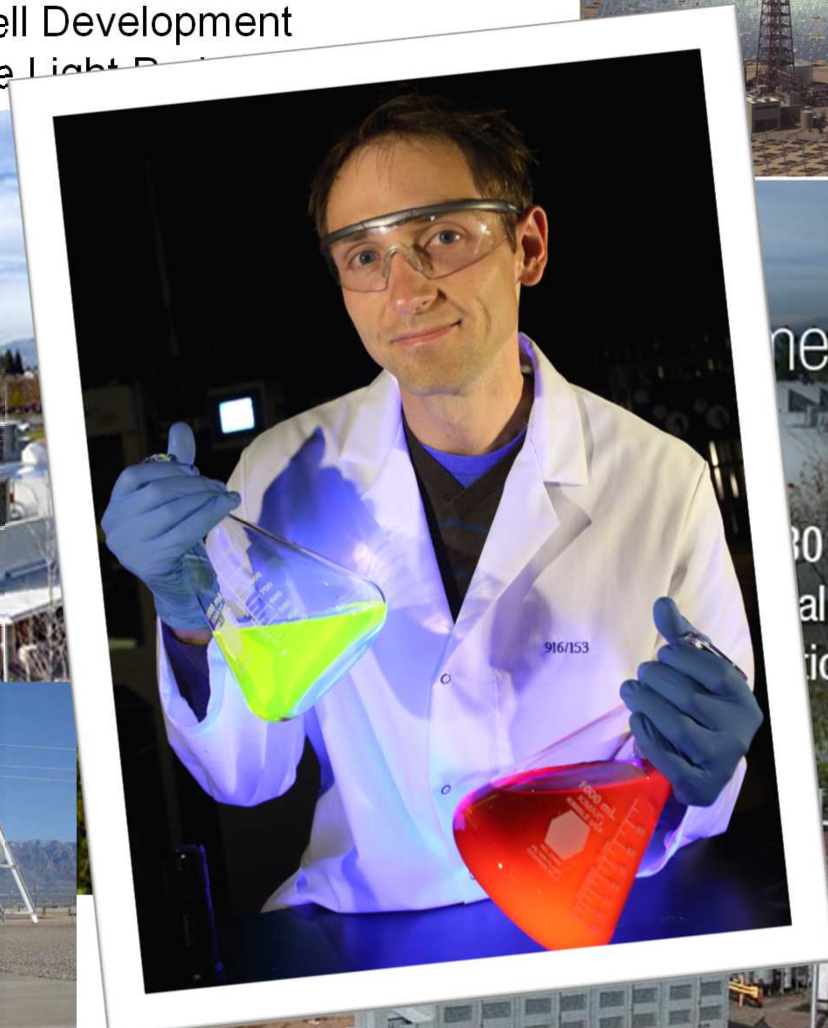
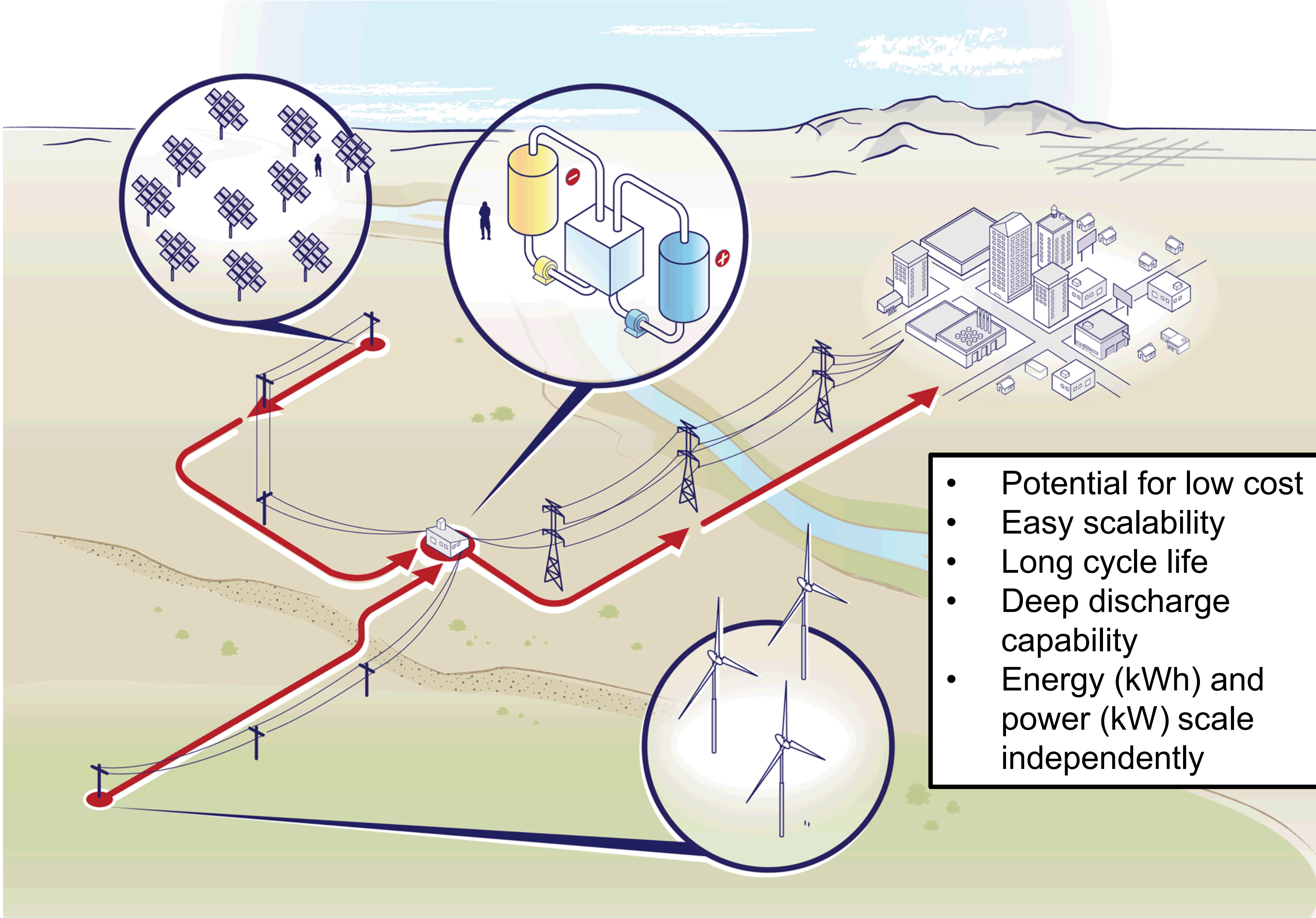


Battery Research
(Na-Sulfur Battery
System)

The Photovoltaic Systems
Evaluation Laboratory (PSEL)

Flow Batteries in the Grid



- Potential for low cost
- Easy scalability
- Long cycle life
- Deep discharge capability
- Energy (kWh) and power (kW) scale independently

Aqueous vs. Non-Aqueous

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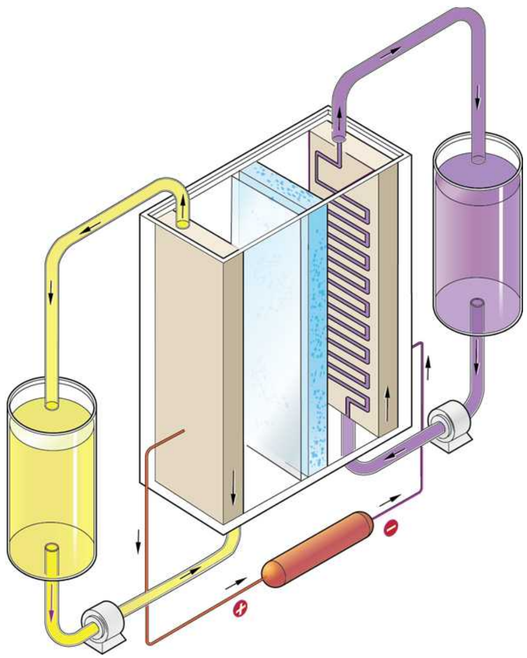
$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$



$$V^{2+} \rightleftharpoons V^{3+} + e^-$$

Open Circuit Potential (OCP) **1.26 V**

Solvent	Electrochemical Window/V
Water	**1.3 V**
Dichloromethane	3.7 V
Tetrahydrofuran	3.7 V
Acetonitrile	4.0 V
Dimethylformamide	4.3 V

- Wider voltage window
- Increased temperature range
- Diverse solubility profiles
- Wide variety of redox-active species

Bard, Inzelt, and Scholz, *Electrochemical Dictionary*, **2012.**

Zanello, Fabrizi de Biani, and Nervi, *Inorganic Electrochemistry: Theory, Practice and Application*, **2012.**

Investigation of Non-Aqueous Chemistry

Industry is optimizing flow battery electrolytes via:

- Higher molarity of active species through ionic liquids, suspensions
- Organic, inorganic, and hybrid systems
- Compounds with many and/or multi-electron redox couples
- Increased stability of redox-active species

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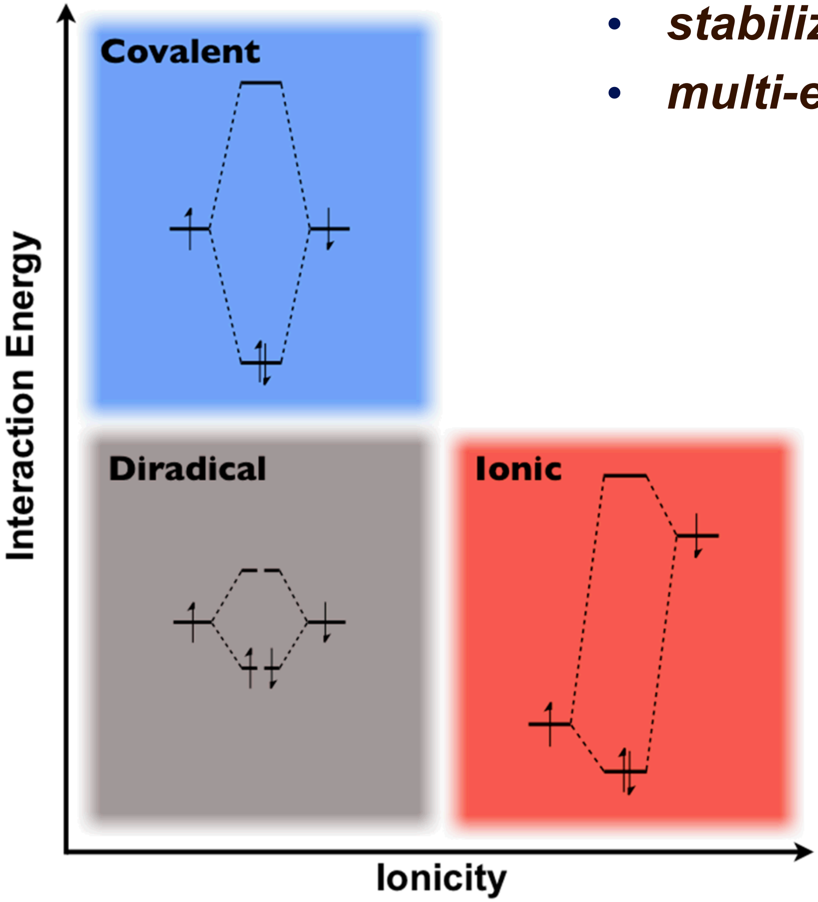
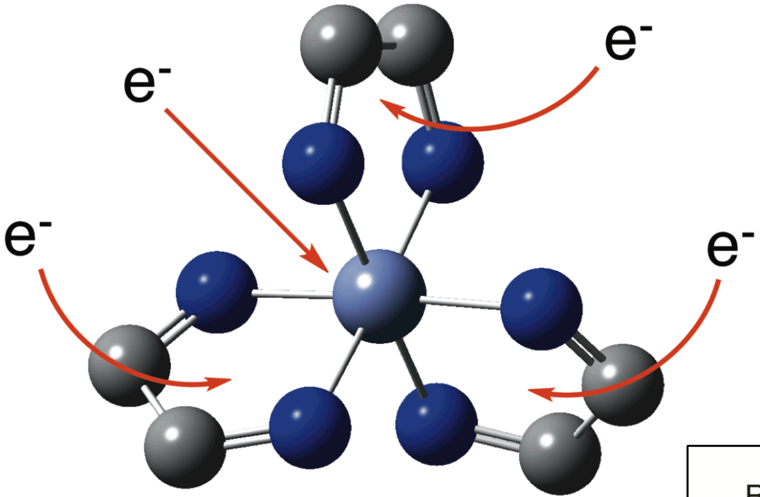
Hidden Potential of Ligands

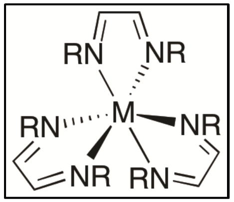
Current paradigm of metal-based electrolytes uses metal as “redox center”

- Metal and Ligands can be isolated *electronically*
  - ***stabilizes highly reduced and oxidized species***
  - ***multi-electron redox events possible***



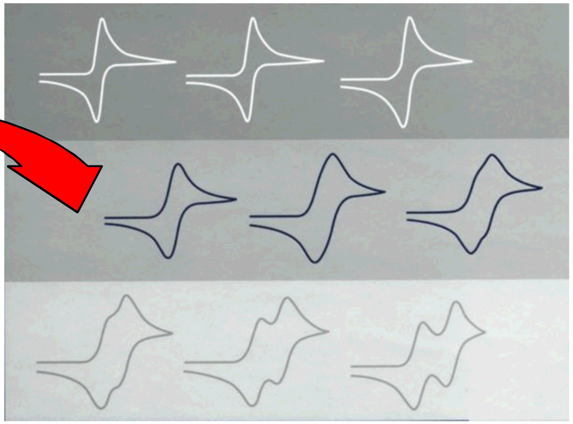


Depiction of Redox Activity with α–Diimine Complex



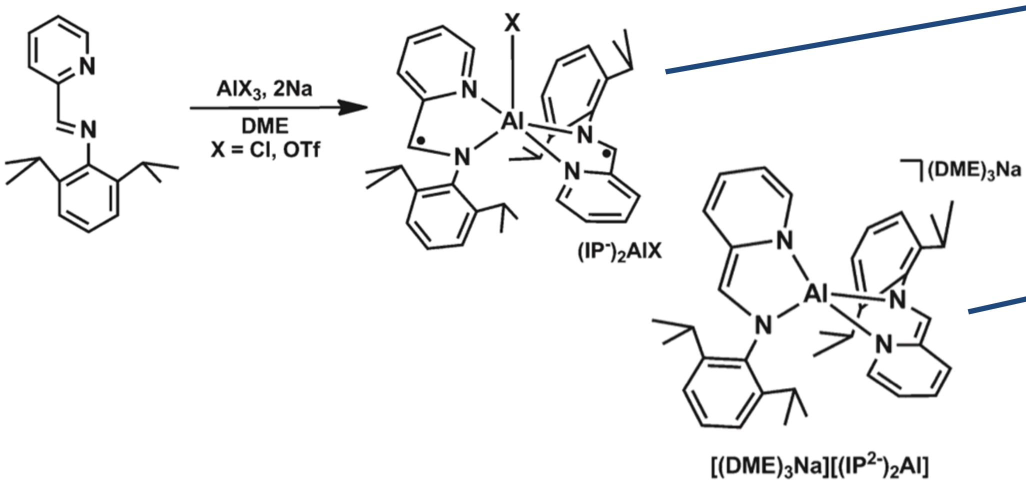
From Potential to Actual

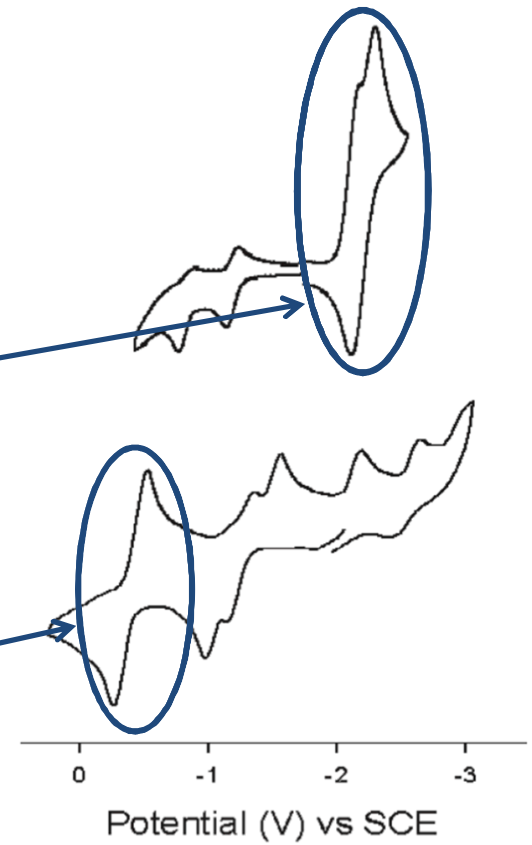
Two major goals:
- single potential, multielectron redox events
- increased cycling performance (long-term stability)



Our strategy: use main group and 1st row transition elements as the central atom and diimines and related imino functionalities for ligand architecture

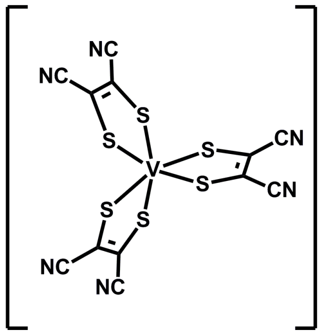
- Main group elements have less electronic orbital overlap with ligands, more efficiently isolating them from one another
- Imines are versatile and widely available; electronic structure is amenable to redox non-innocence

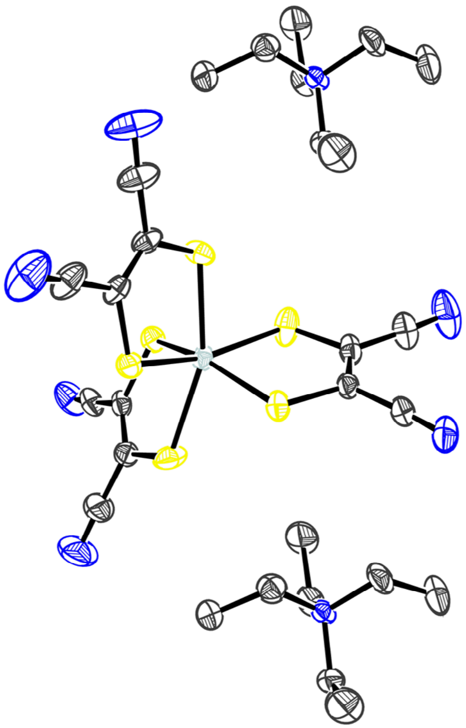


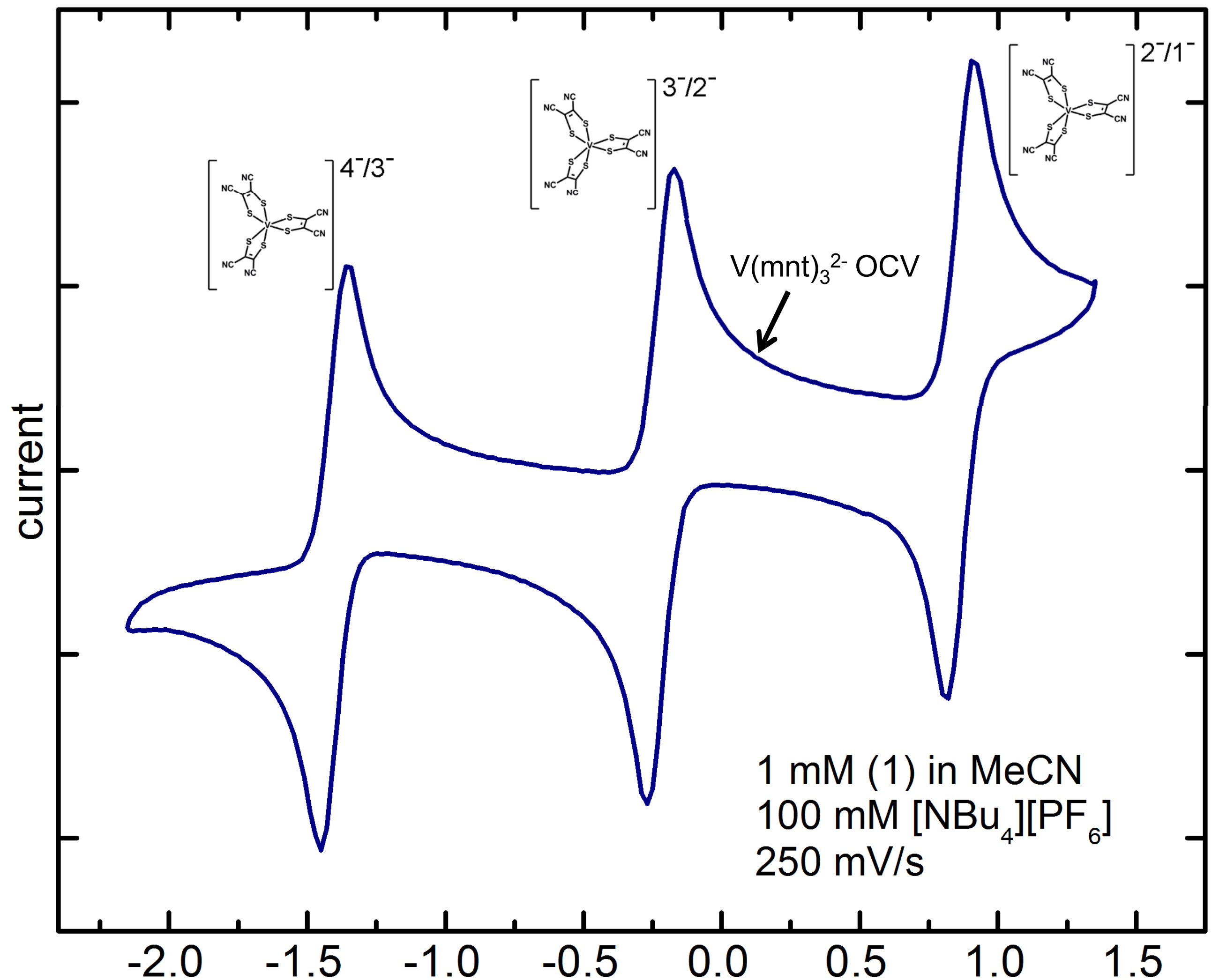


Myers, T. W.; Kazem, N.; Stoll, S.; Britt, R. D.; Shanmugam, M.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 8662–8672.
Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 11865–11867.

Electrochemistry of $V(mnt)_3^{2-}$





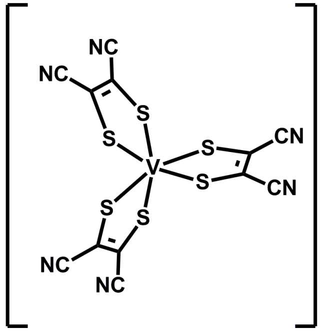


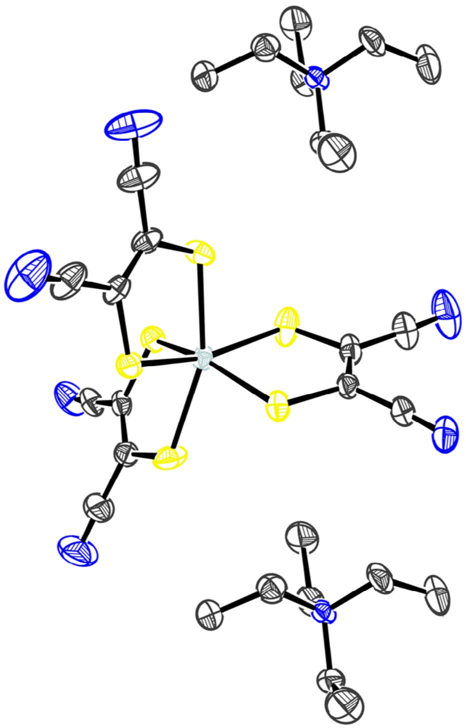
Maximum Concentration is 0.90 M in CH_3CN

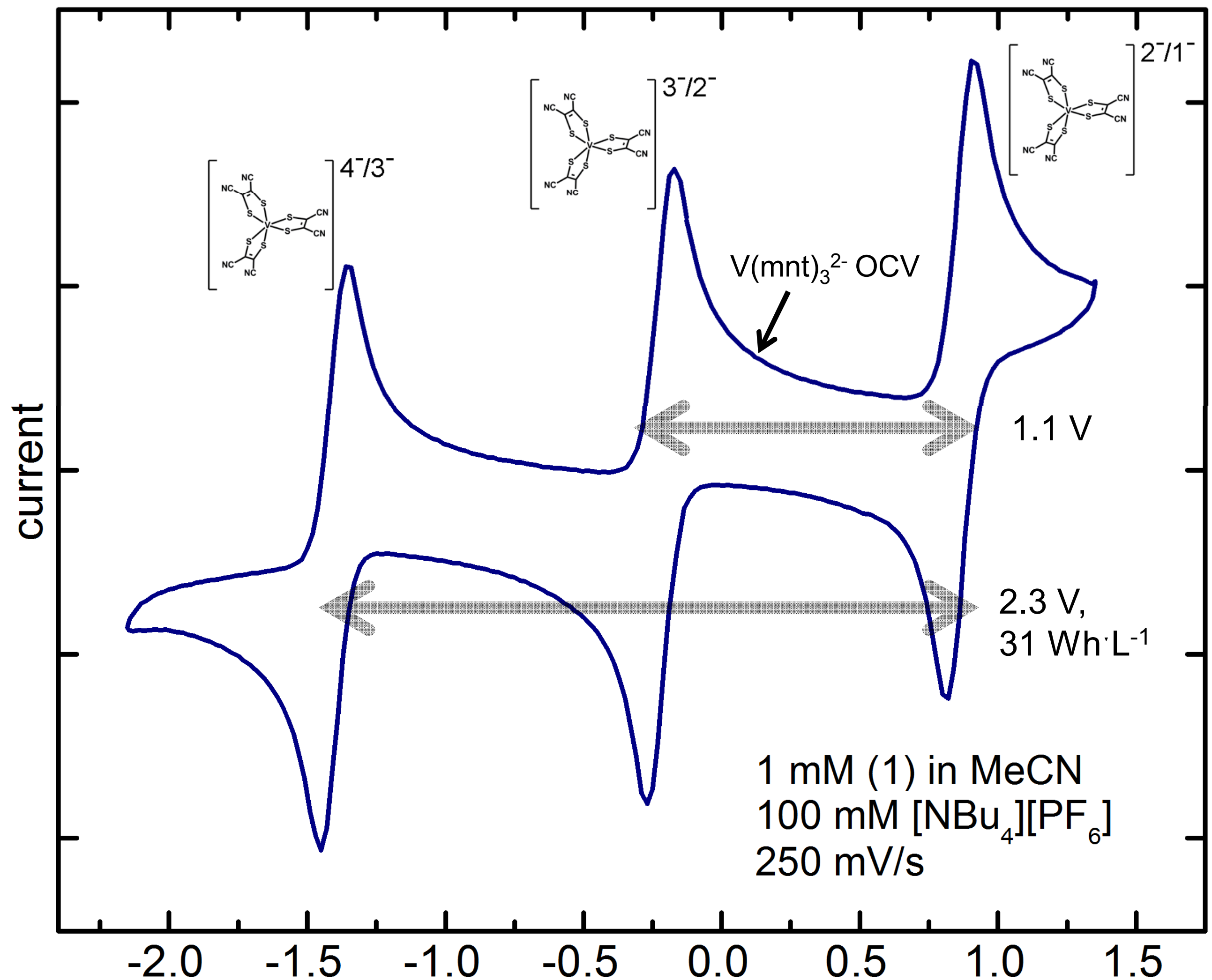
mnt = maleonitriledithiolate

Sproules, S., *et al.*, Inorg. Chem. **2010** , *49* , 5241

Electrochemistry of $V(mnt)_3^{2-}$







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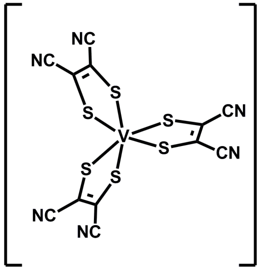
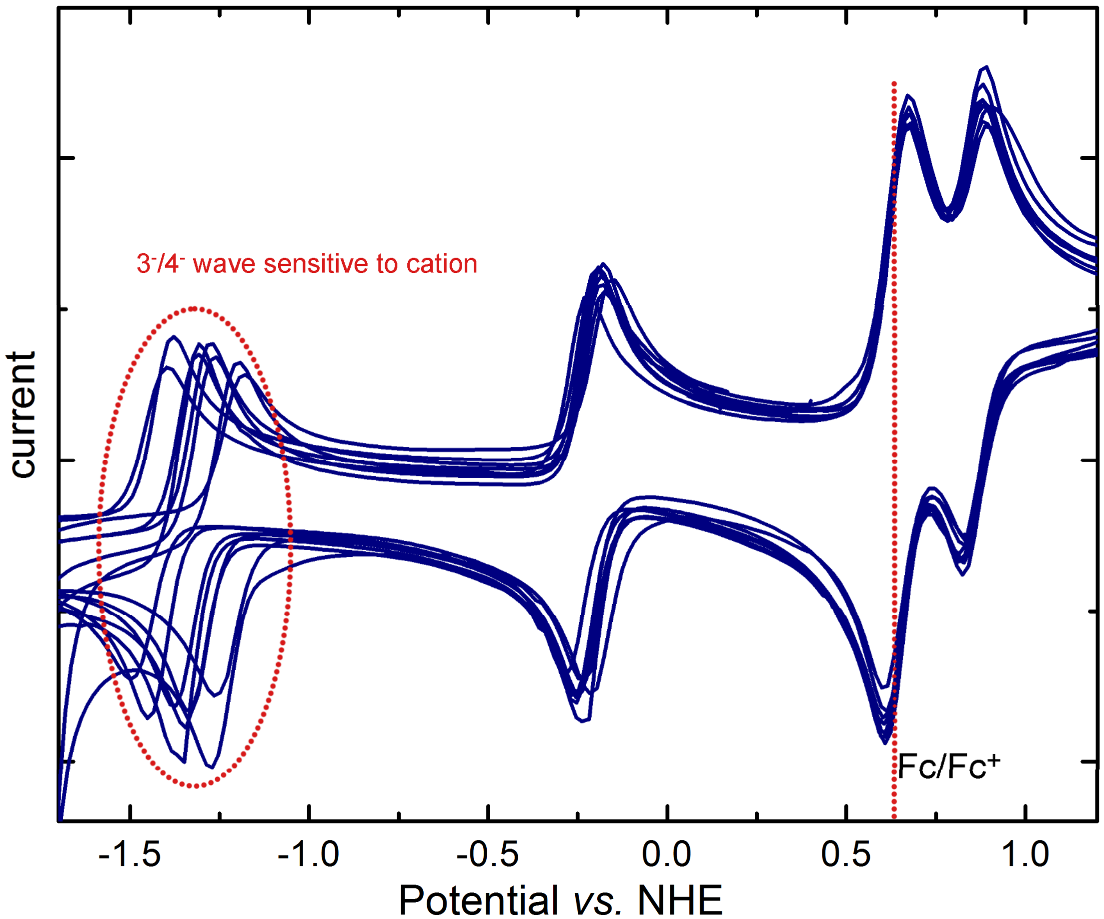
Potential *vs.* NHE

mnt = maleonitriledithiolate

Sproules, S., *et al.*, Inorg. Chem. **2010** , *49* , 5241

Effects of Ion-Pairing





- Hindered or “bulky” cations cannot ion-pair with anionic complex efficiently, resulting in more negative reduction potential
- A method to take full advantage of entire solvent window; increasing voltage of cell without chemical augmentation

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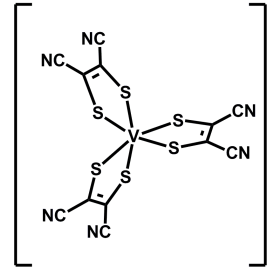

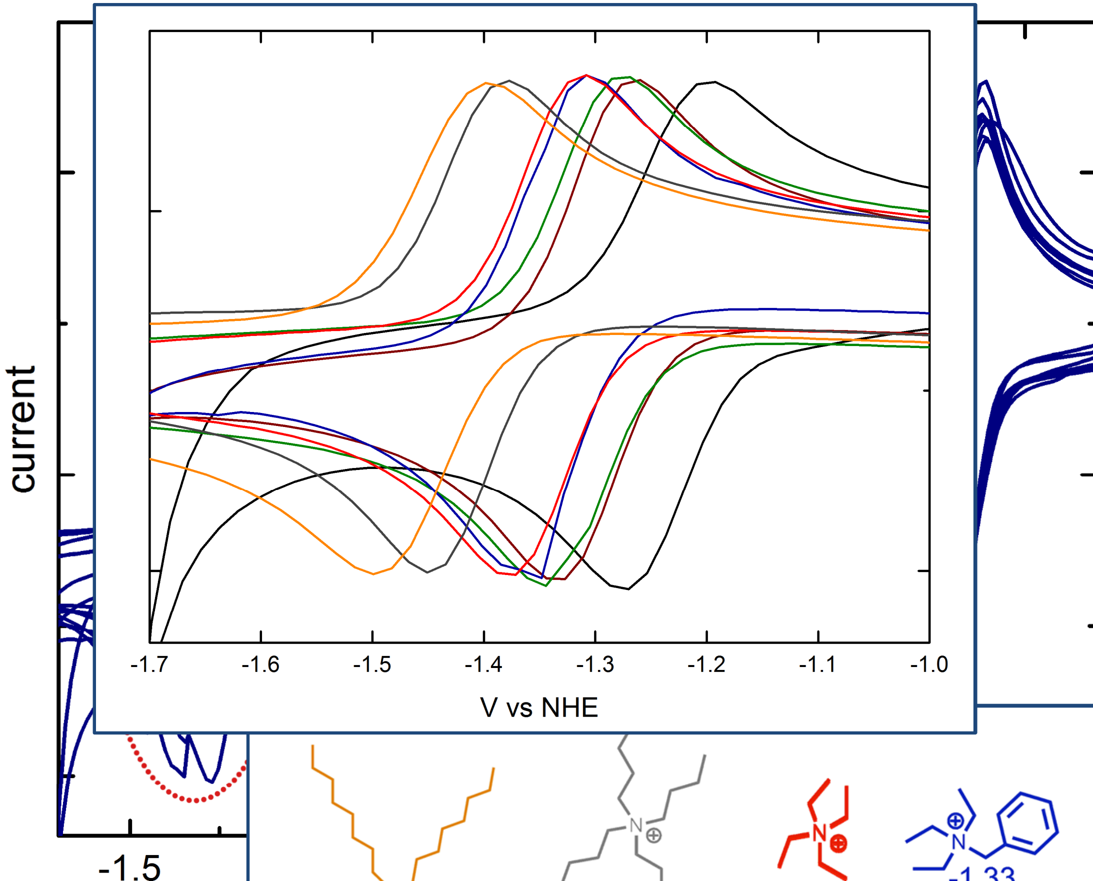

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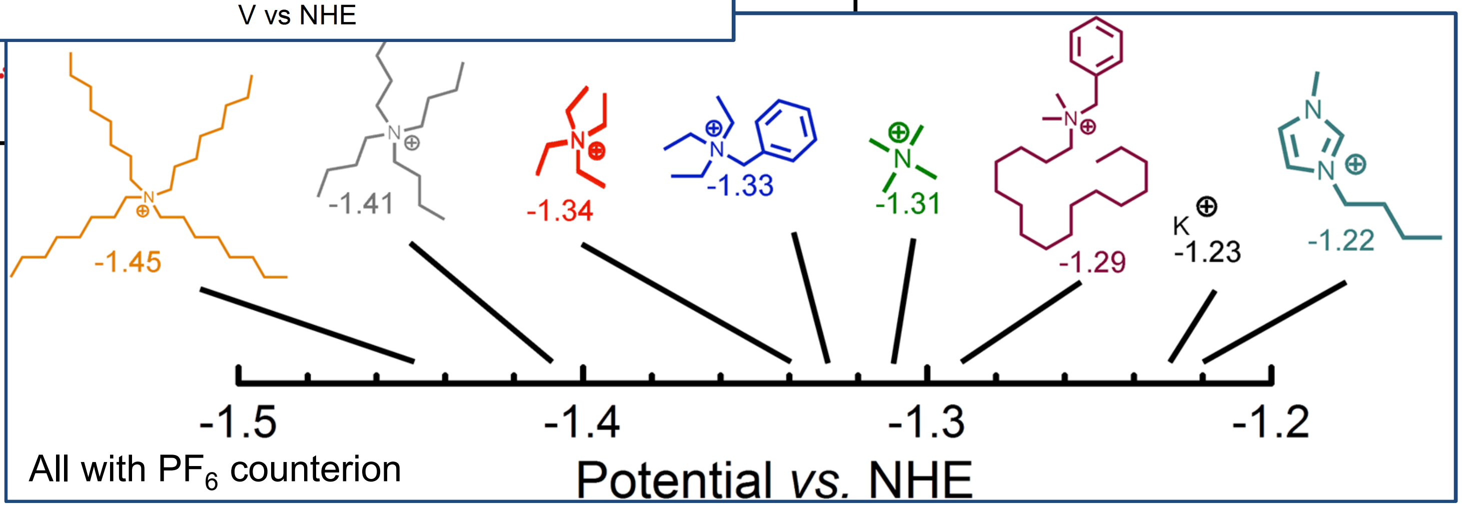
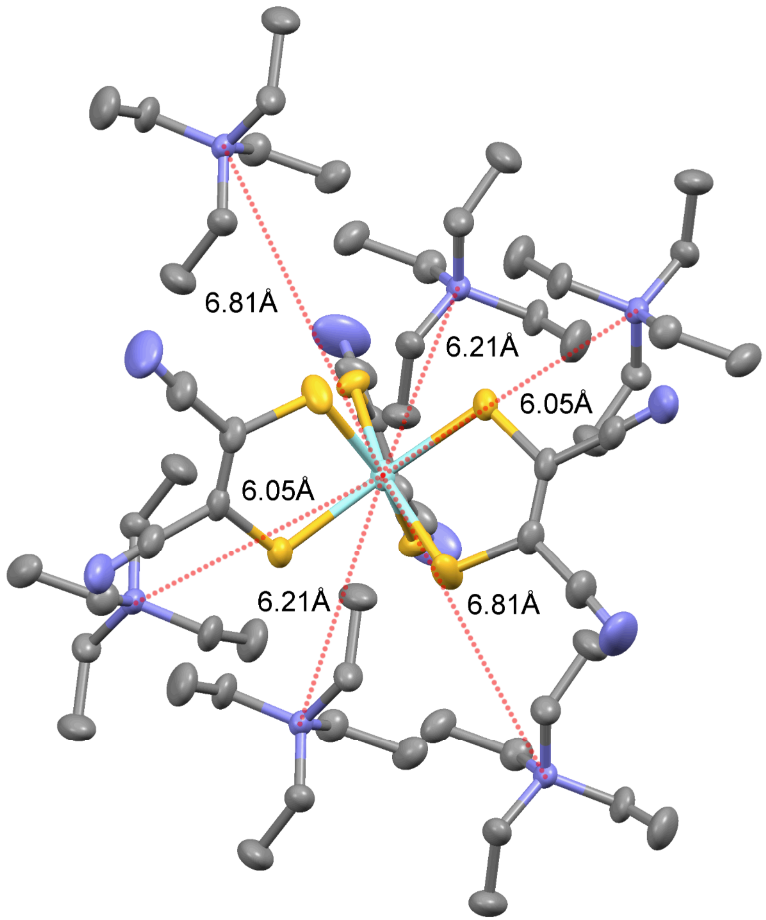
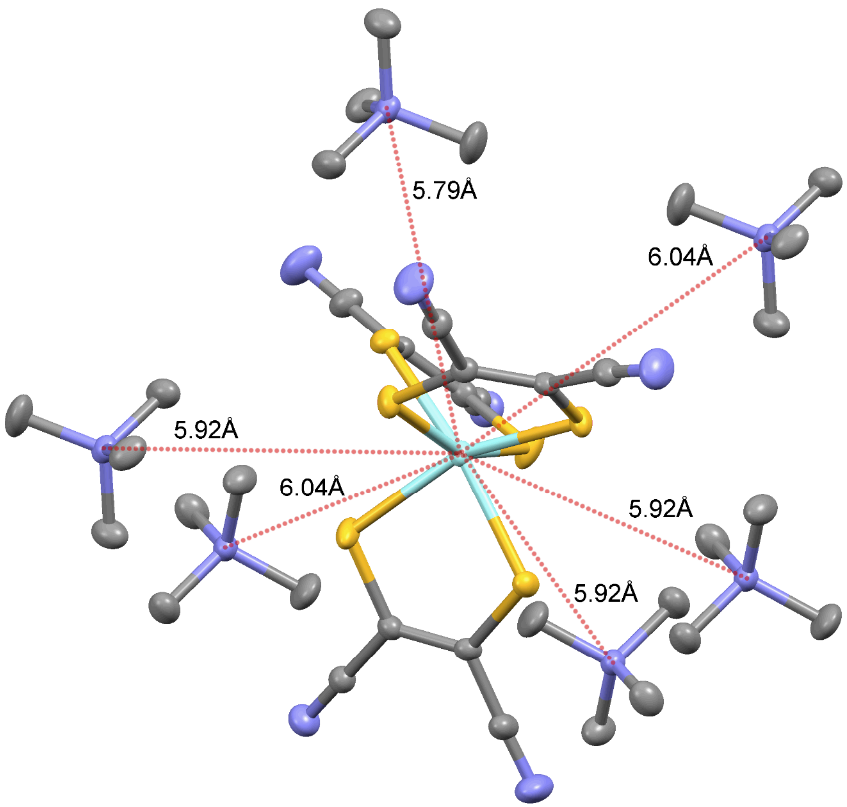


Solid-State Ion-Pairing

- Single-Crystal X-Ray Diffraction analysis shows that there is a significant difference in the ion-pairing between the NR_4^+ and $V(mnt)_3^{2-}$ (6 nearest cations)

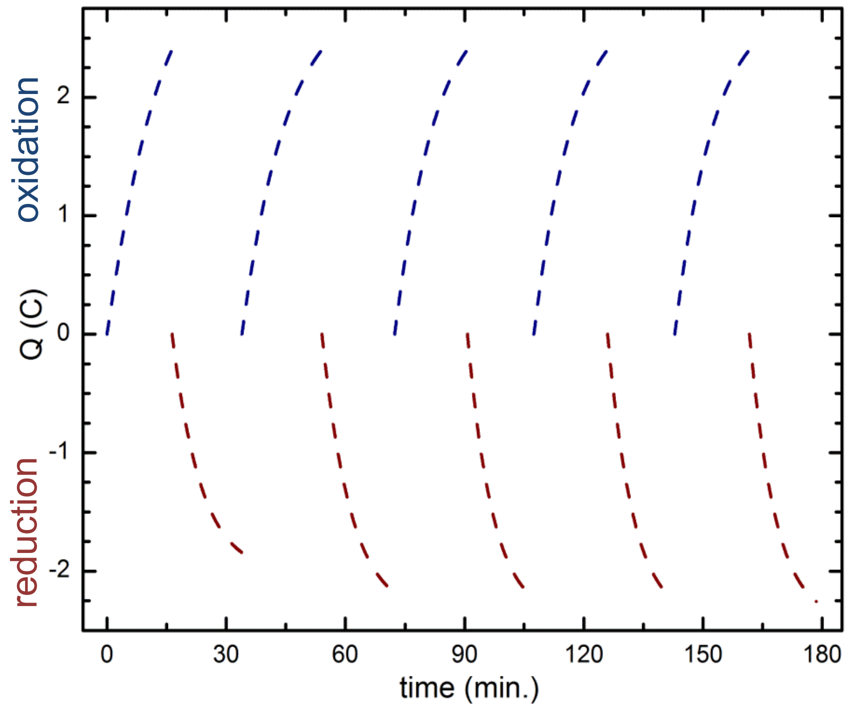


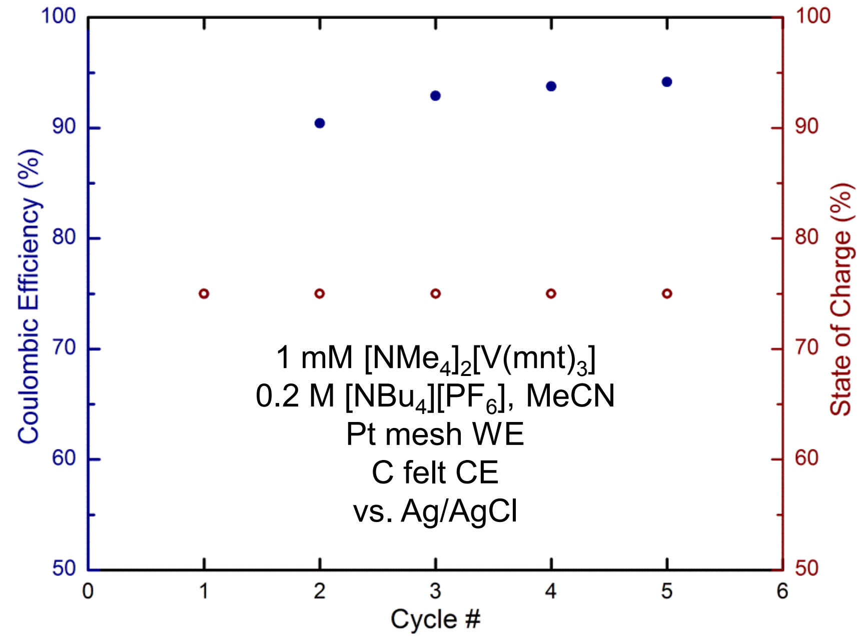


Avg. N-V distance: 6.4 Å

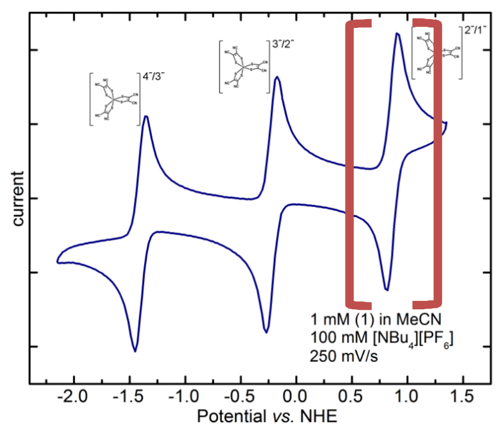
5.9 Å

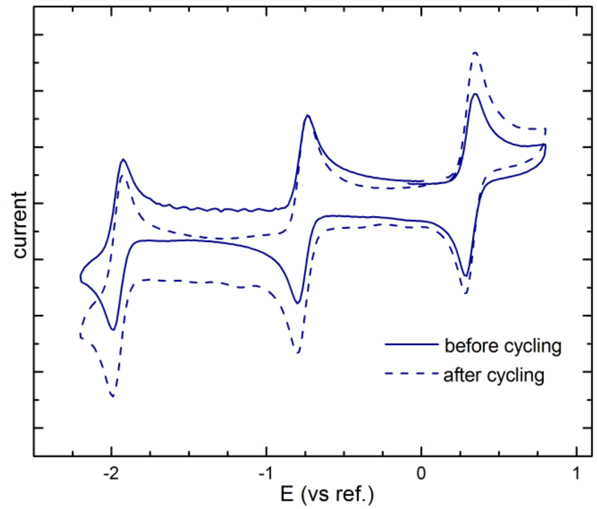
Half Cell Reaction ($V(mnt)_3^{2-} \leftrightarrow V(mnt)_3^{1-}$)



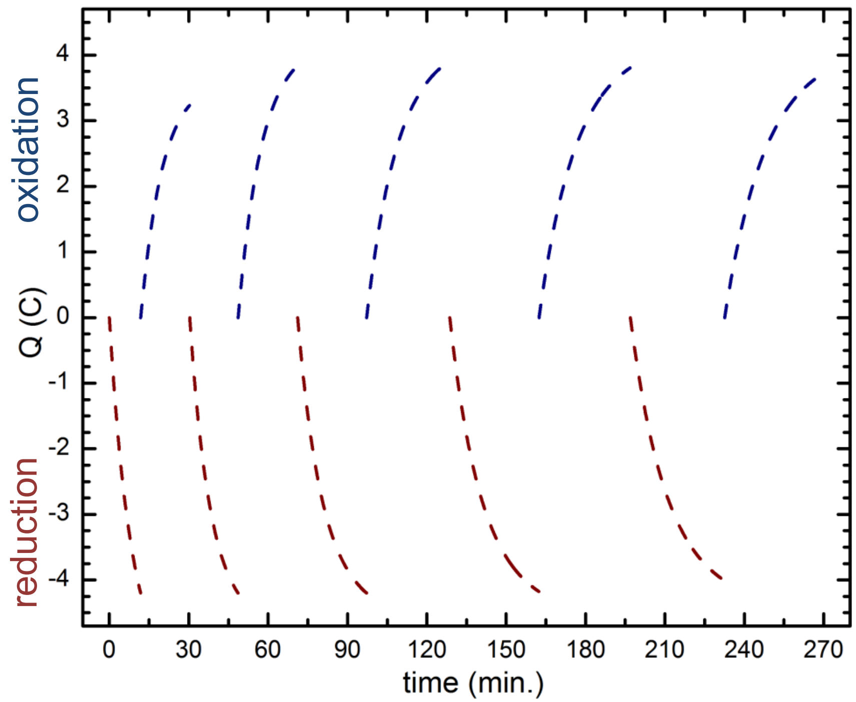


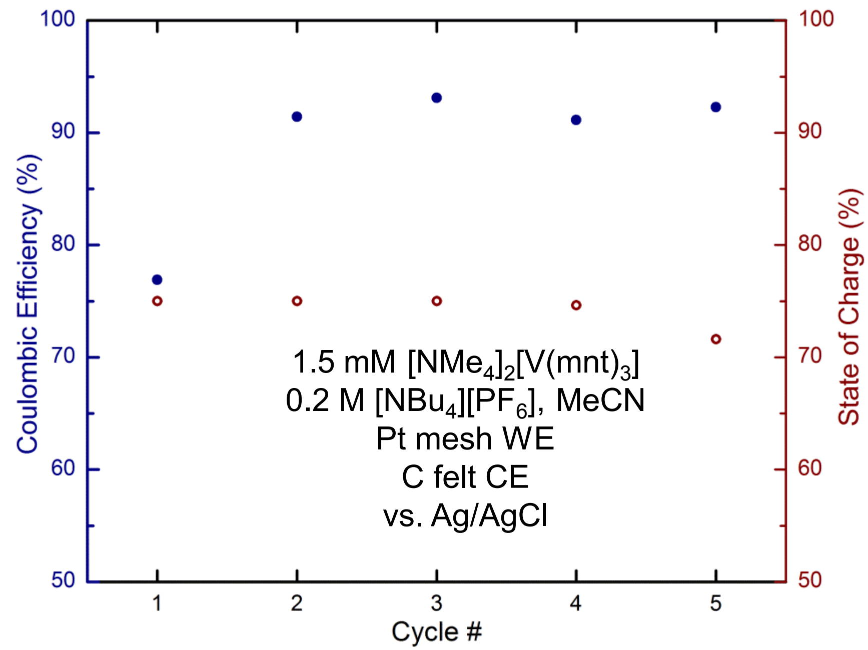
- E_{WE} = 0.5 V, bulk oxidation
- E_{WE} = -0.5 V, bulk reduction
- 75% SOC, 5 cycles
- Approaches 95% CE
- No decomposition observed



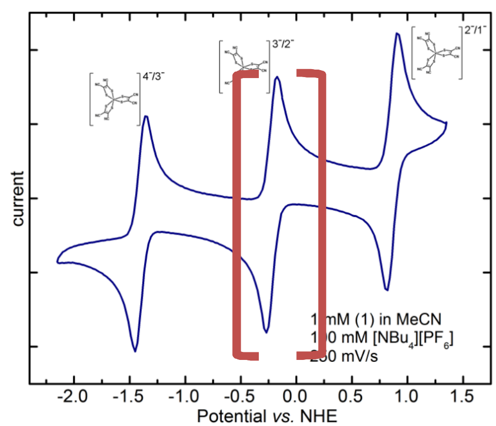


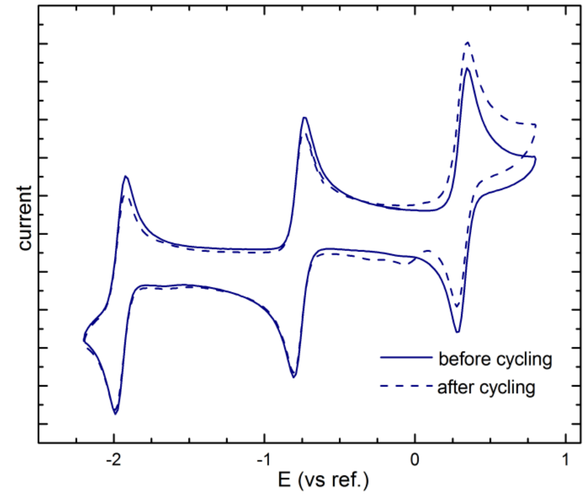
Half Cell Reaction ($V(mnt)_3^{3-} \leftrightarrow V(mnt)_3^{2-}$)



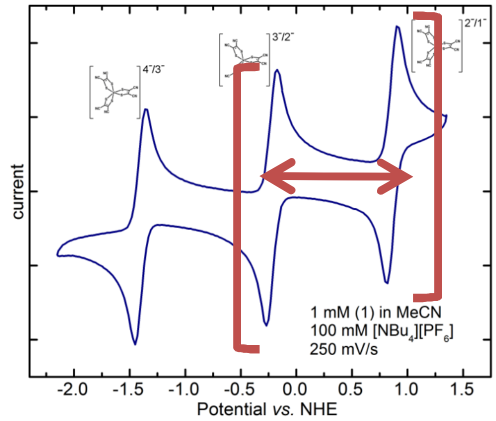


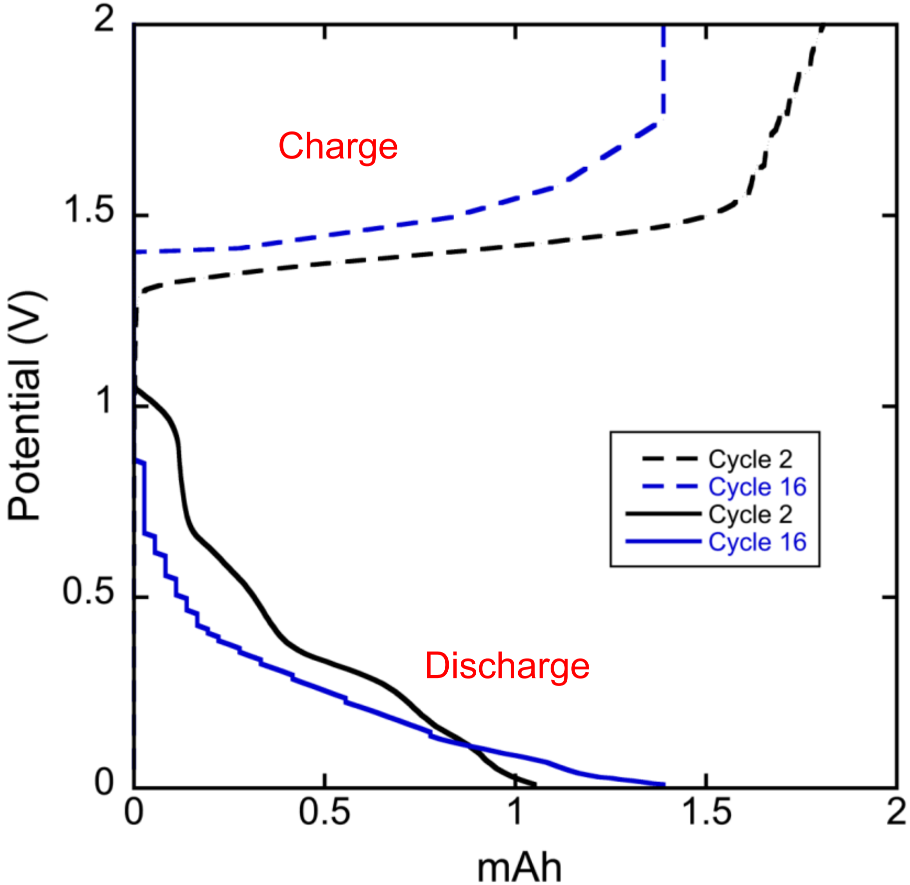
- E_{WE} = -1.2 V, bulk reduction
- E_{WE} = -0.2 V, bulk oxidation
- 75% SOC, 5 cycles
- >90% CE
- No decomposition observed





Poor Initial Results from Static Cell Testing

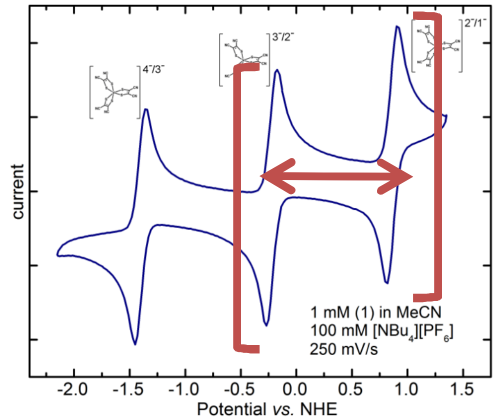




- What is the origin of the gradual drop in discharge potential?
  - Decomposition of $V(mnt)_3$
  - Membrane crossover
  - Inefficient cell design
  - Electrode degradation

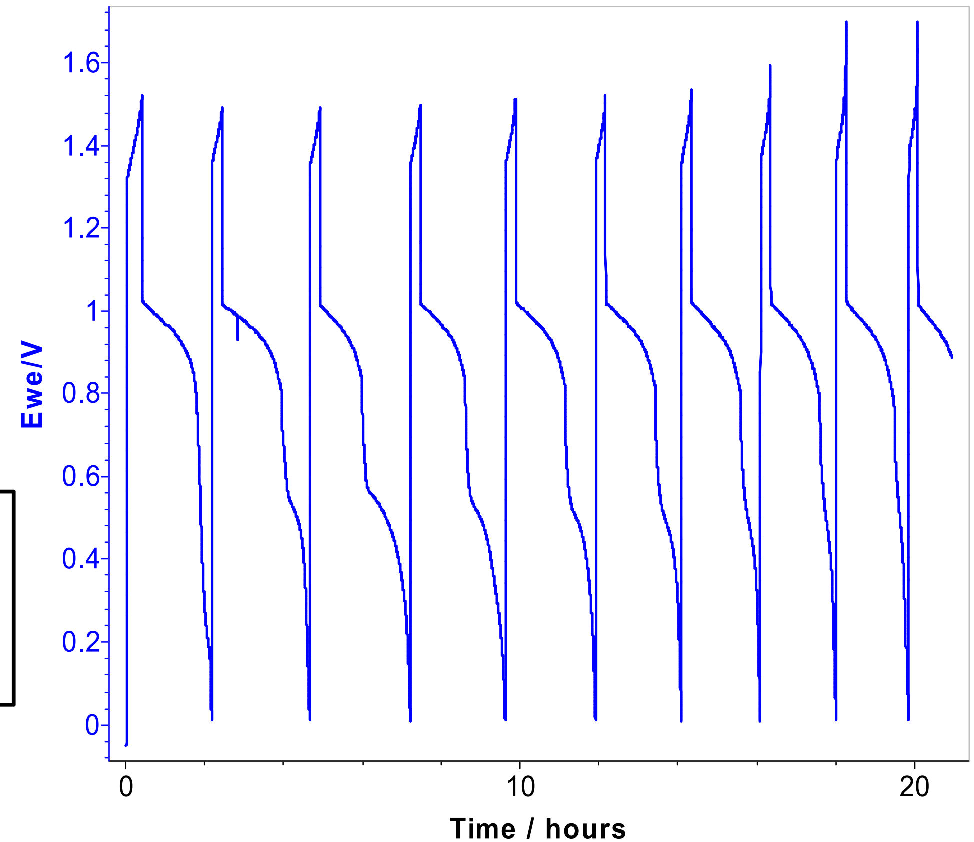
H-cell conditions:
- graphite electrodes ($1 cm^2$)
- microporous separator (Tonen)
- NBu_4PF_6 in MeCN
- 20 mM electrolyte

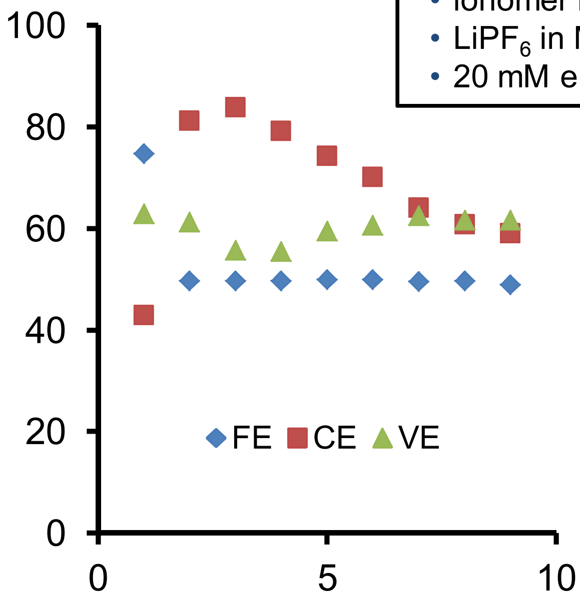
A Change to Li^+



H-cell conditions:

- graphite electrodes ($1 cm^2$)
- ionomer membrane (CEM)
- $LiPF_6$ in MeCN
- 20 mM electrolyte





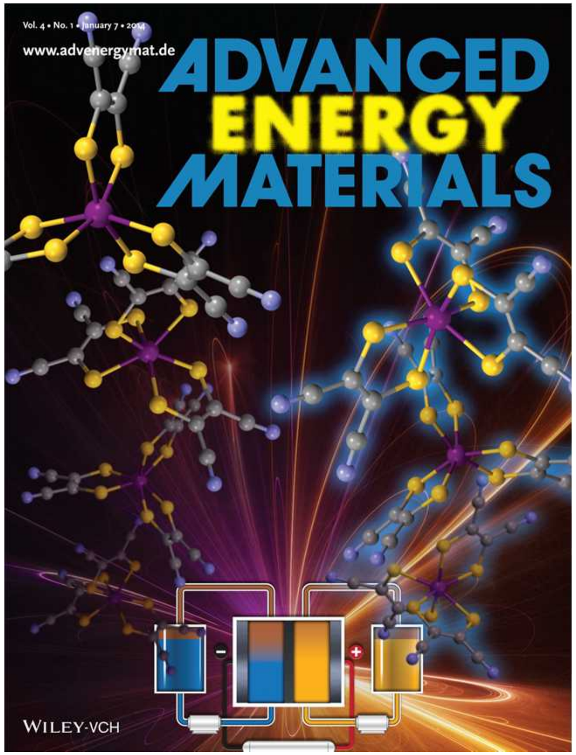
Charged to 75%, discharged to 25% (cycling the middle 50% of total capacity)

Efficiencies decreased slightly but the performance overall has been incredibly improved!

Proof of Concept Complete

- Published results earlier this year in *Advanced Energy Materials*, cover of issue as well
- Invited talks at MRS Fall 2013 and 2014, 1st International Symposium on Energy Challenges and Mechanics in Scotland (July 2014)

- External collaborations with Washington University, University of Pennsylvania



Cover of Jan. 1 issue of Adv. Energy Mater.

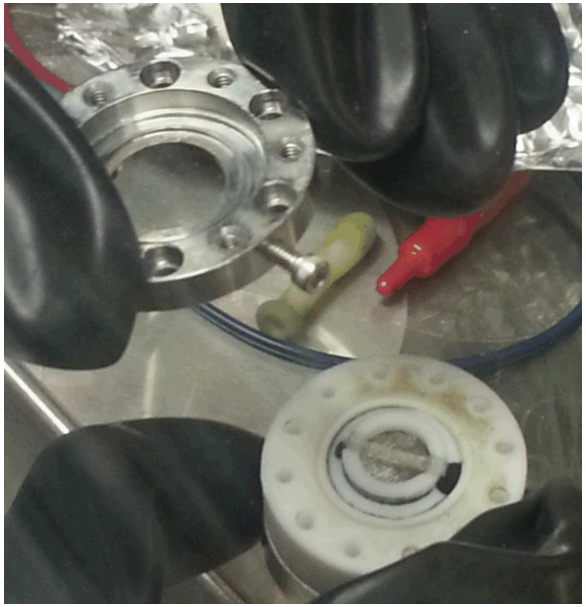
Analytical Techniques for Monitoring

- Our slow initial progress caused us to question our methods for analytical monitoring
- We want methods for *in situ* monitoring state of charge (SOC), electrolyte identity/concentration, decomposition

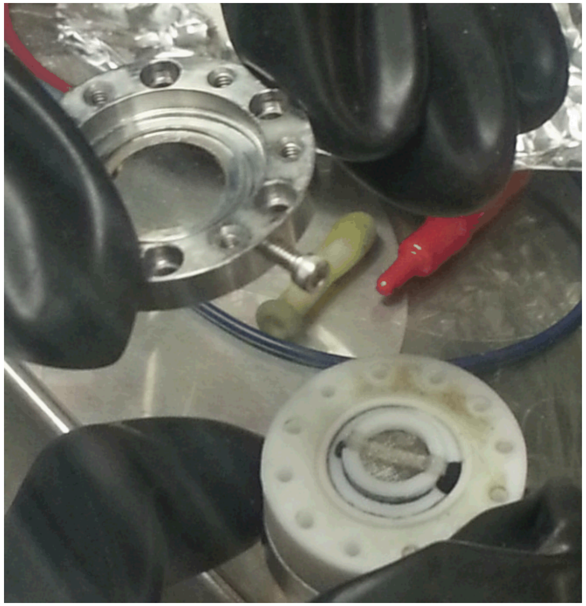
- OCV (Nernst Equation) doesn't work if cell becomes imbalanced; each half-cell's potentials should be monitored but this can be very difficult
- Conductivity, UV-Vis, and IR have all been proposed as alternatives but no real chemical information is learned and concentrations have to be kept low

Raman is a very good method!

- Higher the concentration, the better the measurement
- Peaks are very responsive to changes in oxidation state
- Metal compounds are active in the UV/Vis region, can lead to resonance enhancement of Raman (specific enhancement over solvent or supporting electrolyte!)

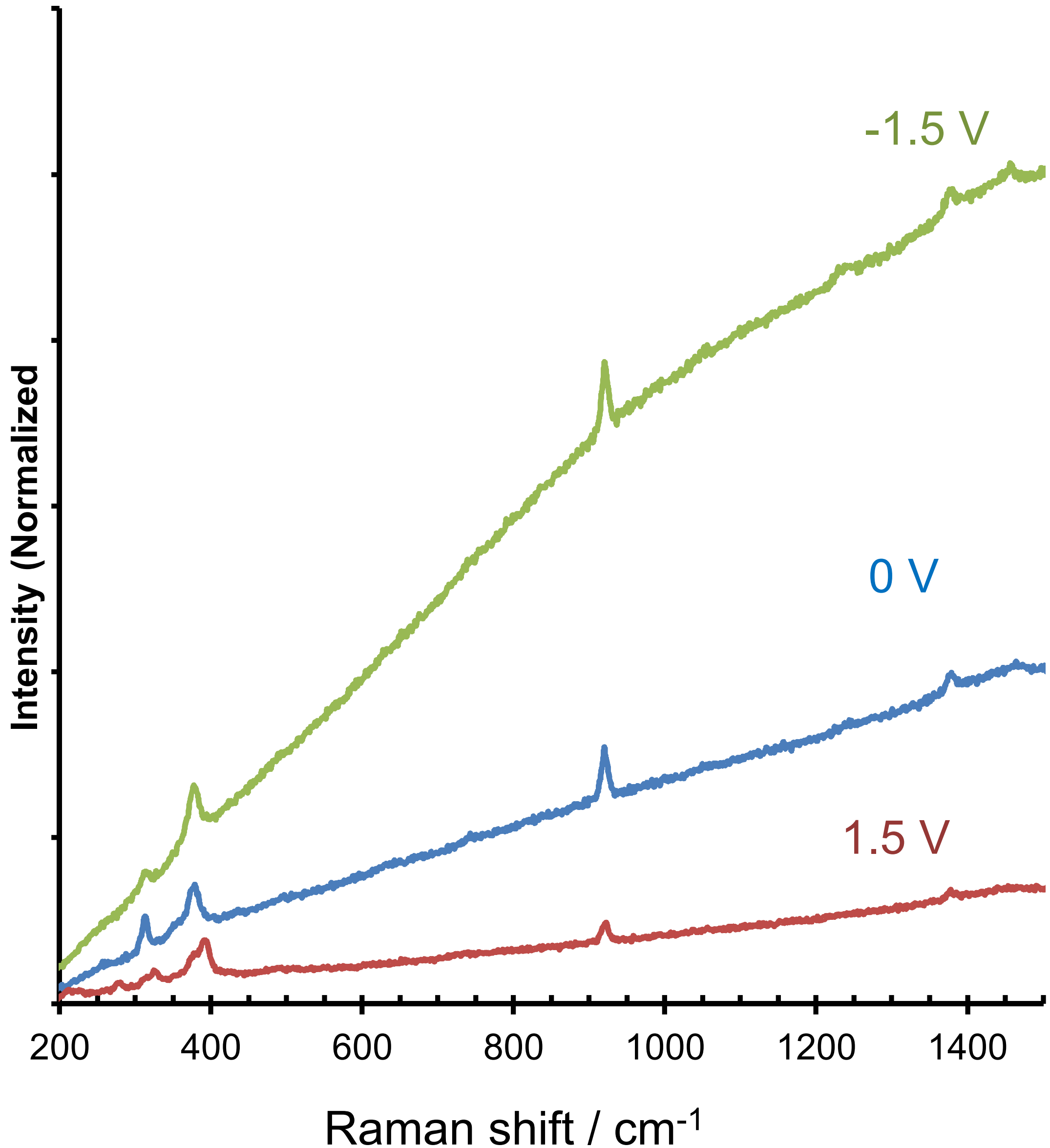


Raman Spectra Changes During Redox



Pt mesh counter
Pt mesh working
< 1mL volume

Cycled E to 1.5V
Back to 0
Cycled E to -1.5V



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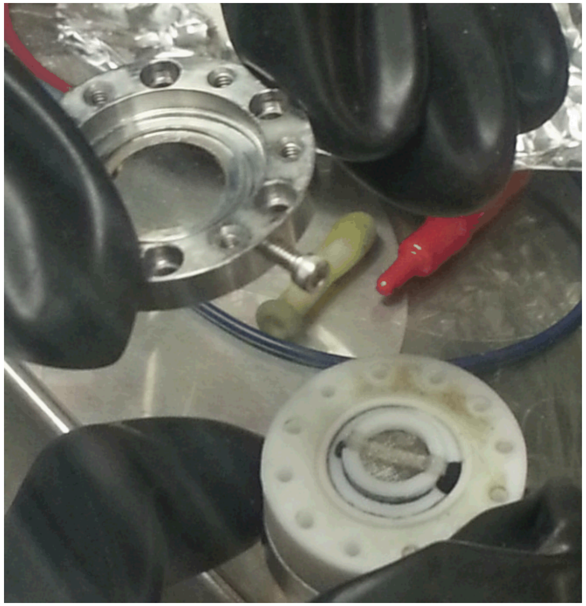

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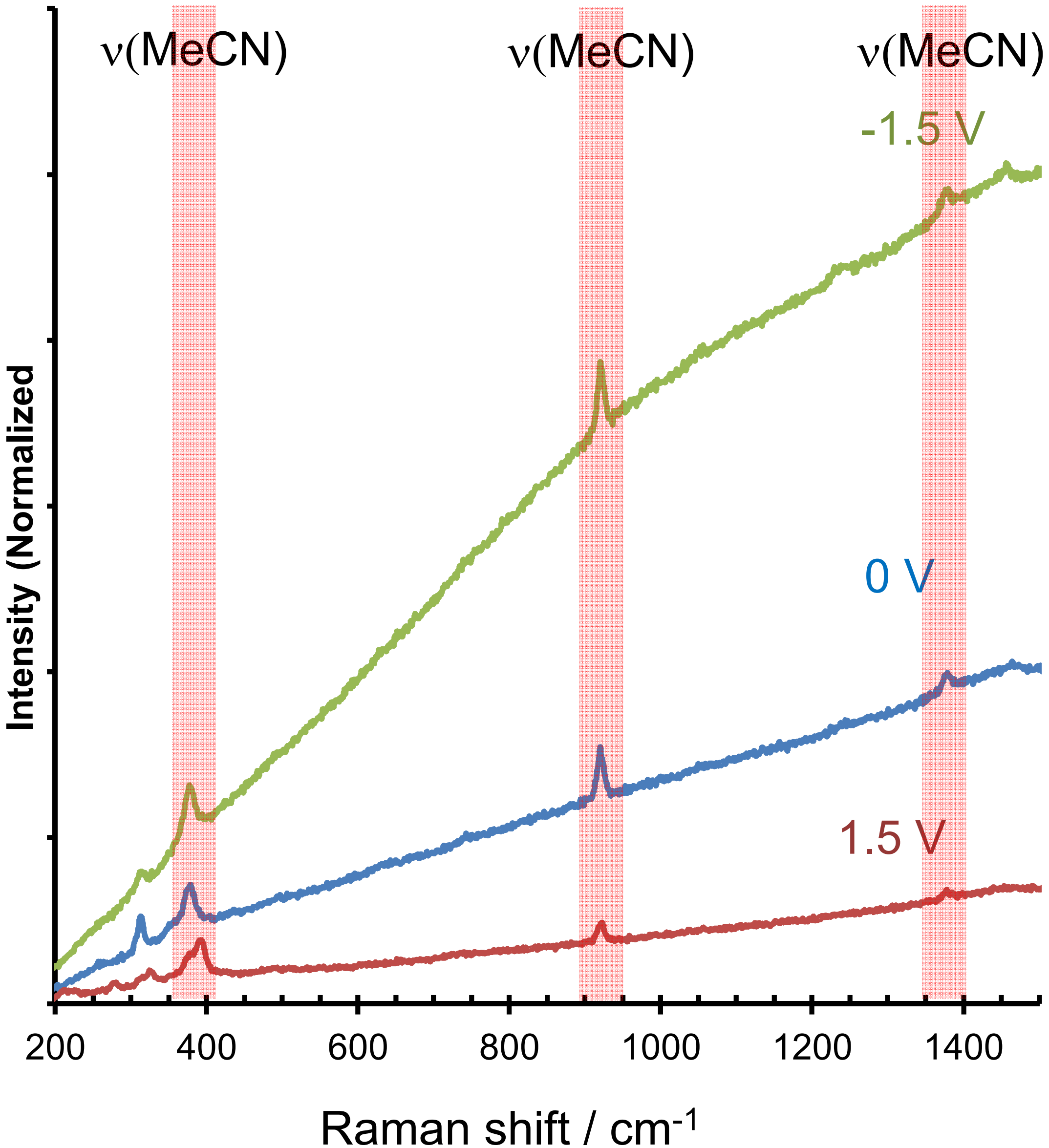

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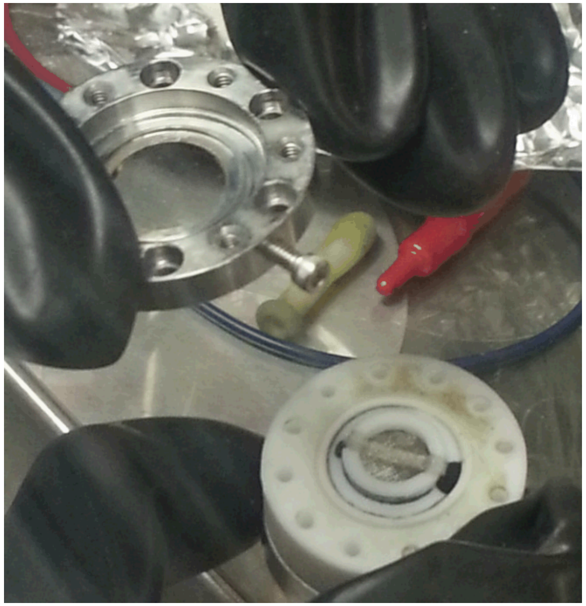

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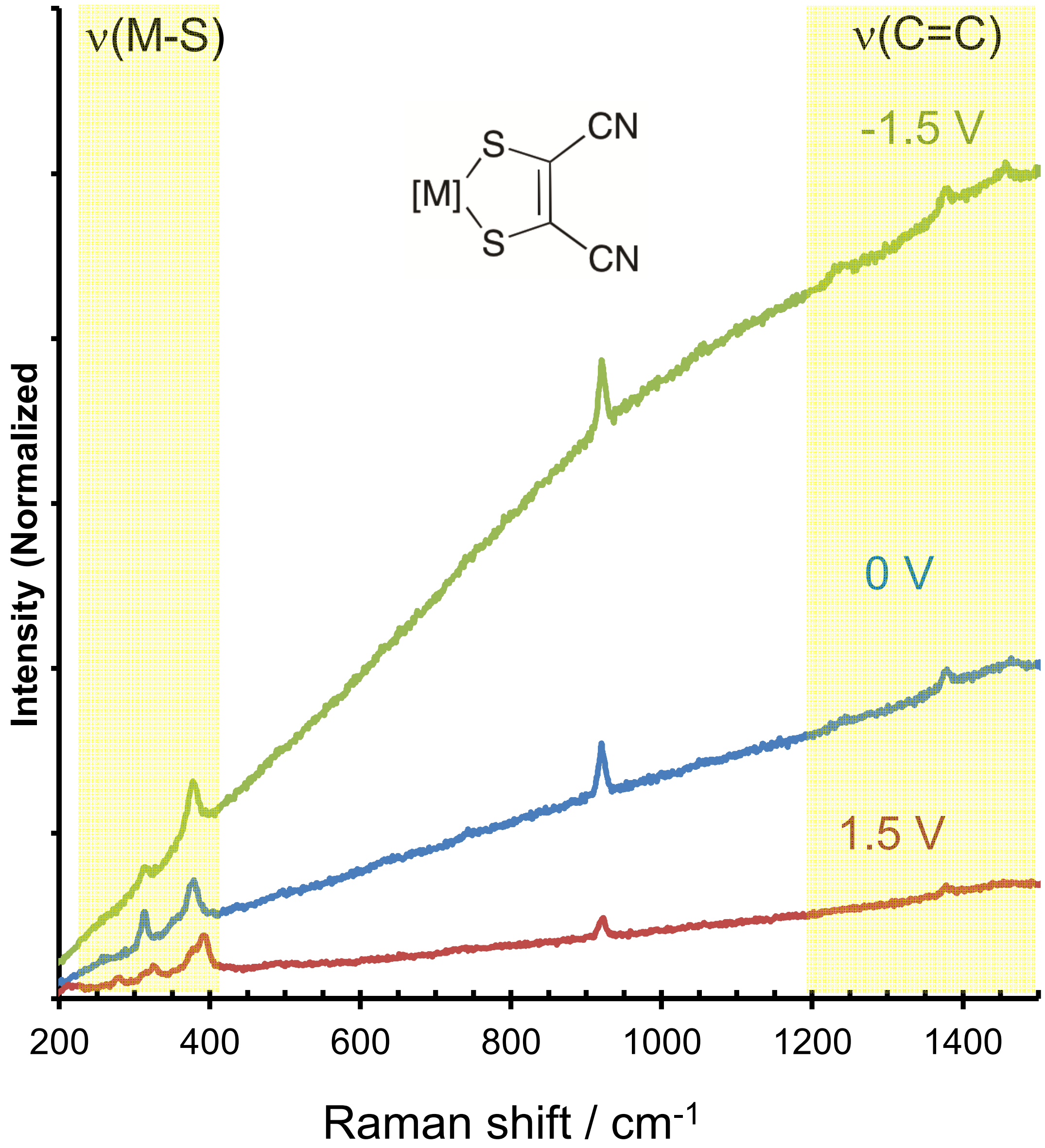

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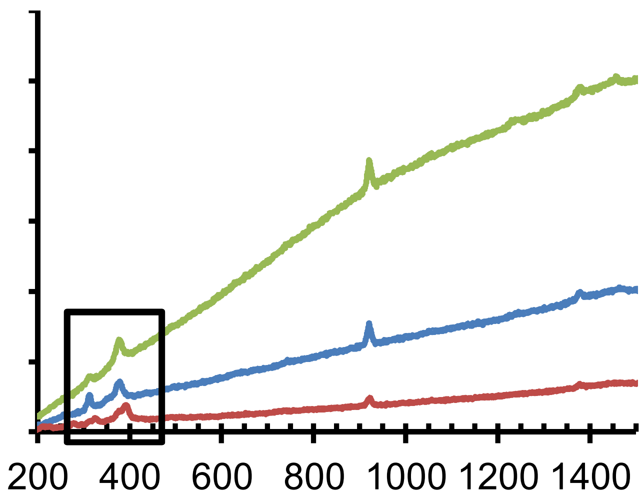
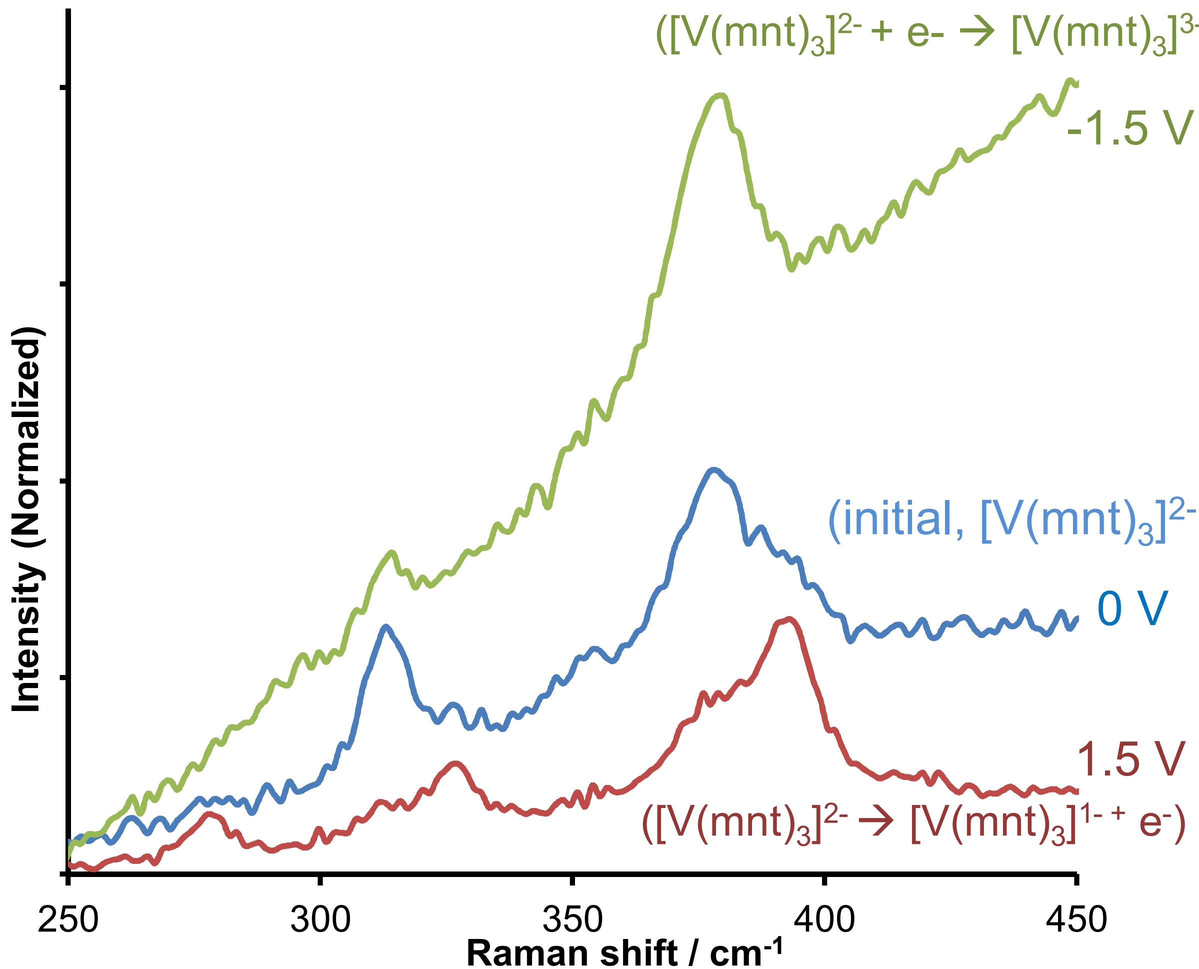
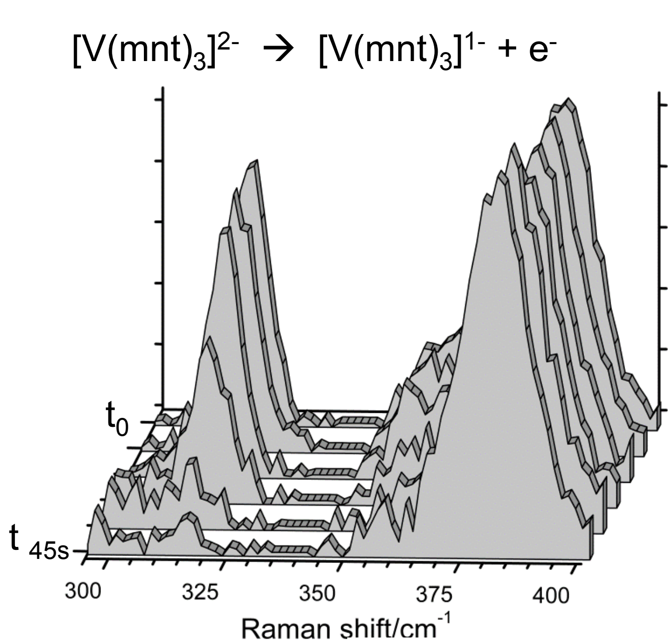
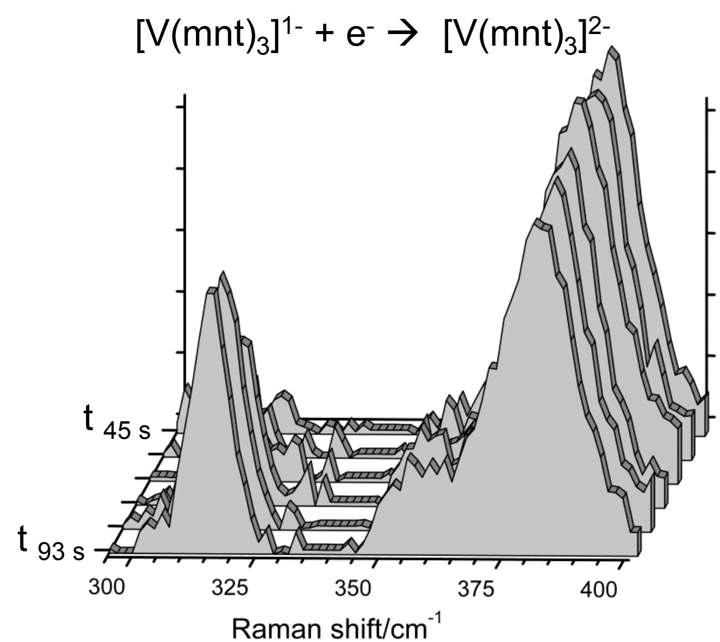
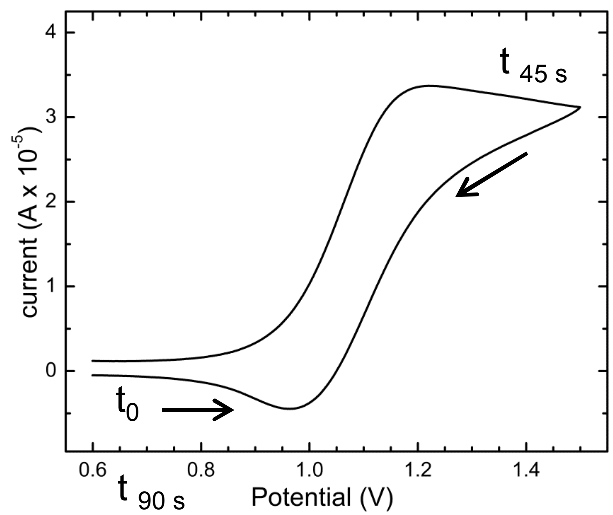




Cycling Between 2- and 1- Ox. States



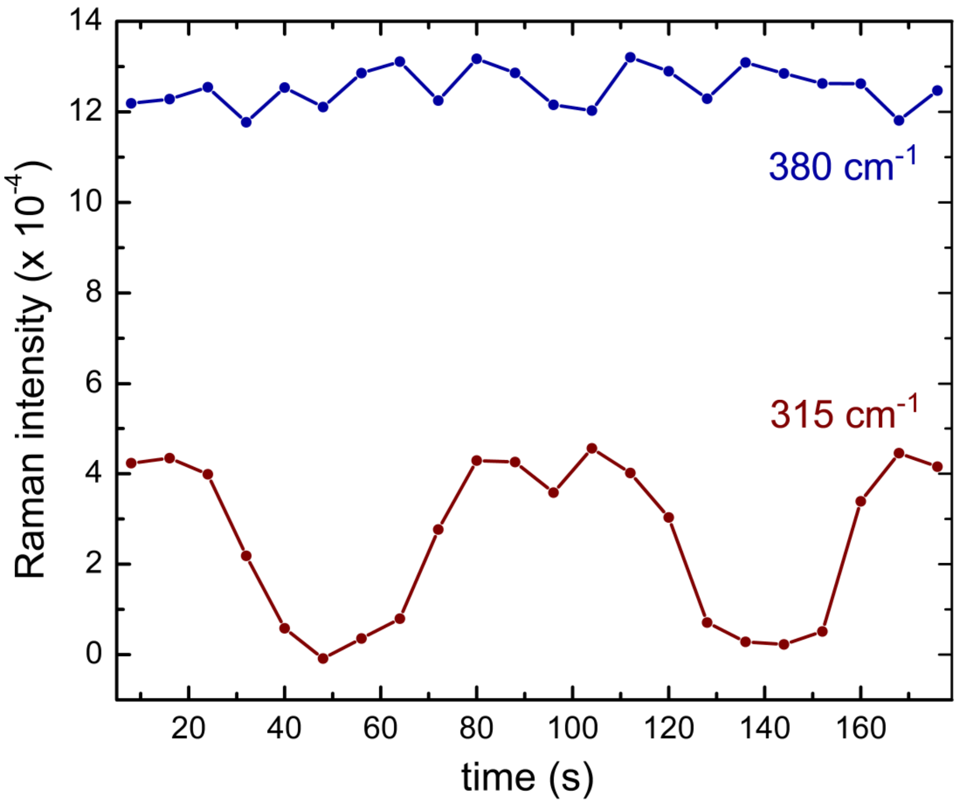




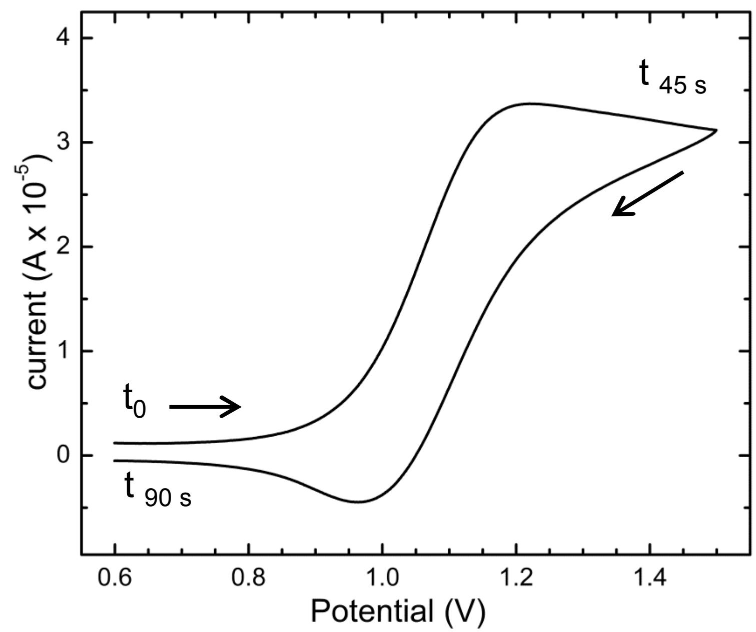
4 mM $[NMe_4][V(mnt)_3]$
0.2 M $[NBu_4][PF_6]$
MeCN
Pt wire WE/CE

20 mV/s scan rate

Cycling Between 2- and 1- Ox. States



Integrated area for regions from 296 to 334 cm^{-1} (315 cm^{-1}) and from 343 to 413 cm^{-1} (380cm^{-1}). The 22 spectra correspond to two complete CV cycles. Spectra were background corrected and integrated using CASAXPS.



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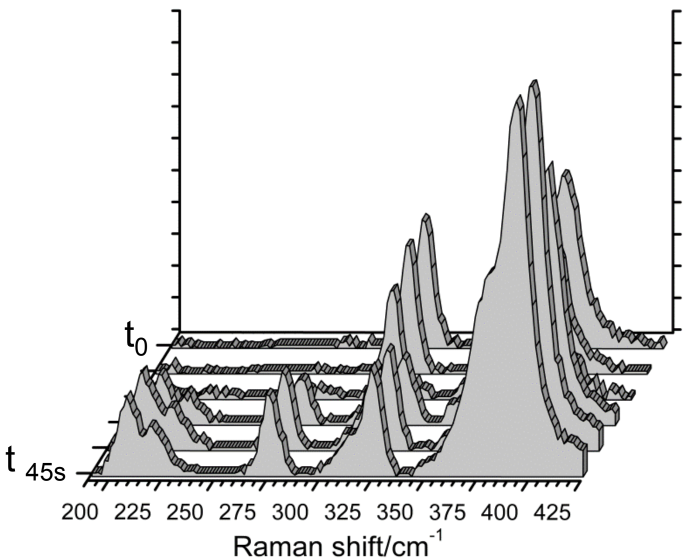
0.2 M $[NBu_4][PF_6]$
MeCN
Pt wire WE/CE

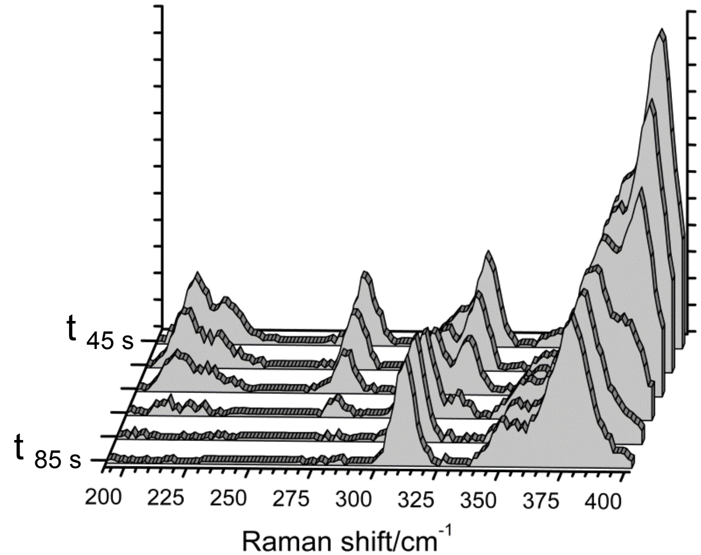
20 mV/s scan rate

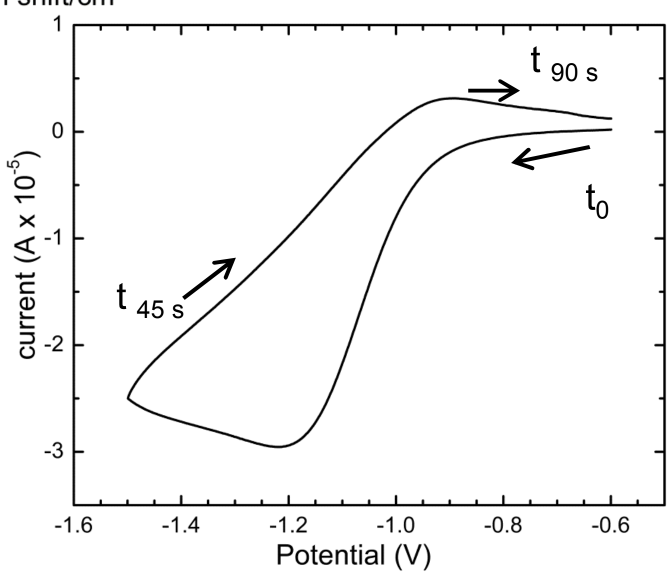
Cycling Between 2- and 3- Ox. States

$[V(mnt)_3]^{2-} + e^- \rightarrow [V(mnt)_3]^{3-}$



$[V(mnt)_3]^{3-} \rightarrow [V(mnt)_3]^{2-} + e^-$





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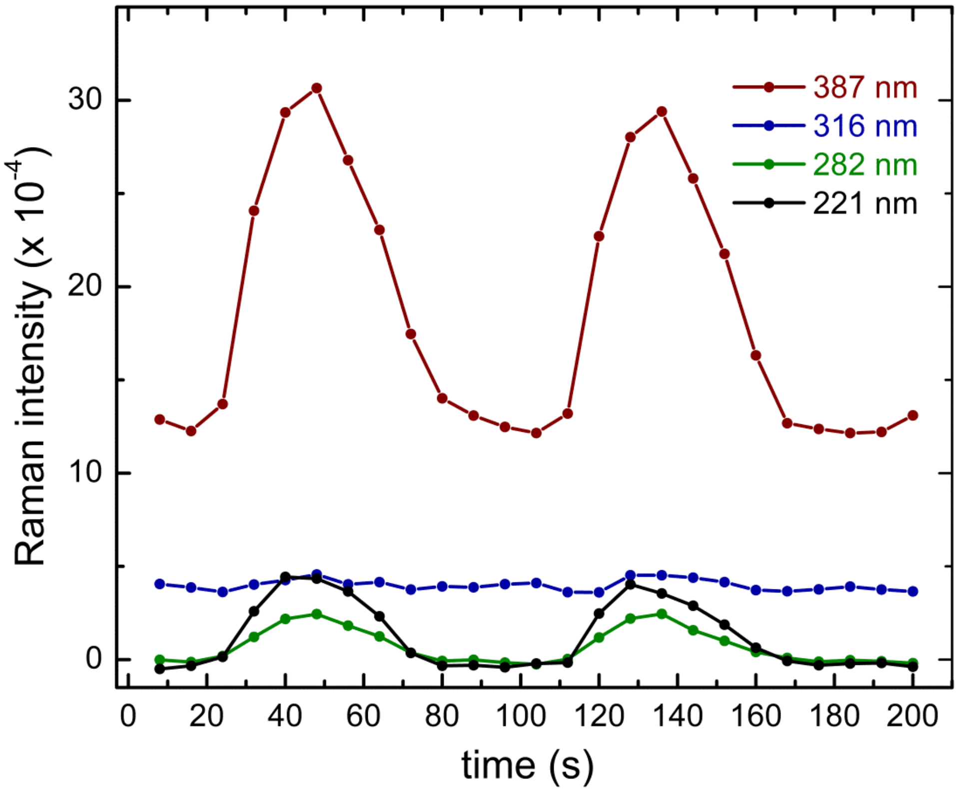
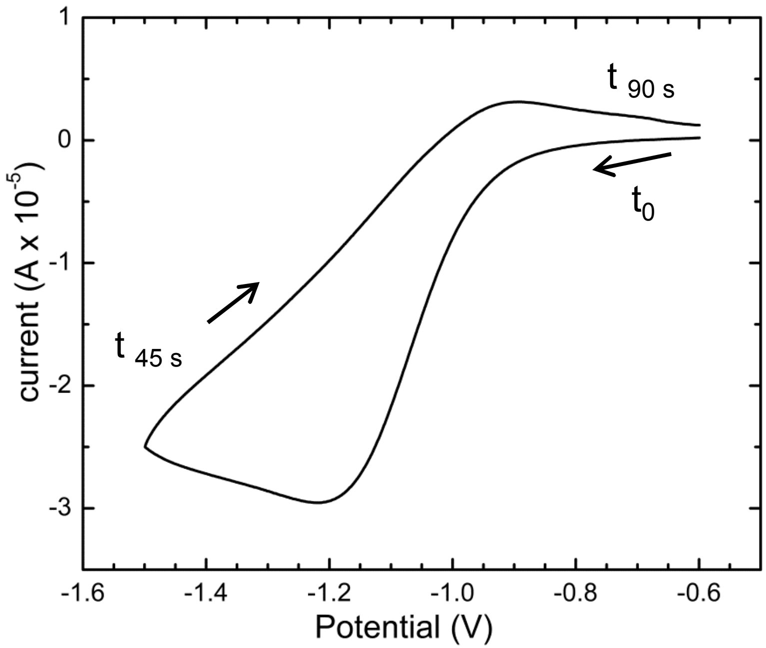
0.2 M $[NBu_4][PF_6]$
MeCN
Pt wire WE/CE

20 mV/s scan rate

Cycling Between 2- and 1- Ox. States





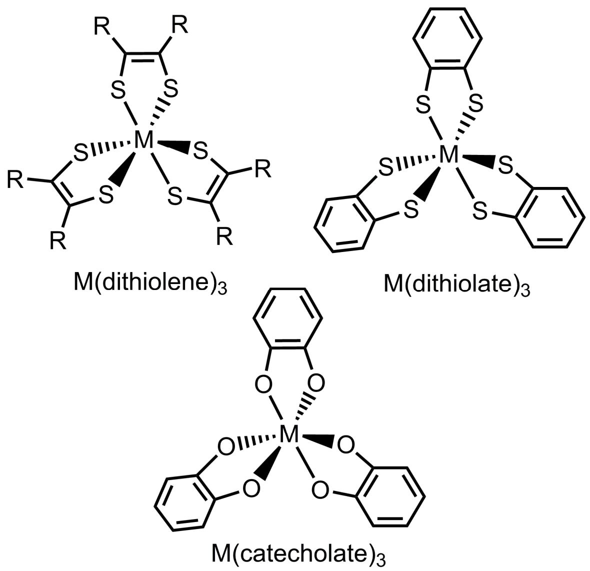
4 mM $[NMe_4][V(mnt)_3]$
0.2 M $[NBu_4][PF_6]$
MeCN
Pt wire WE/CE

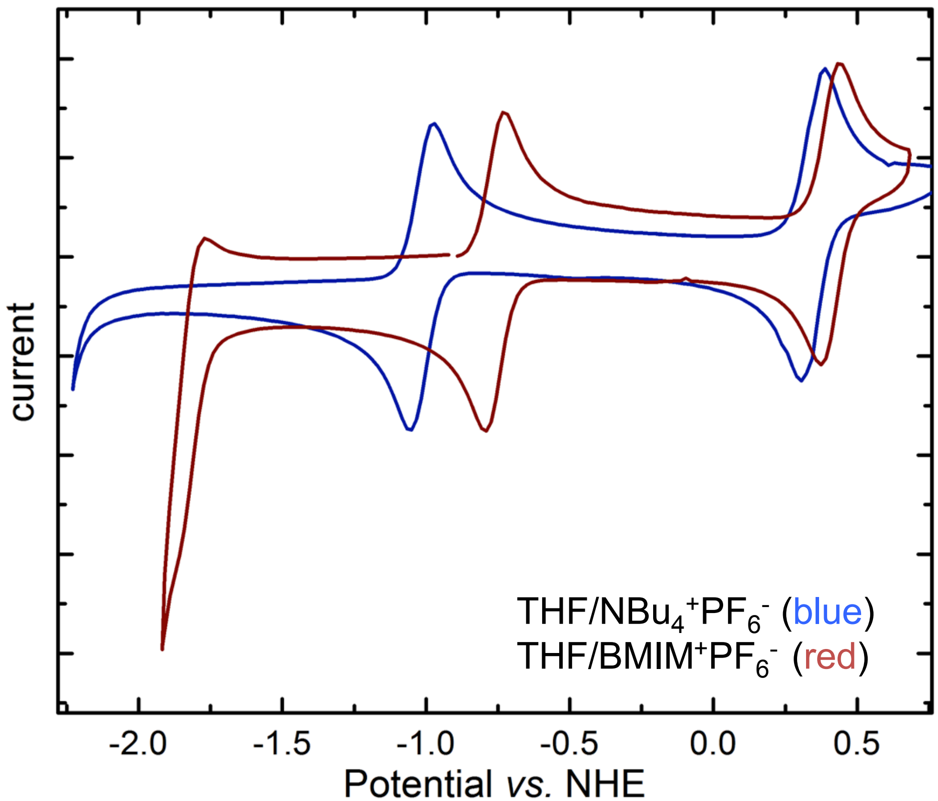
20 mV/s scan rate

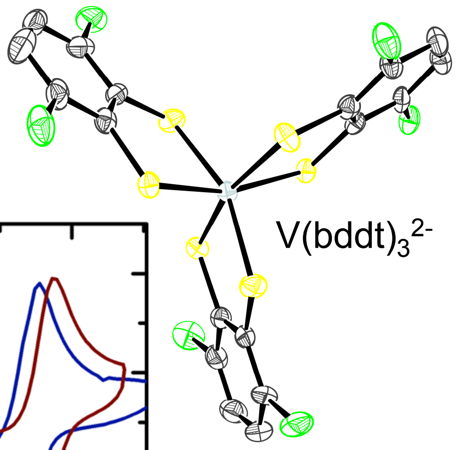
Integrated area for regions from 344 to 430 cm^{-1} (387 cm^{-1}), 298 and 334 cm^{-1} (316 cm^{-1}), 273 and 290 cm^{-1} (282 cm^{-1}) and 198 and 244 cm^{-1} (221 cm^{-1}). The 25 spectra correspond to two complete CV cycles. Spectra were background corrected and integrated using CASAXPS.

New Candidates: Benzenedithiolates

Continuing on with new complex development, we have expanded to Benzenedithiolates for more anolyte materials







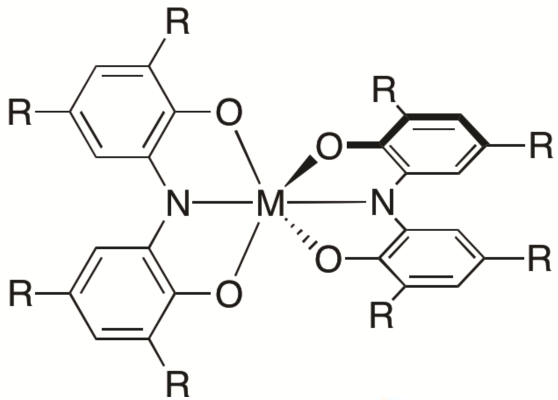
$V(bddt)_3^{2-}$

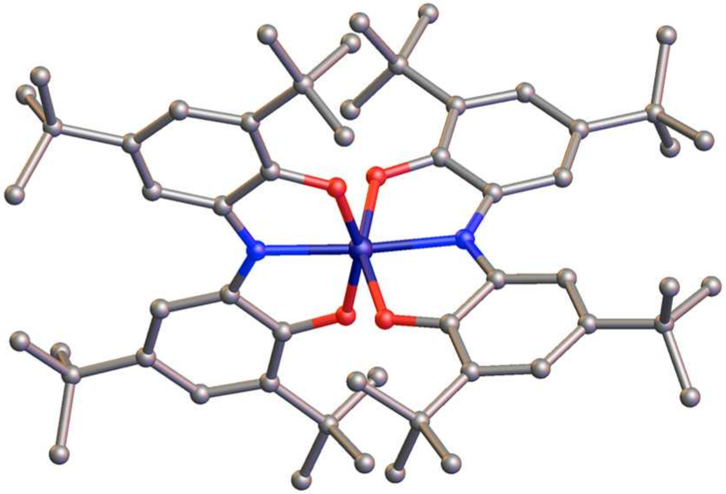
A third, unknown, redox couple is present by using cation to “pull” reduction more positive

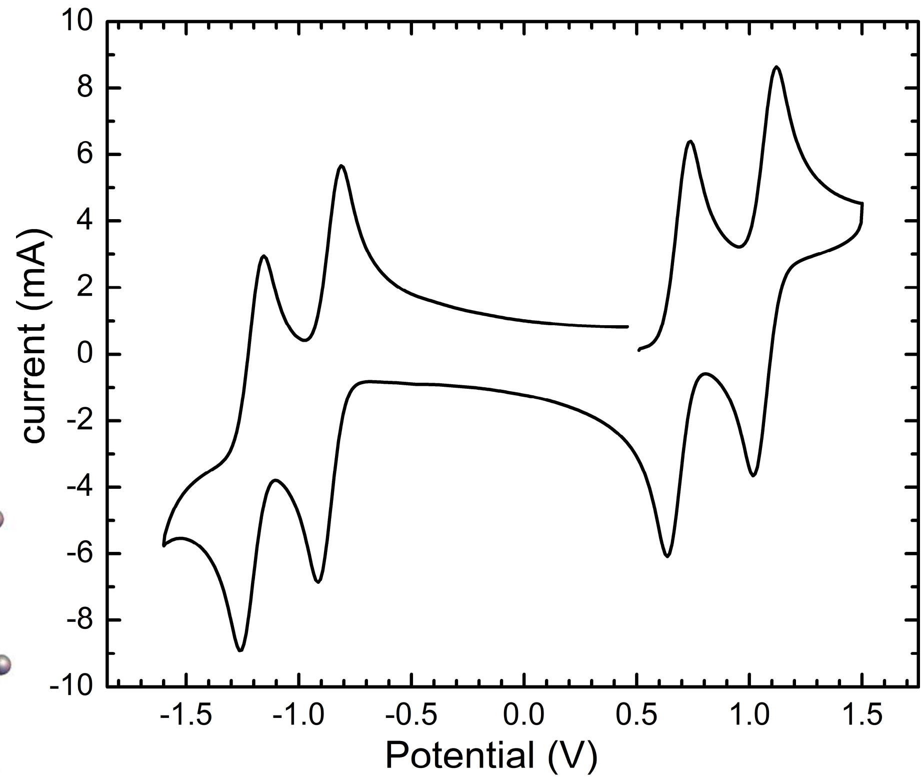
New Candidates: Nickel ONOs

Sandia National Laboratories

The ONO (Oxygen-Nitrogen-Oxygen) ligand motif is versatile and robust; offers catecholate-type redox chemistry but with 3 binding atoms



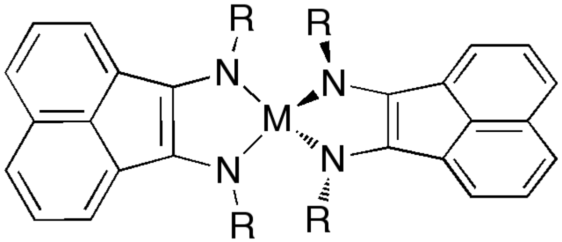


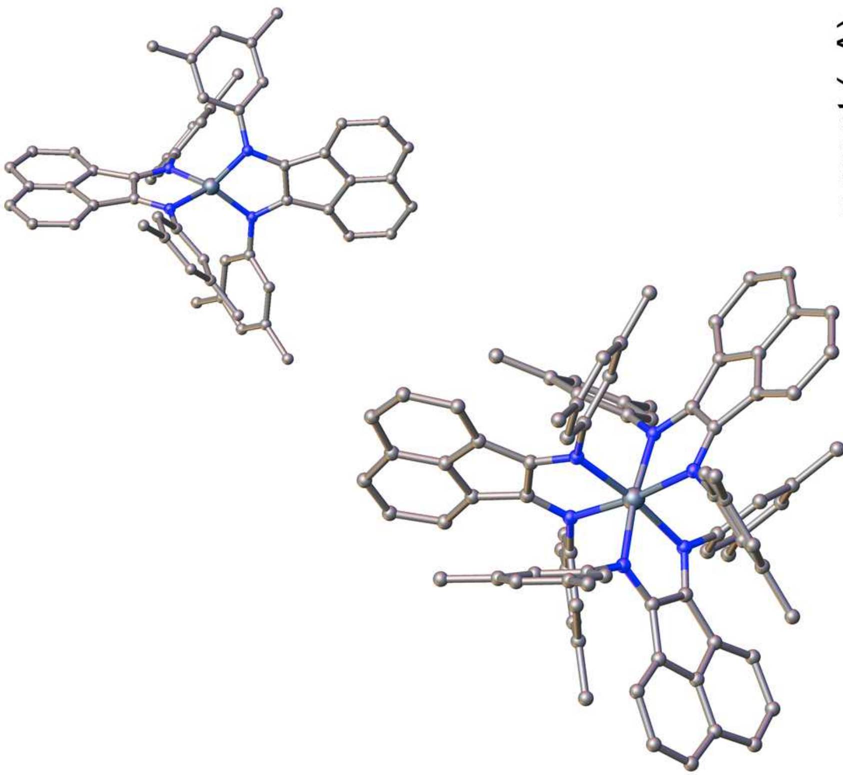


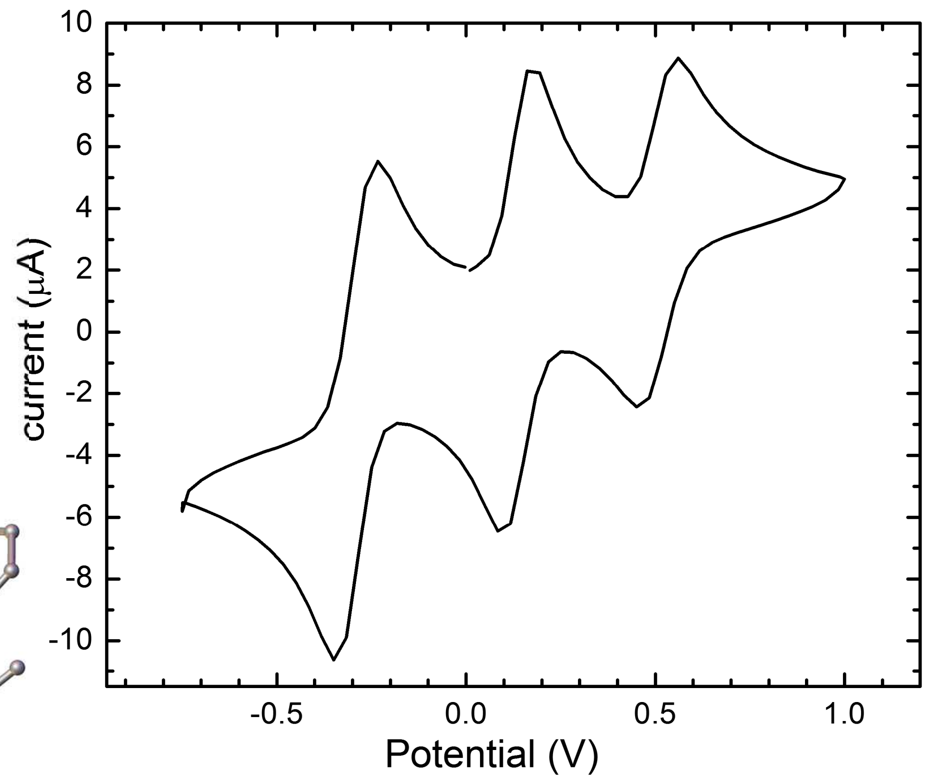
Interesting electrochemical feature is the closely spaced pairs of redox events, why are they close and can we move them closer?

New Candidates: Main Group Bisimines

Logical design of multi-electron redox: interest in main group complexes comes from the lack of redox chemistry they exhibit; the barrier to MO interaction between ligands

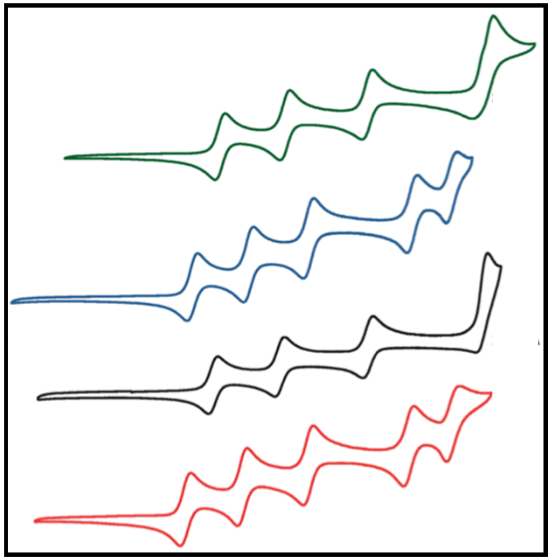


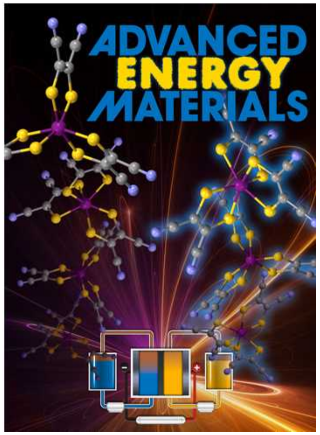




Summary

- New strategy for NRFB electrolytes with increased energy density
- Ion-pairing effects > 200 mV shift in OCP
- Half reactions for $[V(mnt)]_3^{n-}$, $2^-/1^-$ and $2^-/3^-$ are reversible, efficient
- Focus now on cell optimization and elucidating other promising electrolytes





Cappillino, P. J.; Pratt, H. D., III; Hudak, N. S.; Tomson, N. C.; Anderson, T. M.*; Anstey, M. R.* *Adv. Energy Mater.* **2013**, published on the Web.

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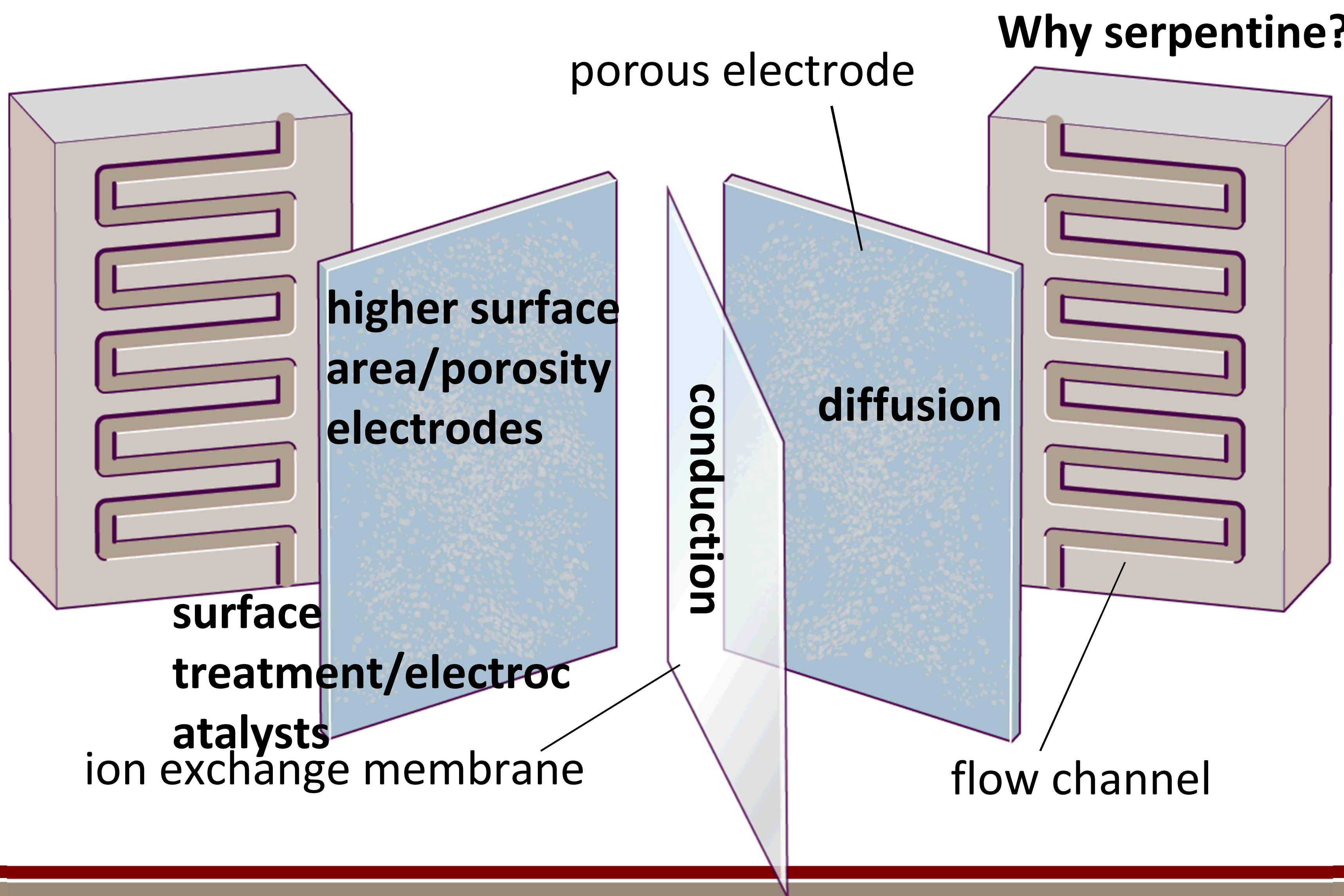
Babu Chalamala, SunEdison, Inc.

End of Talk, Supplemental Slides Follow

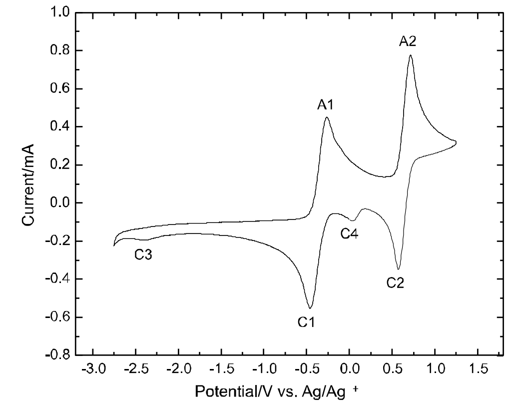
Cell Configuration



Examples

Metal Acetylacetonate (acac) Complexes (U. Michigan)

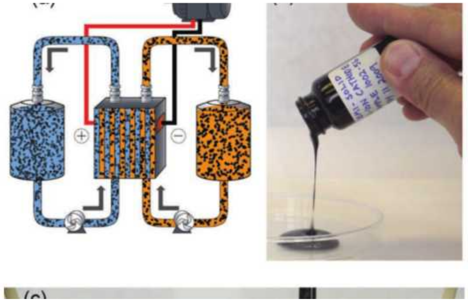
Metal	Cell Potential
Vanadium	2.2 V
Manganese	1.1 V
Chromium	3.4 V



Solvent/Supporting Electrolyte: acetonitrile/$TEABF_4$

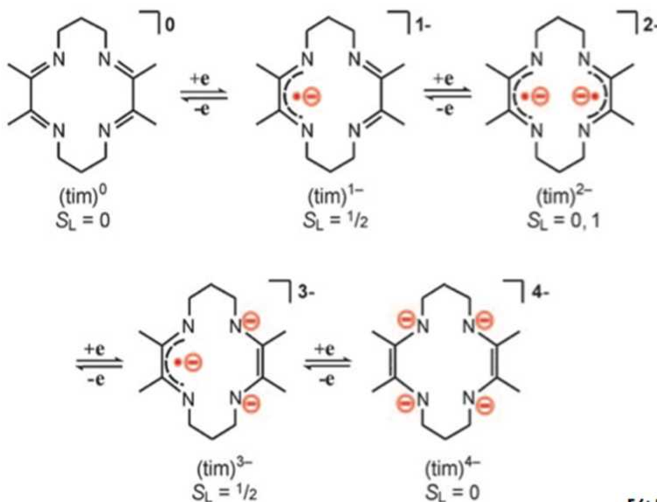
Semi-Solid Lithium Ion (MIT/24M)

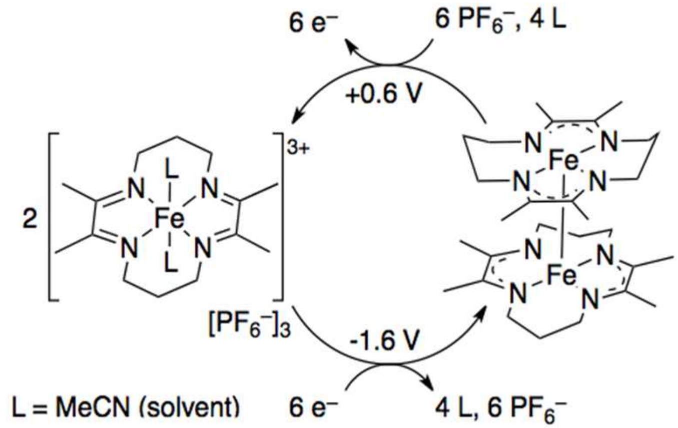
Cathodes	Anodes
$LiCoO_2$	$Li_4Ti_5O_{12}$
$LiFePO_4$	graphite
$LiNi_{0.5}Mn_{1.5}O_4$	Si

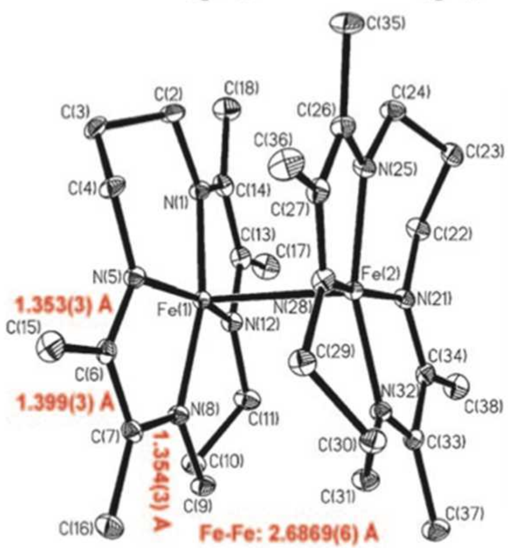


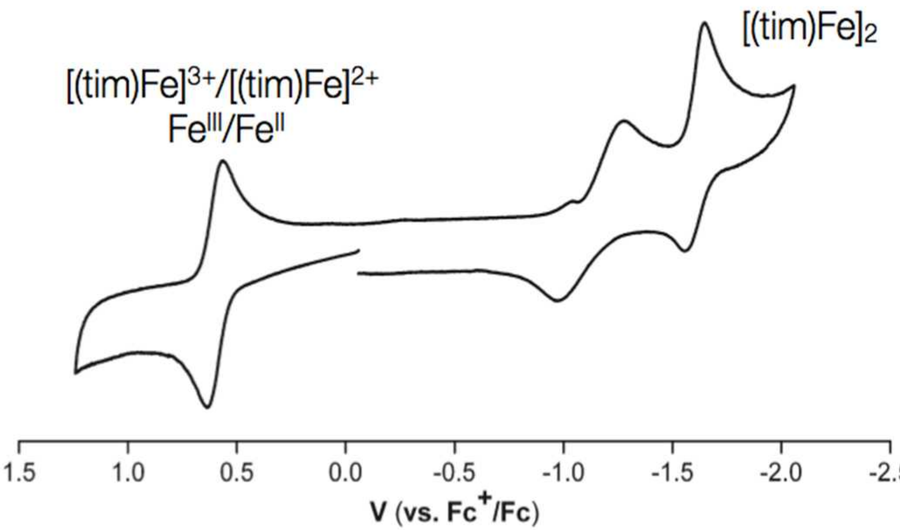
Iron-based Diimine Complex

Sandia National Laboratories



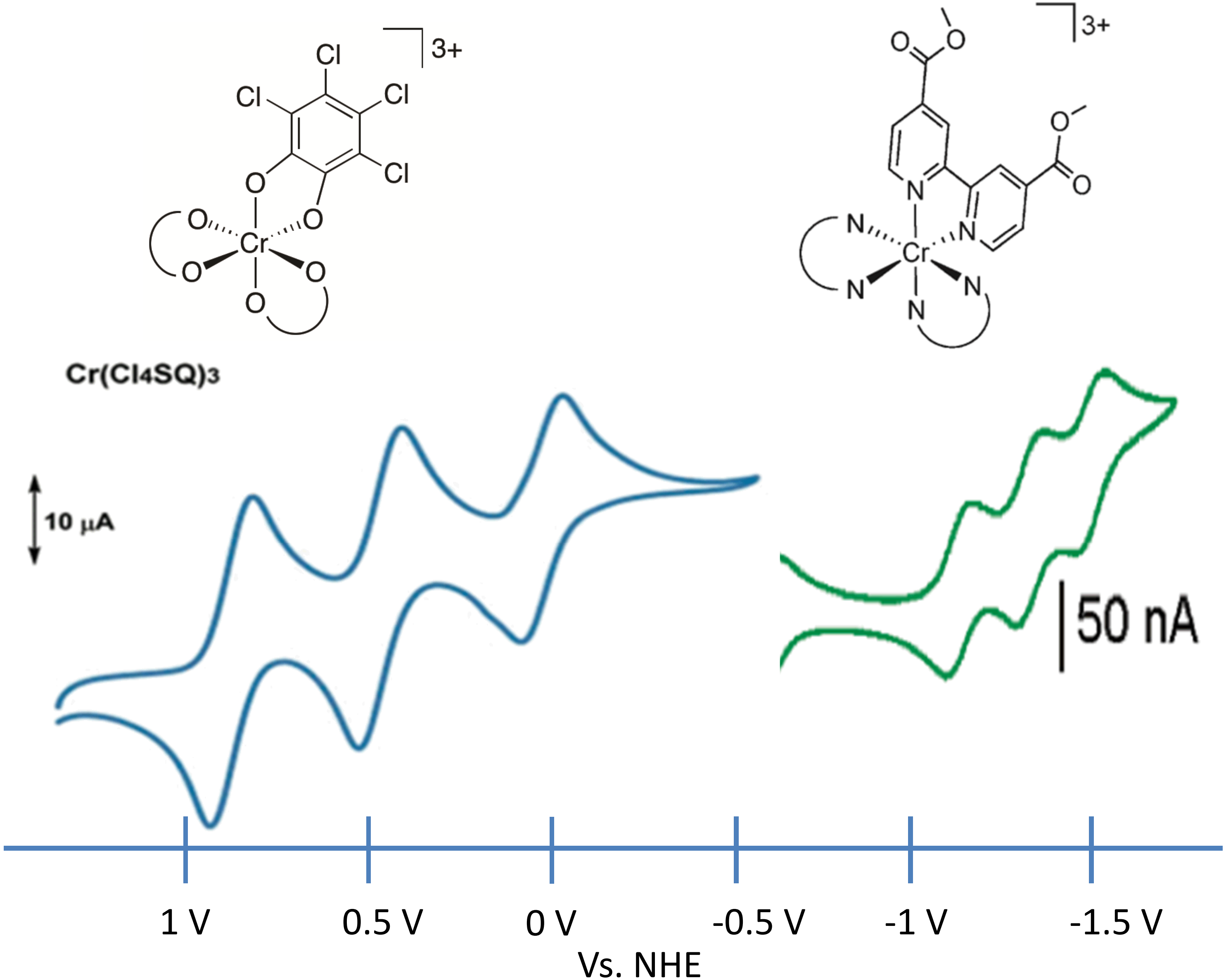




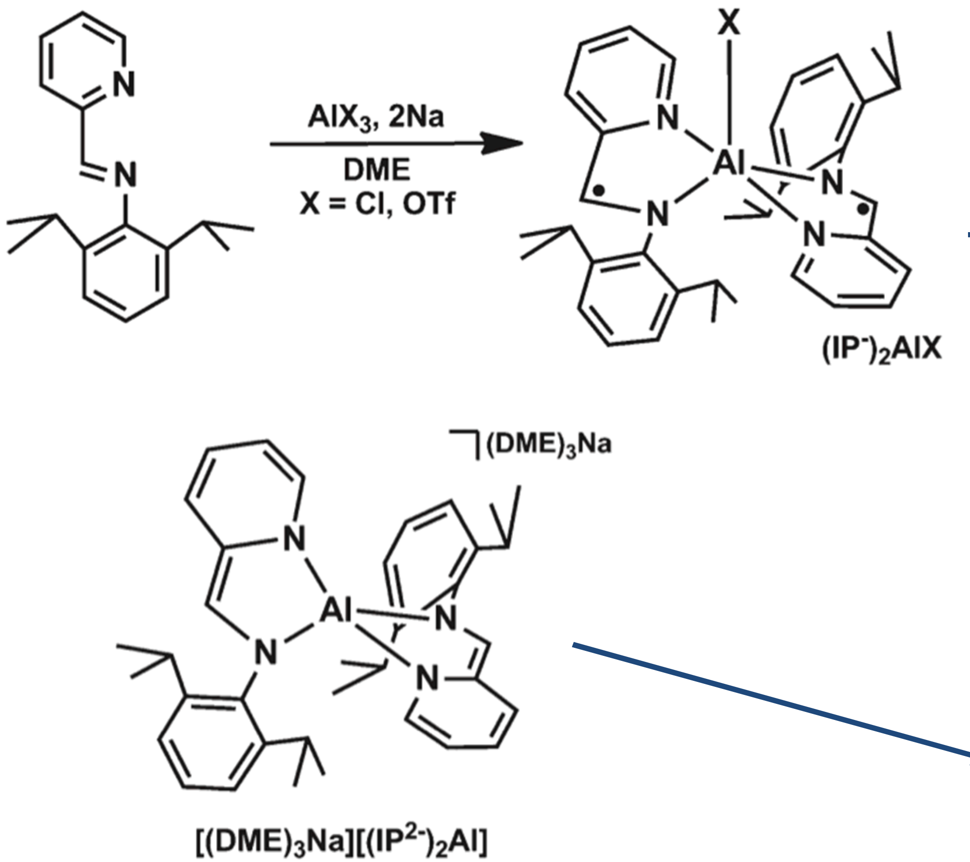


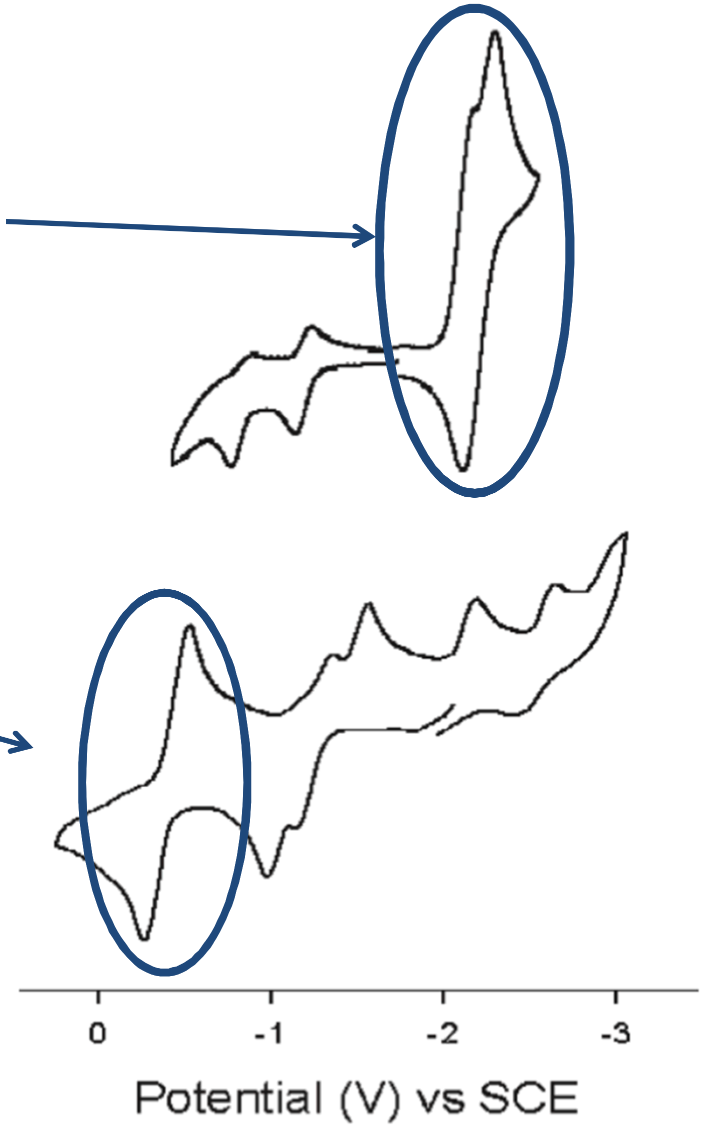
Hess *et. al. Angew. Chem. Int. Ed.* **2009**, *48*, 3703.
Hess *et. al. Angew. Chem. Int. Ed.* **2010**, *49*, 5686.

Chromium Anolyte and Electrolyte



Bipyridines and Imines

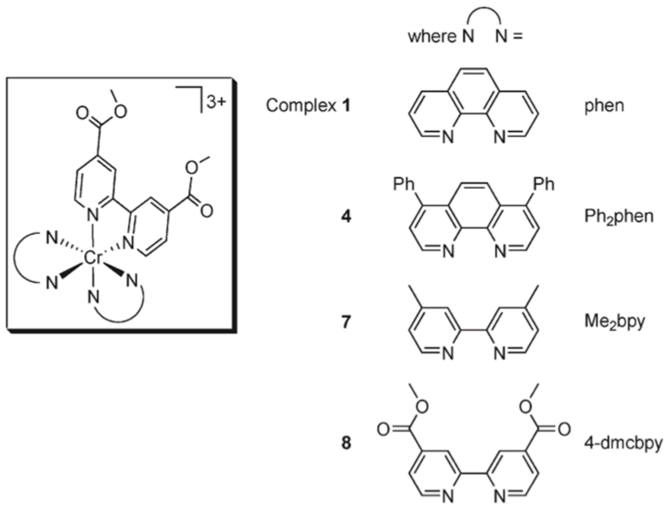


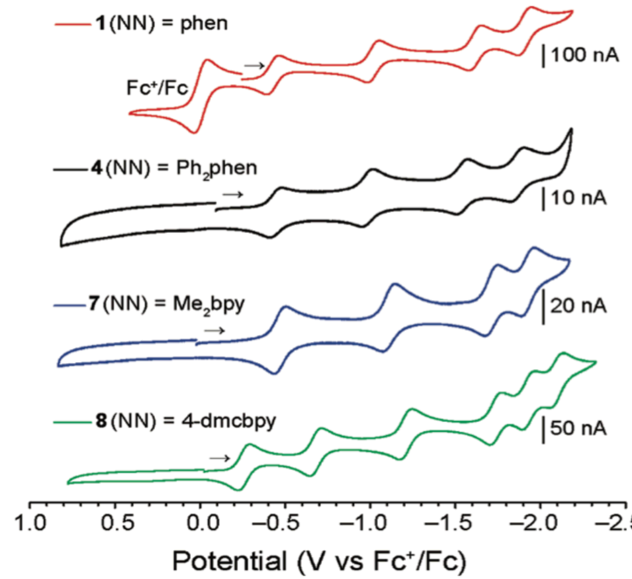


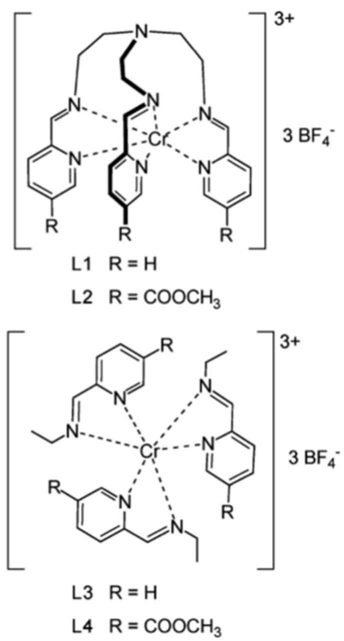
These two redox couples have been characterized as 2-electron processes spaced roughly 2V apart

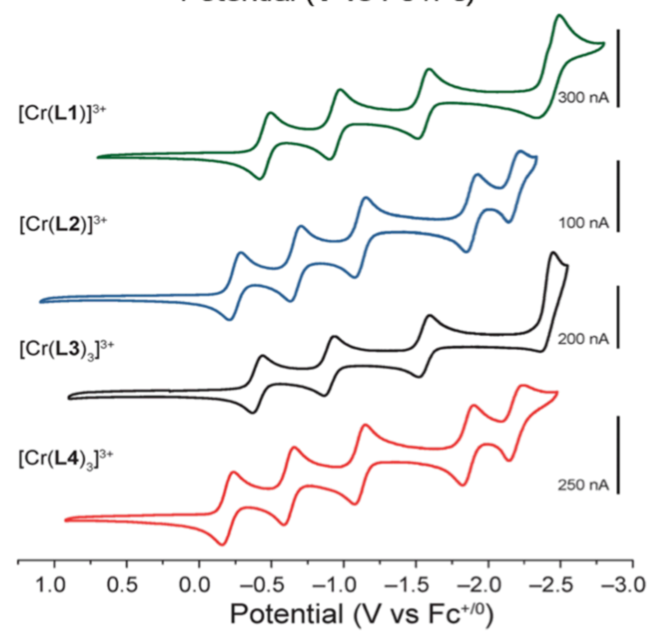
Myers, T. W.; Kazem, N.; Stoll, S.; Britt, R. D.; Shanmugam, M.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 8662–8672.
Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 11865–11867.

Bipyridines and Imines



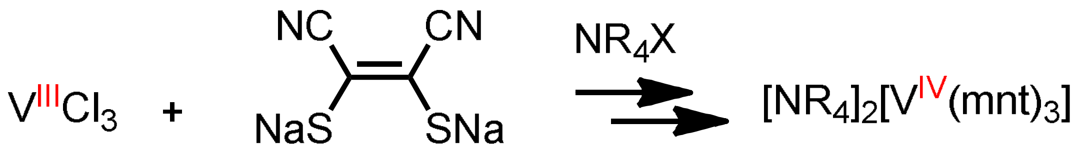






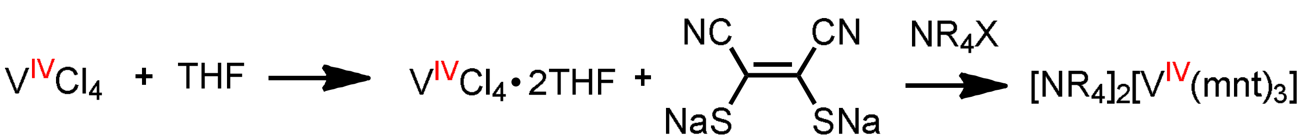
McDaniel, A. M.; Tseng, H.-W.; Damrauer, N. H.; Shores, M. P. *Inorg Chem* **2010**, *49*, 7981–7991.
McDaniel, A. M.; Tseng, H.-W.; Hill, E. A.; Damrauer, N. H.; Rappé, A. K.; Shores, M. P. *Inorg Chem* **2013**, Advance Article.

Scalable, High Yield Synthesis



~50% yield

Davison, A., *et al.,* J. Am. Chem. Soc. 1964 , 86 , 2799

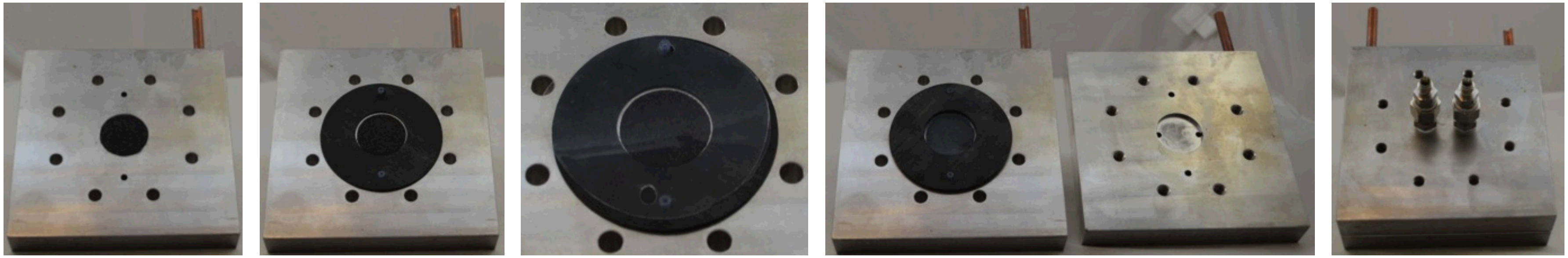


>90% yield after recrystallization

Heyn, B., et al., *Anorganische Synthesechemie: ein integriertes Praktikum*, Springer-Verlag , Berlin, Germany **1990**

Cappillino *et al.*, Adv. Energy Mater. (2013), in press

Flow Cell Tester

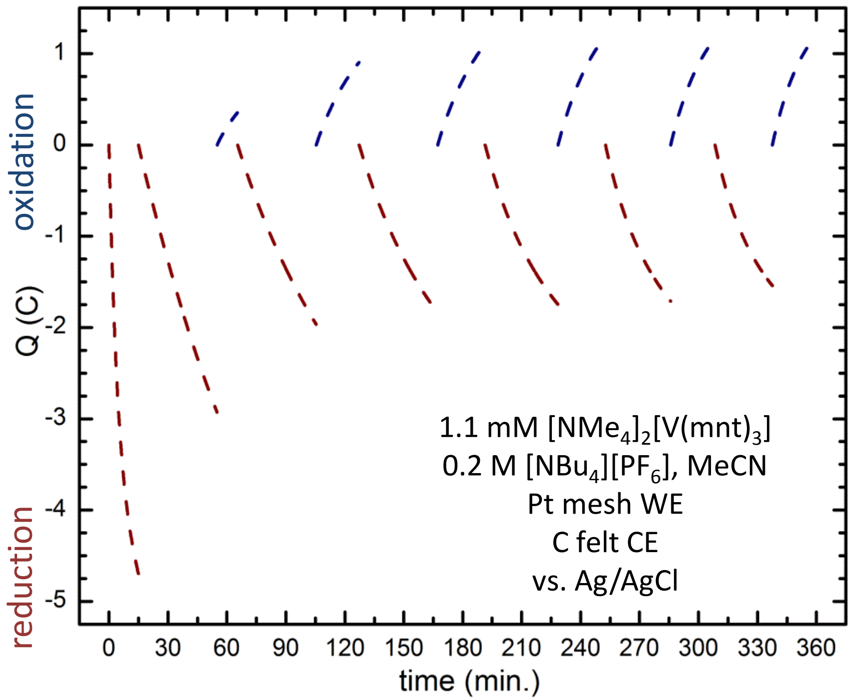


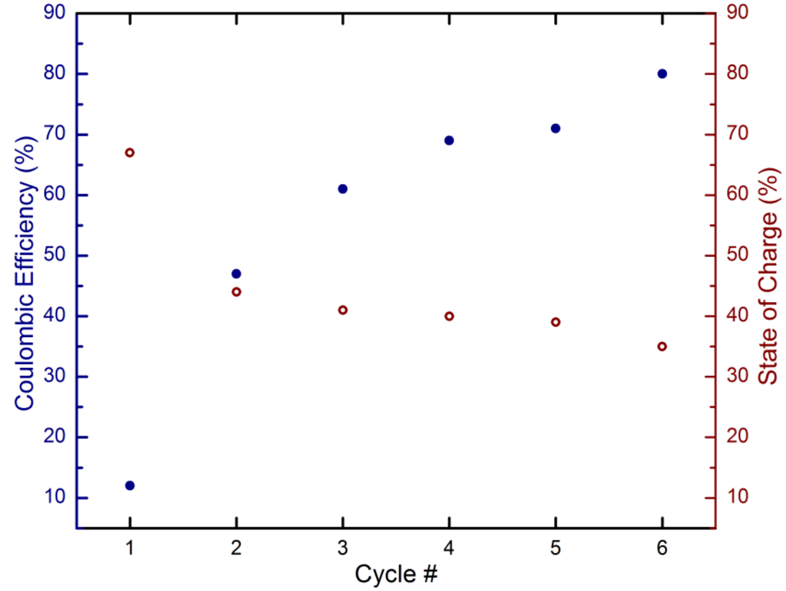
assembly

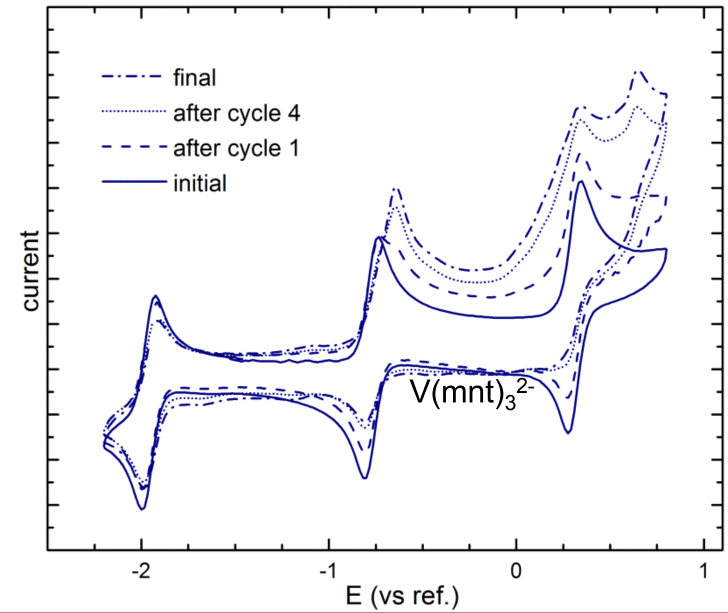
Key Issues:

- Force fluid against gravity
- Avoid sharp turns
- Membrane material
- Carbon felt/membrane contact
- Wettability

Half Cell Reaction ($V(mnt)_3^{4-} \leftrightarrow V(mnt)_3^{3-}$)

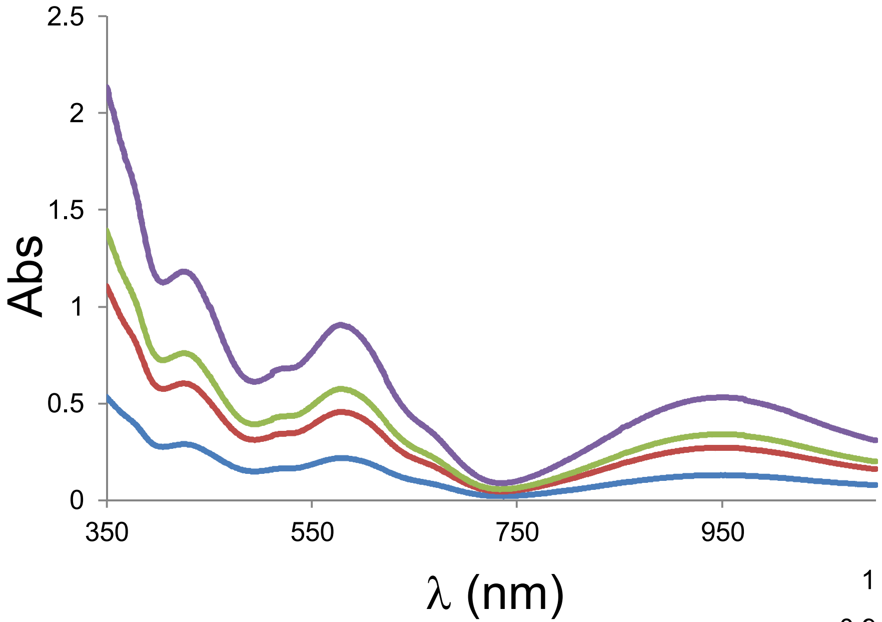




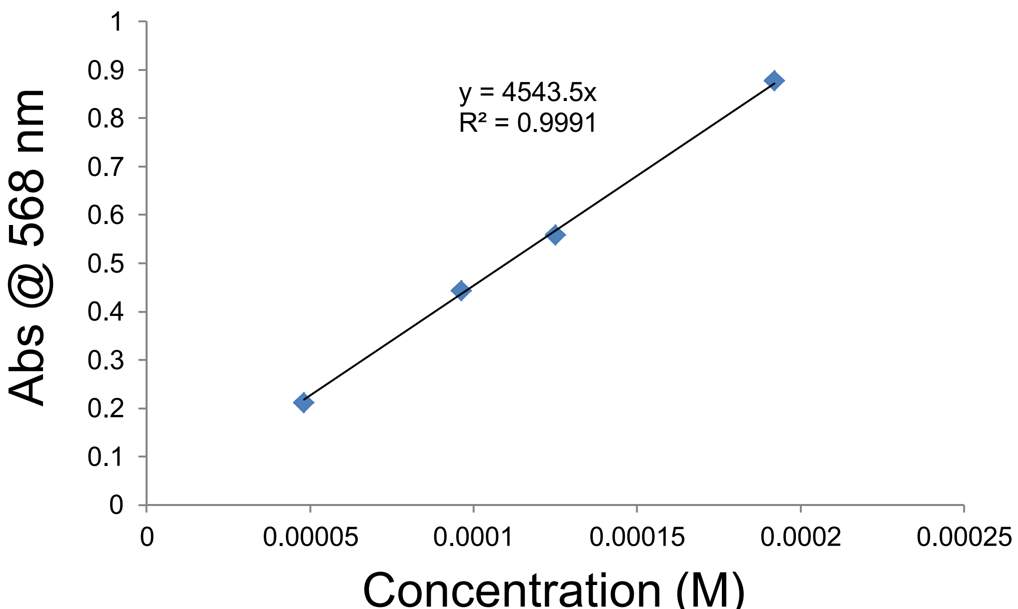


- E_{WE} = -2.2 V, bulk reduction
- E_{WE} = -1.4 V, bulk oxidation
- Lower SOC attained
- Low CE, gradually improves
- decomposition observed

Determination of Concentration



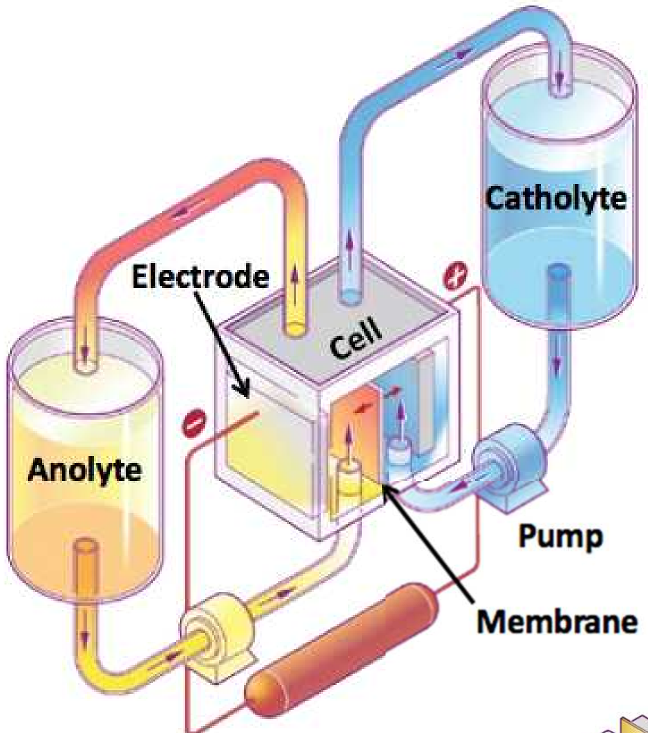
- Several features in visible region
- Use 568 nm to determine concentration
- Prepared $[NEt_4]_2[V(mnt)_3]$ standards between 0.05 and 0.2 mM

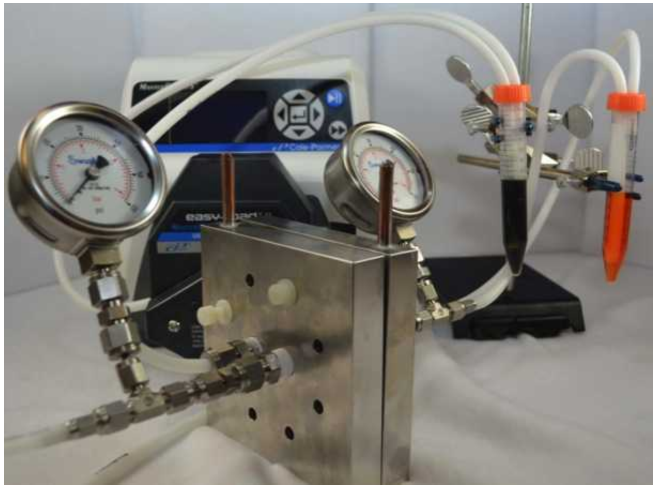


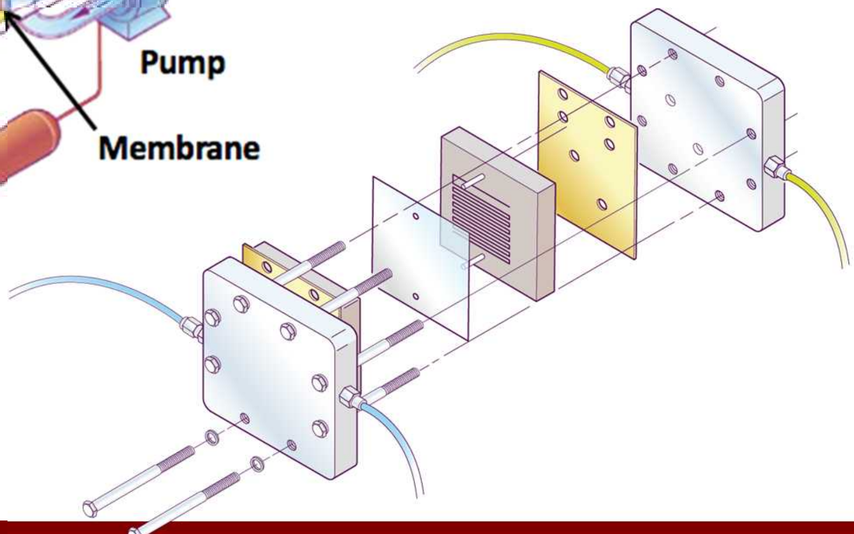
- Determined ε_{568} = 4540 $M^{-1}cm^{-1}$
- Solutions of $[NEt_4]$ and $[NMe_4]$ salts of $[V(mnt)_3]^{2-}$ made, diluted to determine max concentration
- Plastic is good (polypropylene).

Flow Battery

Energy storage technology utilizing redox states of various species for charge/discharge purposes

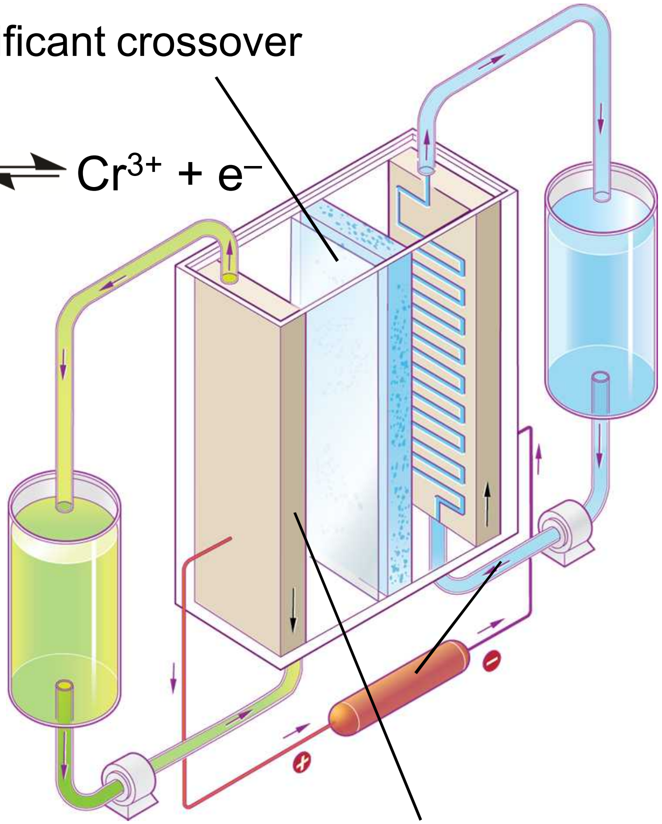




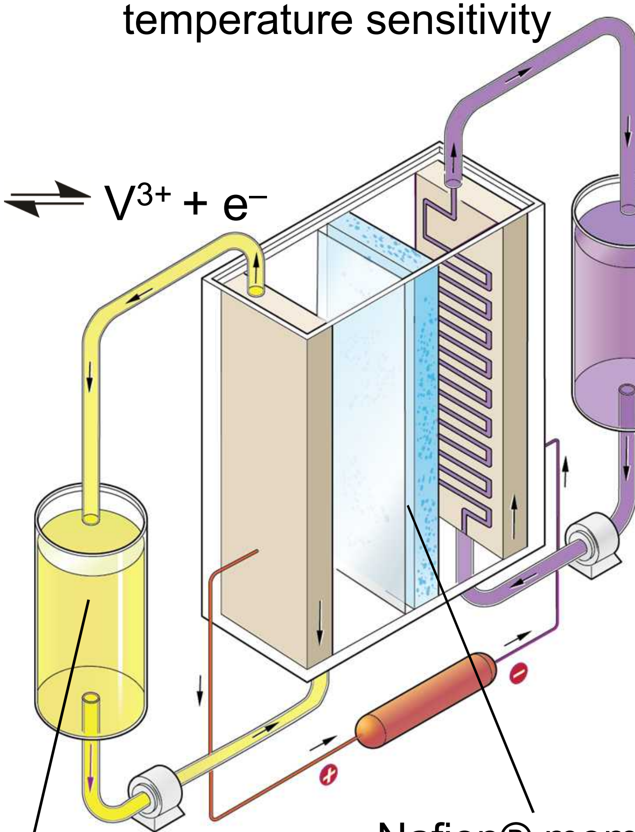


- Potential for low cost
- Easy scalability
- Long cycle life
- Deep discharge capability
- Energy (kWh) and power (kW) scale independently

Early Development (Aqueous)

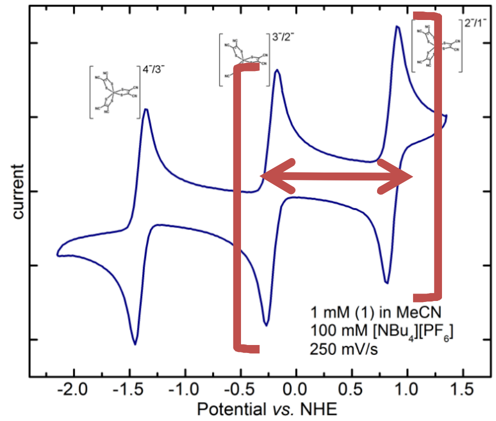


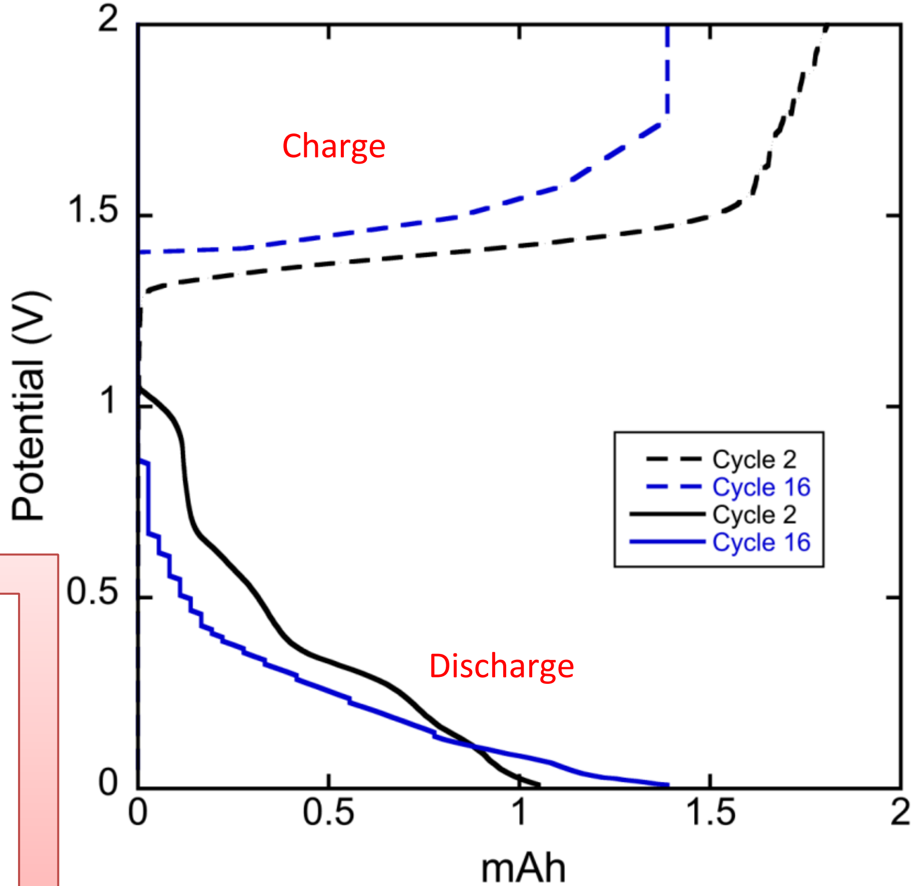
Open Circuit Potential (OCP) **1.18 V**



Open Circuit Potential (OCP) **1.26 V**

Implications for the Static Cell Tests



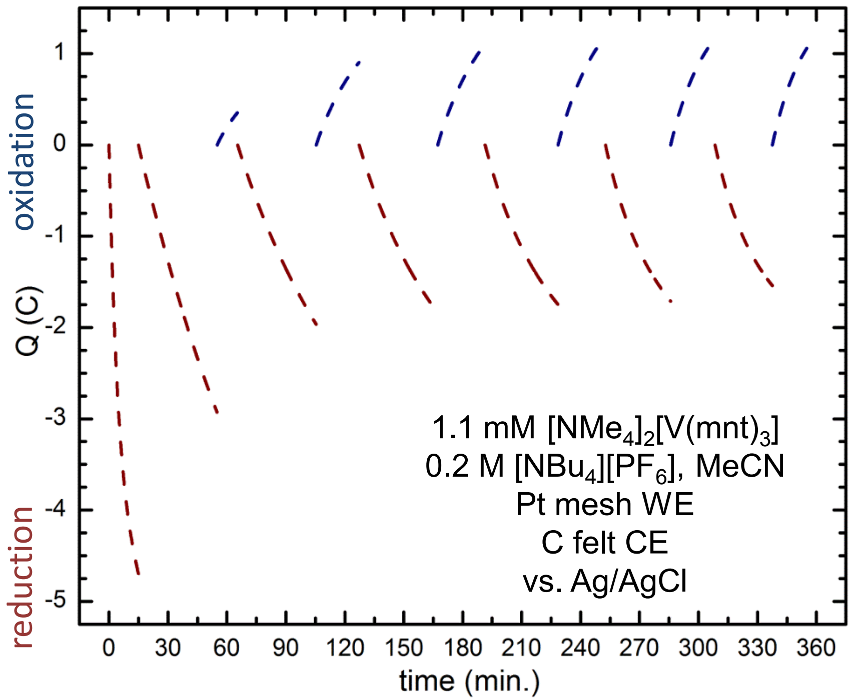


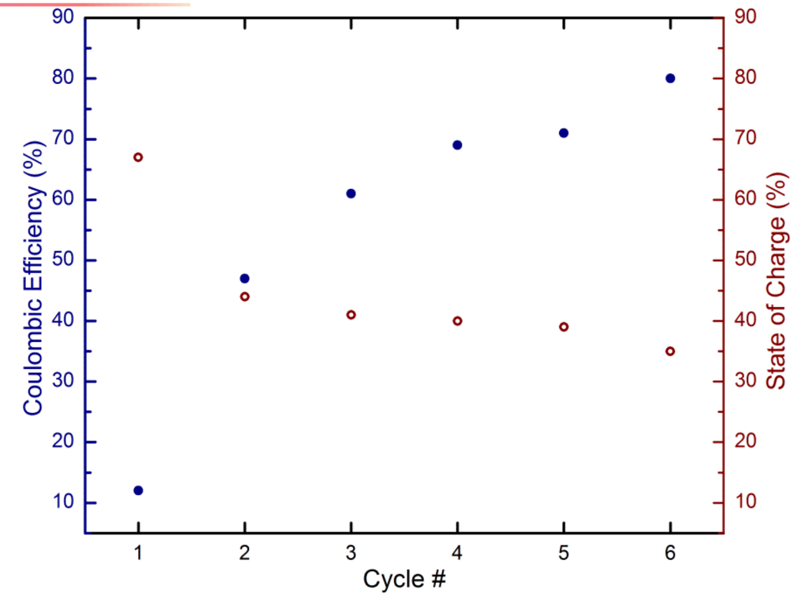
- What is the origin of the gradual drop in discharge potential?
  - ~~Decomposition of $V(mnt)_3$~~
  - Membrane crossover
  - Inefficient cell design
  - Electrode degradation

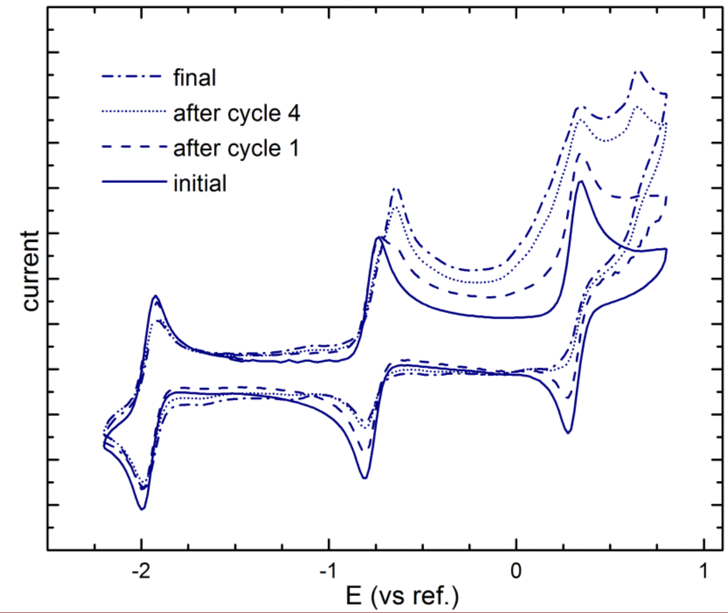
H-cell conditions:

- graphite electrodes ($1 cm^2$)
- microporous separator (Tonen)
- NBu_4PF_6 in MeCN
- 20 mM electrolyte

Half Cell Reactions ($V(mnt)_3^{3-}$ ←→ $V(mnt)_3^{4-}$)







- E_{WE} = -2.2 V, bulk reduction
- E_{WE} = -1.4 V, bulk oxidation
- Lower SOC attained
- Low CE, gradually improves
- decomposition observed

Some suggestion of polymerization of 4^- in literature…