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Metal Complexes With Redox-Active Ligands As High Energy Density Nonaqueous Redox Flow Battery Electrolytes

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Flow Battery Basics

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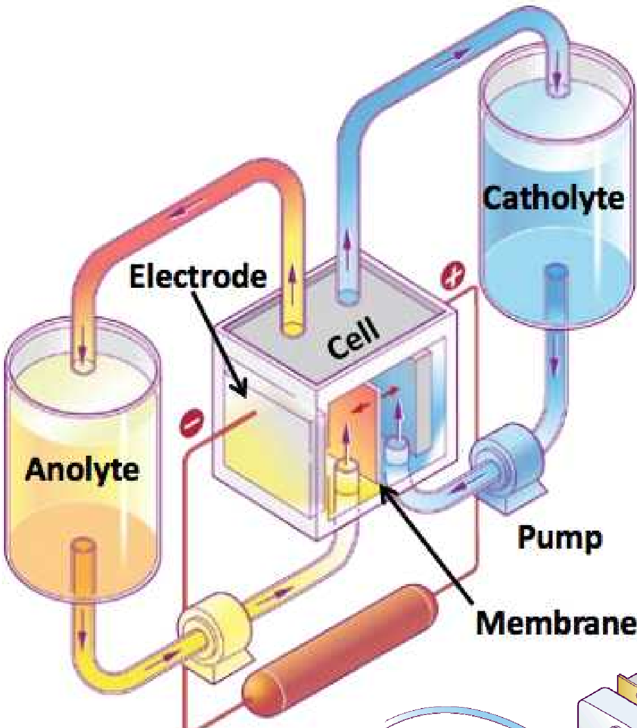
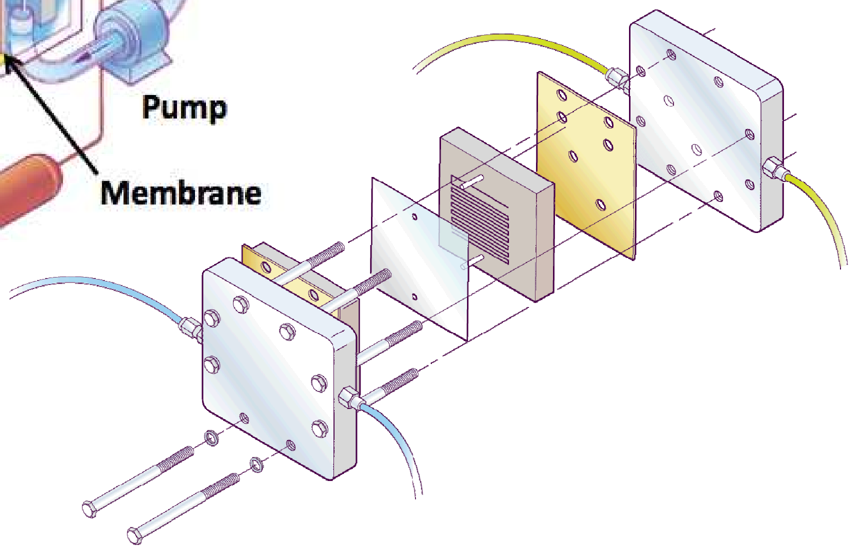
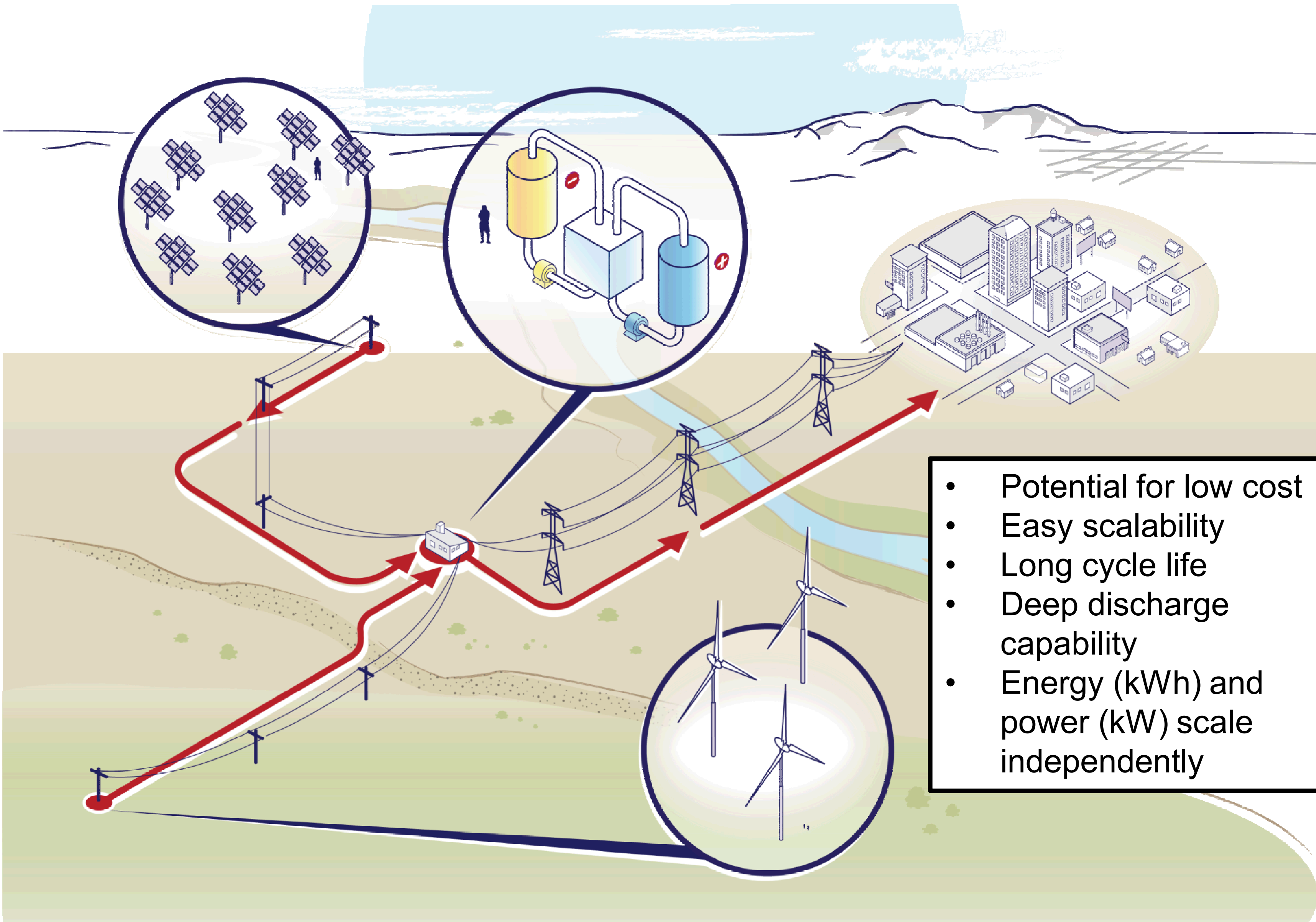
Energy storage technology utilizing redox states of various species for charge/discharge purposes





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

Flow Batteries in the Grid



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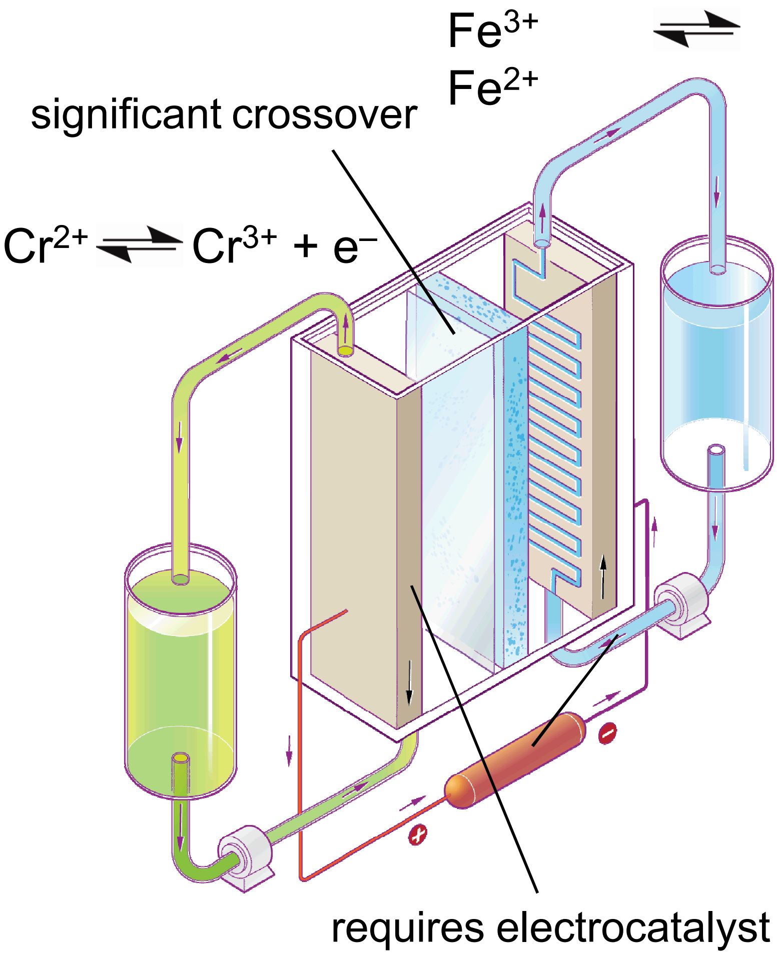
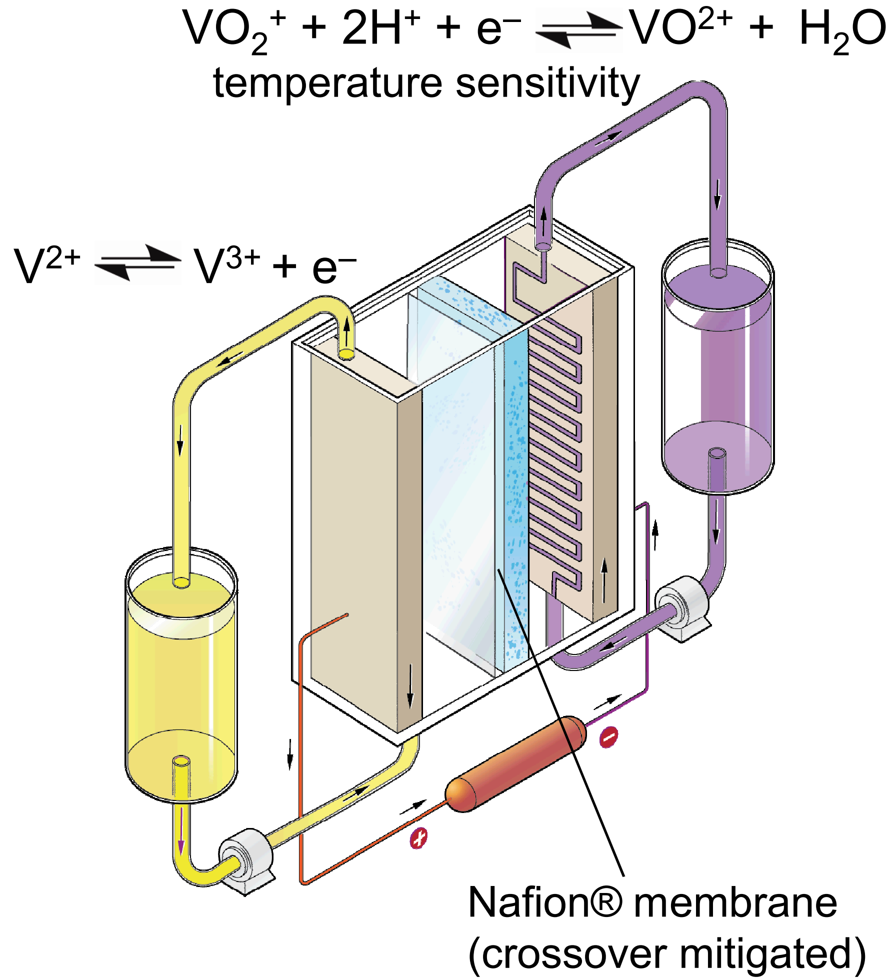
Early Development (Aqueous)



Open Circuit Potential (OCP) **1.2 V**[1]



Open Circuit Potential (OCP) **1.3 V**[2]

[1]Skyllas-Kazacos, M. J. Electrochem. Soc., 158 (8) R55-R79 (2011)

[2]Li, L. *et al.,* Adv. Energy Mater. 2011, 1, 394–400

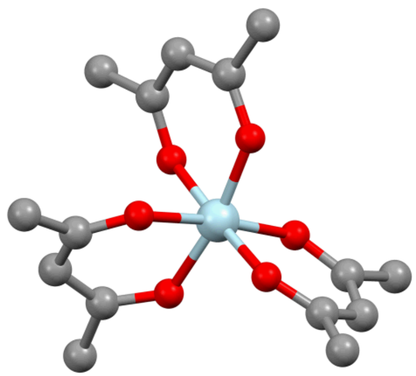
Non-Aqueous Chemistry

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
- Higher charge cycle efficiency
- Decreased temperature sensitivity
- Increased cycle life

Bard, Inzelt, and Scholz, *Electrochemical Dictionary*, **2012**.
Zanello, Fabrizi de Biani, and Nervi, *Inorganic Electrochemistry: Theory, Practice and Application*, **2012.**

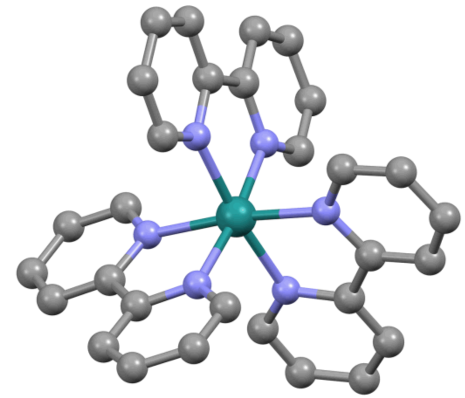
State of the Art in Electrolytes



$V(acac)_3$

2.2 V OCP
1 mol□L^{-1}
29 Wh□L^{-1}

$V^{III}(L)_3 \,|\, V^{IV}(L)_3 \,\|\, V^{III}(L)_3 \,|\, V^{II}(L)_3$



$[Ru(bpy)_3]^{2+}$

2.6 V OCP
0.2 mol□L^{-1}
7 Wh□L^{-1}

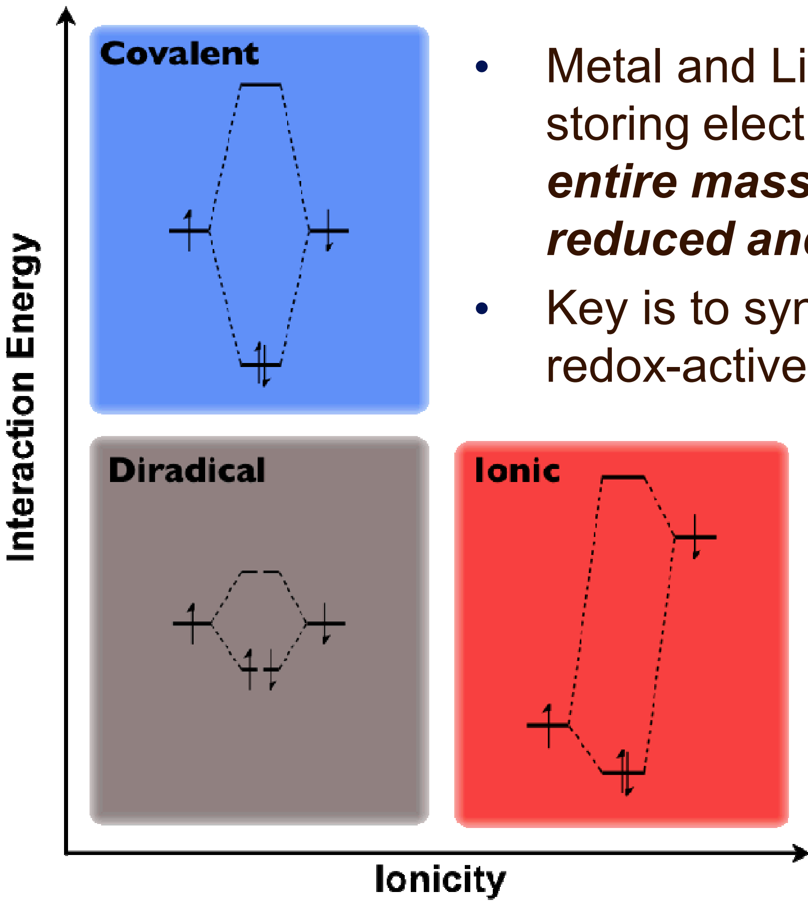
$Ru^{II}(L)_3 \,|\, Ru^{III}(L)_3 \,\|\, Ru^{II}(L)_3 \,|\, Ru^{I}(L)_3$

Liu, Q., et al. Electrochem. Commun. 11 (2009) 2312–2315

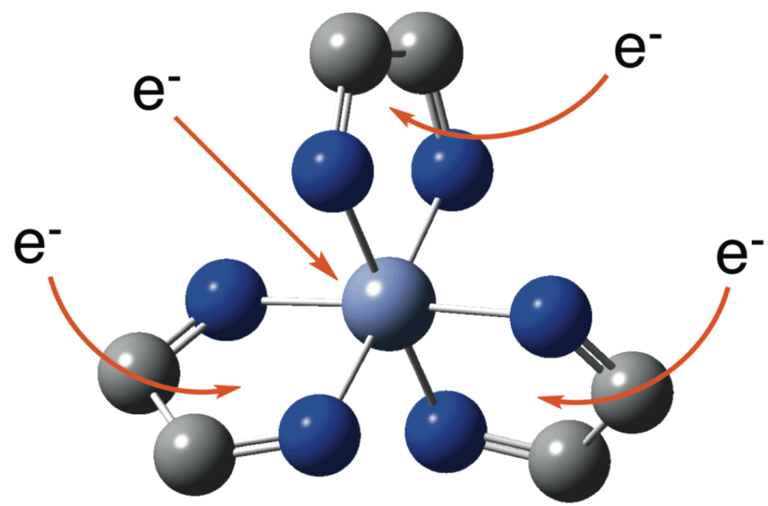
Matsuda, Y. *et al.*, J. Appl. Electrochem. 18 (1988) 909-914

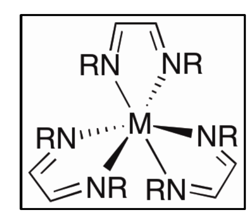
Hidden Potential of Ligands

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



- Metal and Ligands can be isolated, *electronically*, with each storing electrons separately, ***makes better use of the entire mass of the electrolyte*** and ***stabilizes highly reduced and oxidized species***
- Key is to synthesize and test compounds with the feature of redox-active ligands

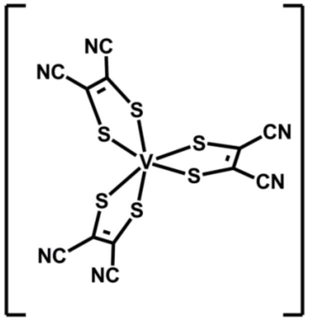


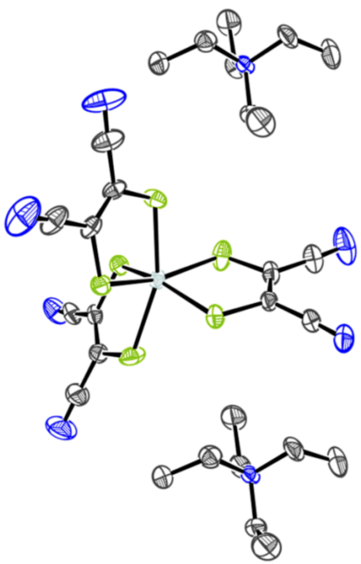


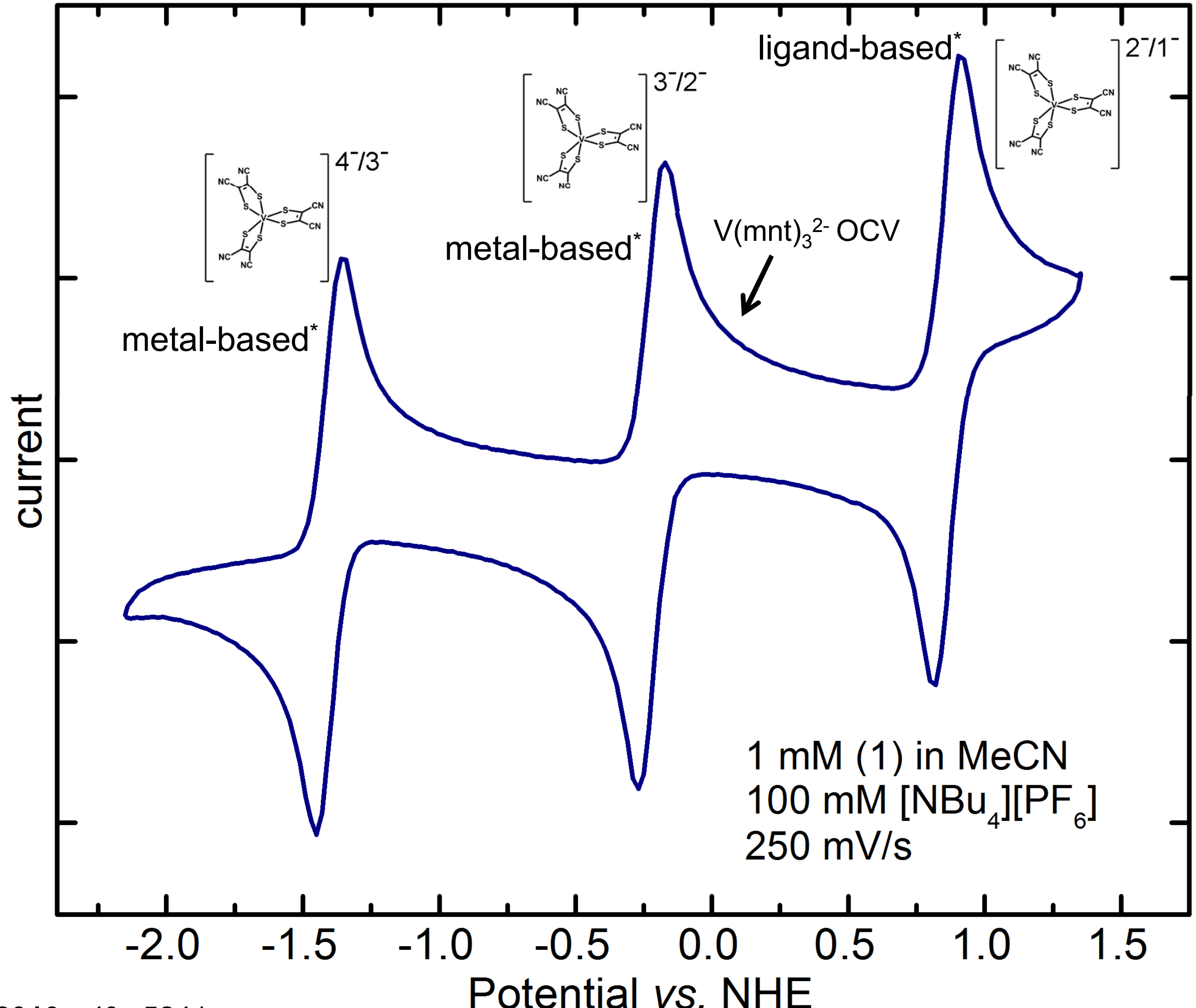
$\ddot{M}^{(n)+} — L^{0}$ or $\dot{M}^{(n+1)+} — \dot{L}^{1-}$ or $M^{(n+2)+} — \ddot{L}^{2-}$

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

mnt = maleonitriledithiolate

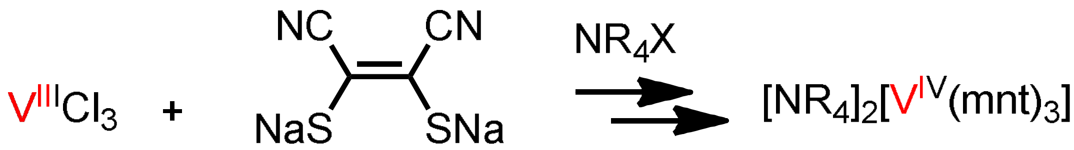






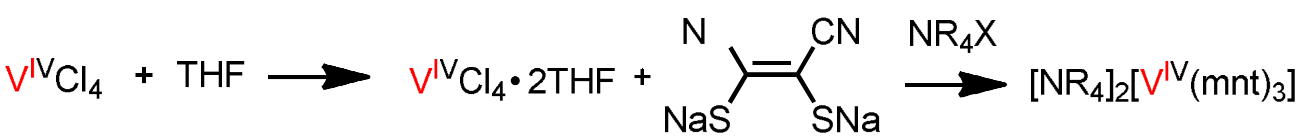
*Sproules, S., *et al.*, Inorg. Chem. **2010** , *49* , 5241

Scalable, High Yield Synthesis



~50% yield

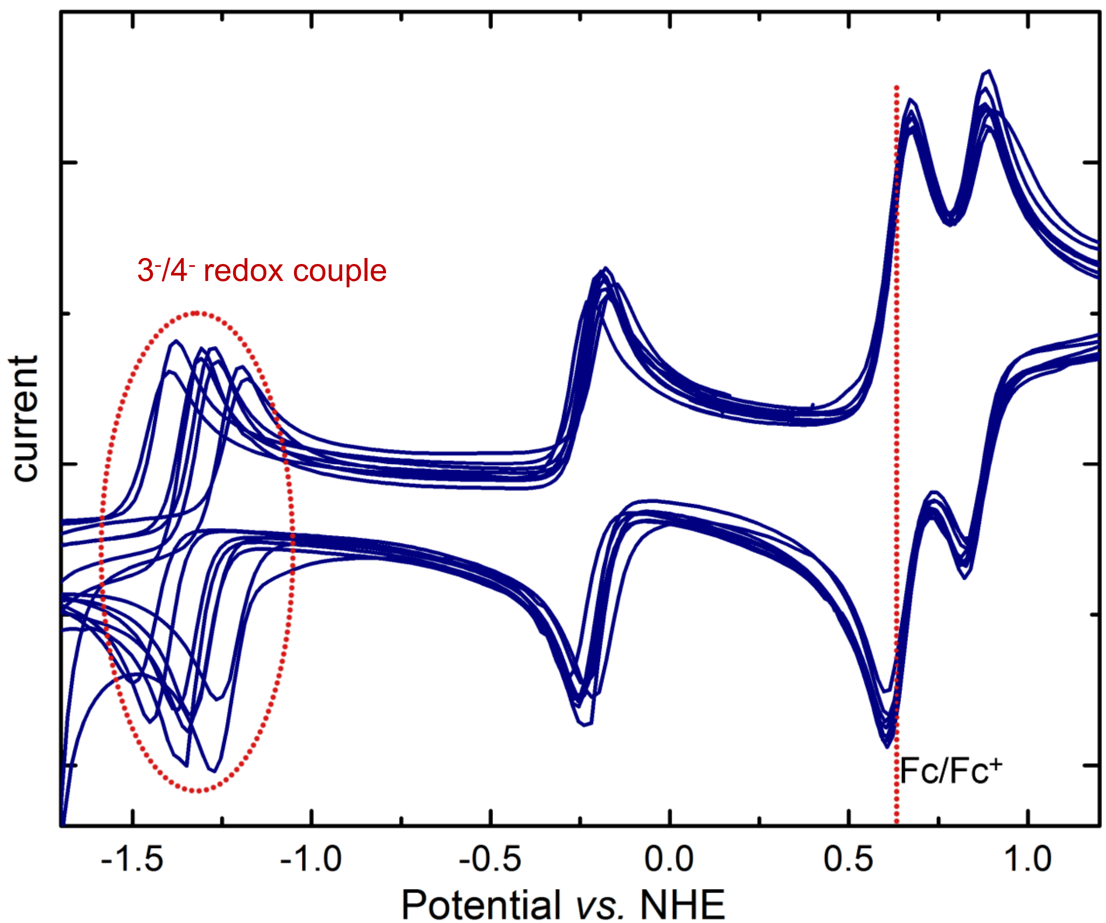
Davison, A., *et al.,* J. Am. Chem. Soc. 1964 , 86 , 2799

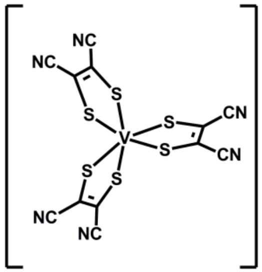


>90% yield after recrystallization

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

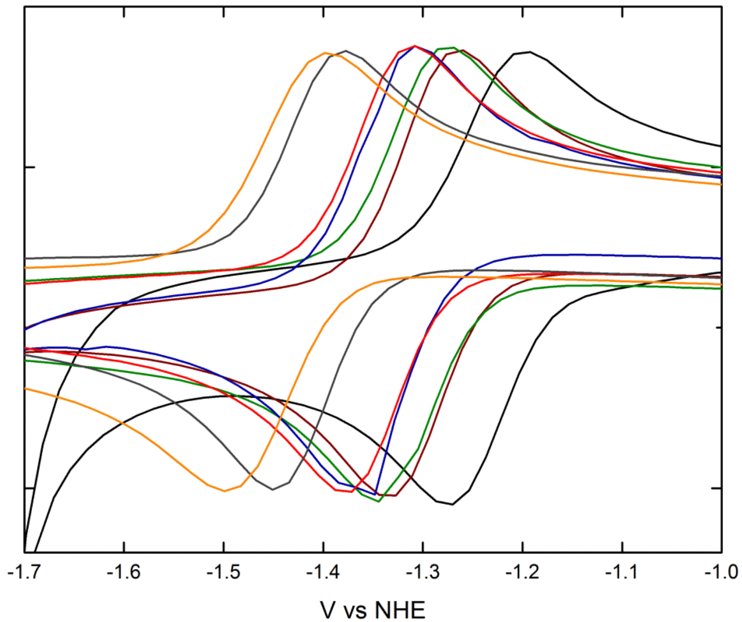
Effects of Ion-Pairing

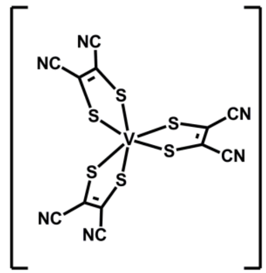




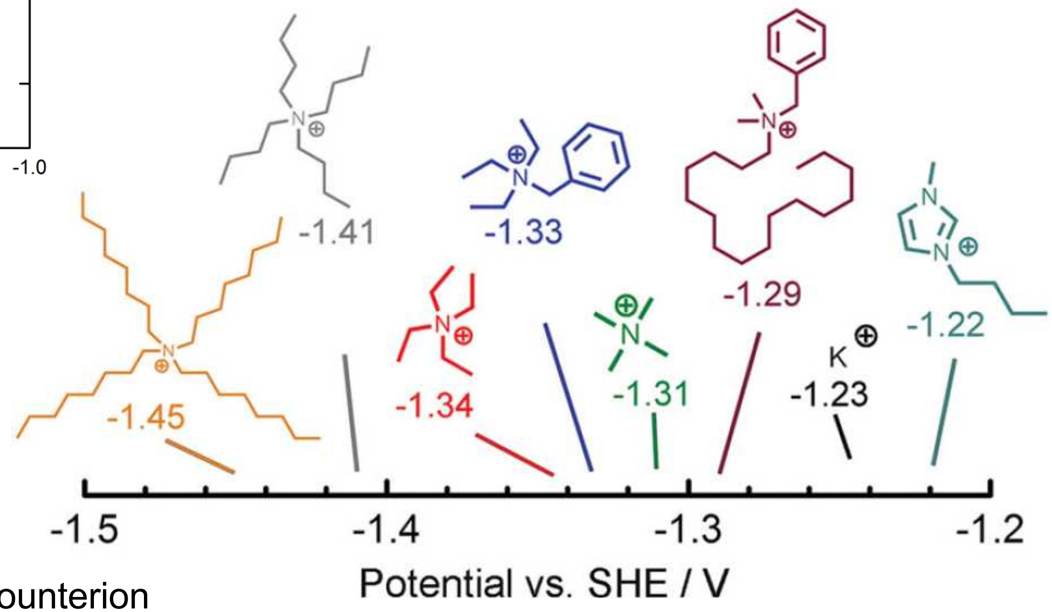
- Identity of supporting electrolyte cation affects electrochemistry
- Shift apparent in $3^-/4^-$ redox couple

Effects of Ion-Pairing





- 230 mV shift in potential
- Bulkier cations are shifted to lower E



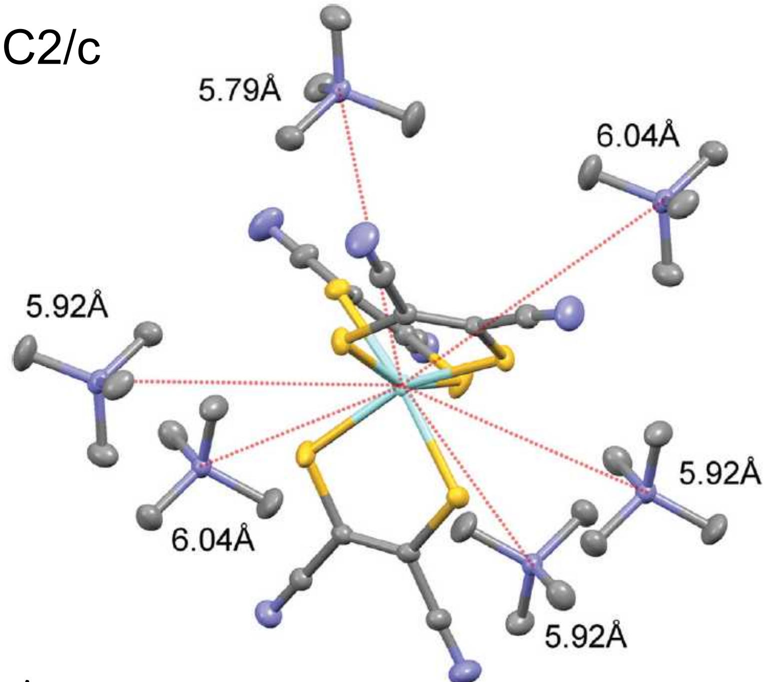
- Steric bulk prevents close approach
- Less effective ion-pairing

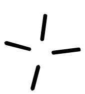
All with PF_6^- counterion

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)

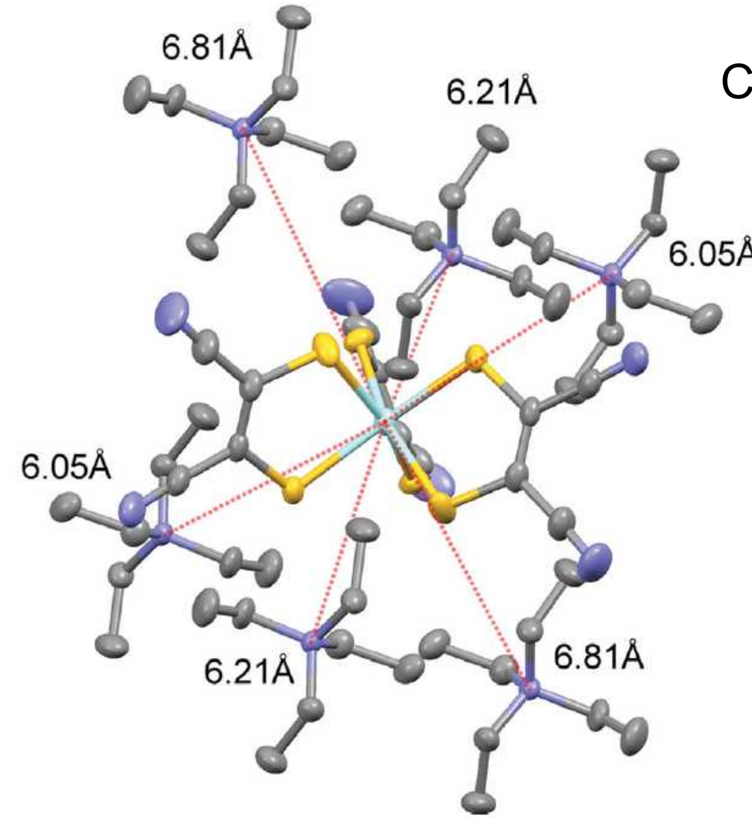
C2/c



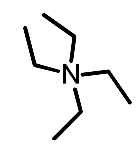


$[NMe_4]^+$

C2/c



$[NEt_4]^+$



Avg. N-V distance: 5.9 Å, 6.4 Å

Static Cell Testing of $V(mnt)_3^{2-}$

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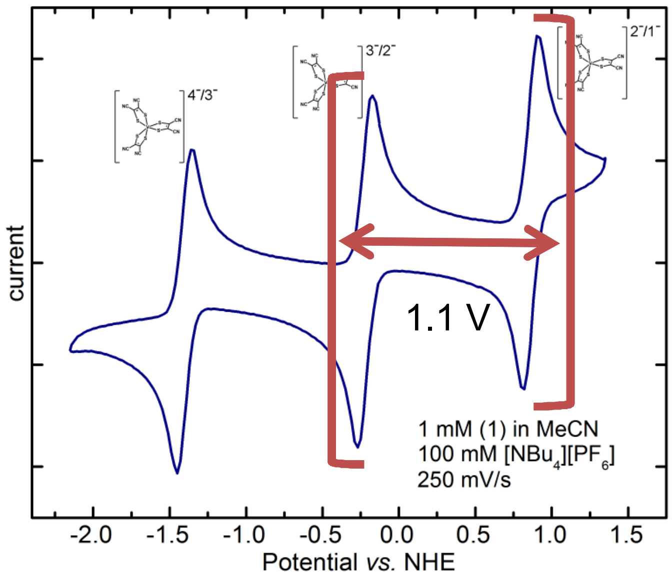
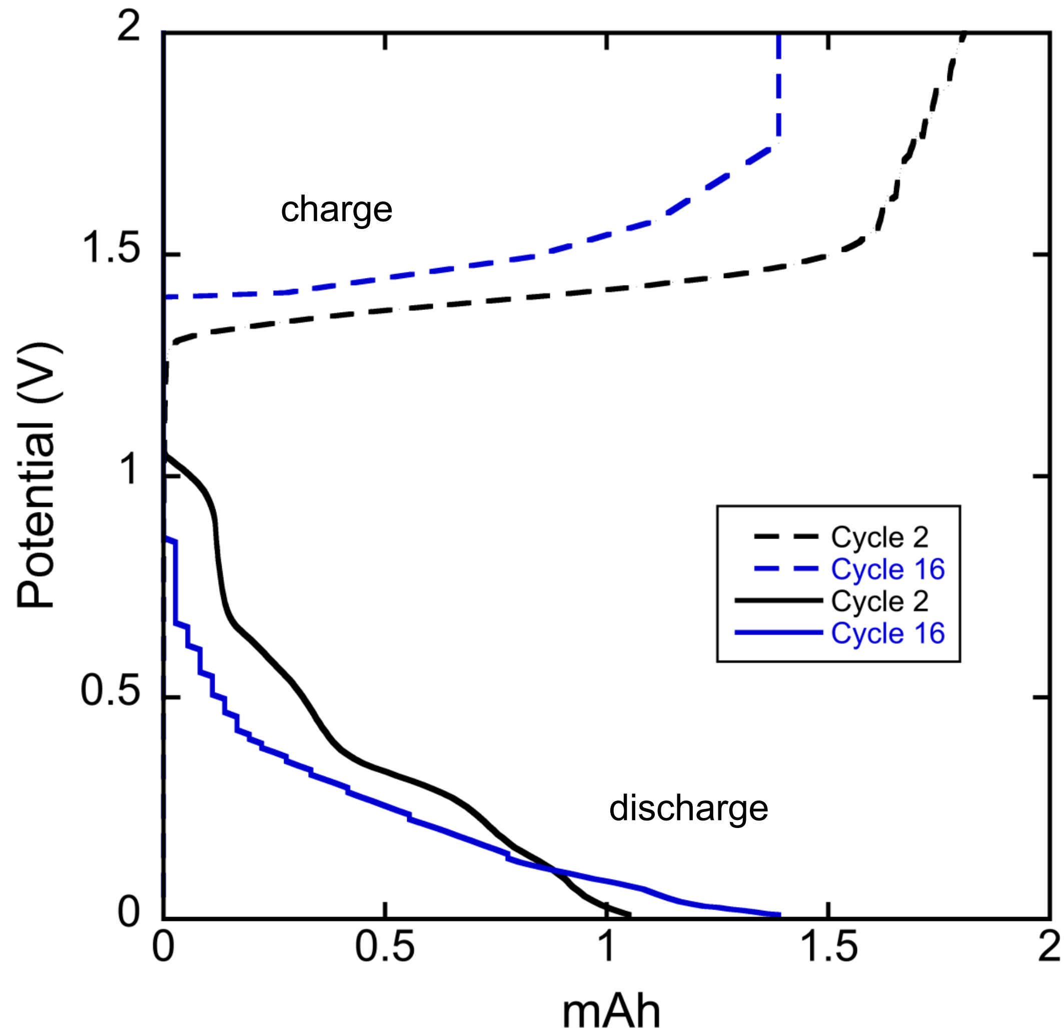
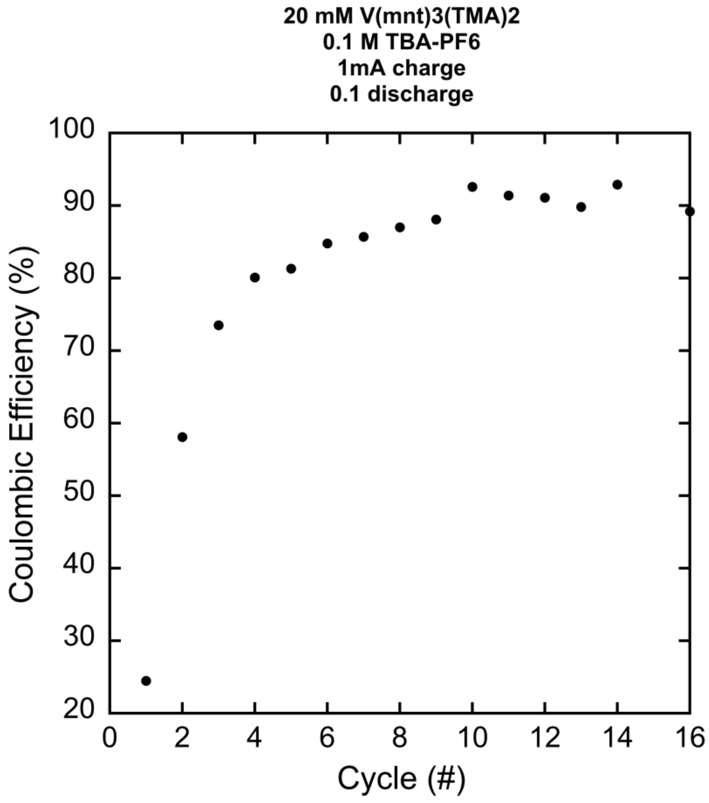
- Static "H-Cell" testing of the $V(mnt)_3^{2-}$ shows stable and flat charge (1 mA) characteristics, discharge (0.1 mA) begins at ~1 V but drops over time
- CV looks good, so gradual drop in discharge voltage is most likely from unoptimized H-Cell geometry and membrane crossover

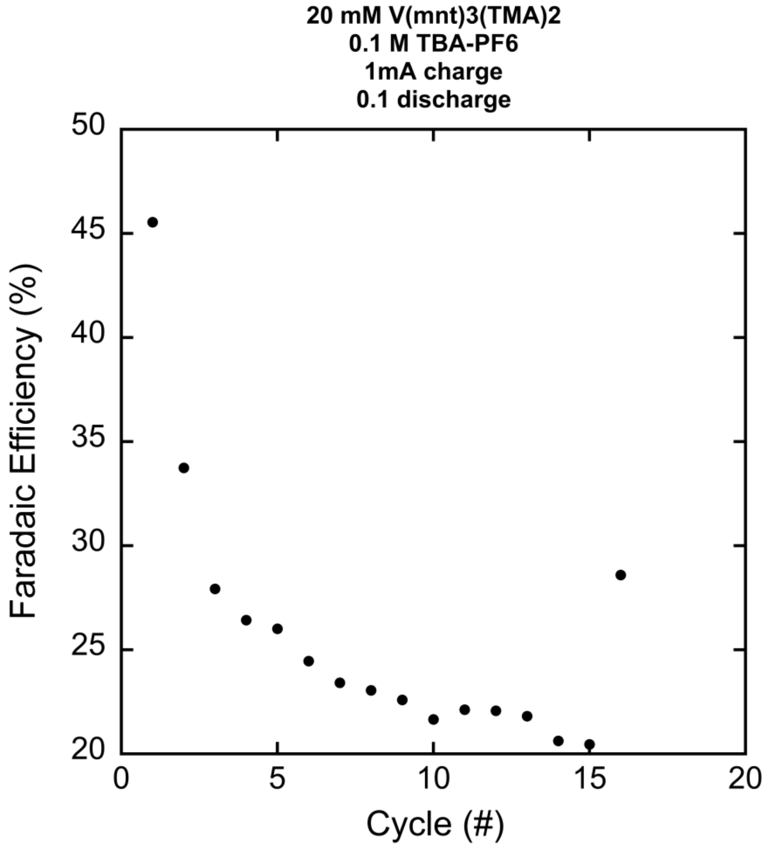




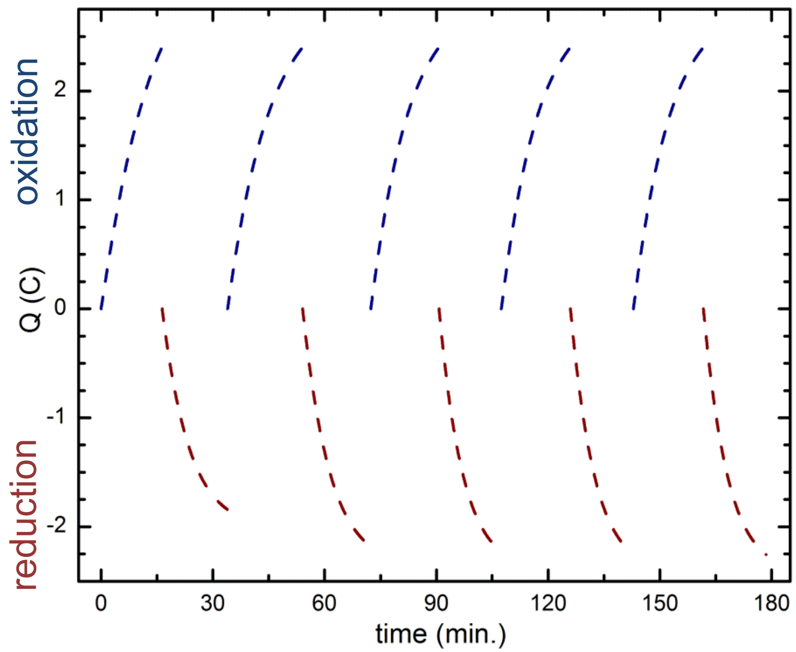
Coulombic and Faradaic Efficiencies

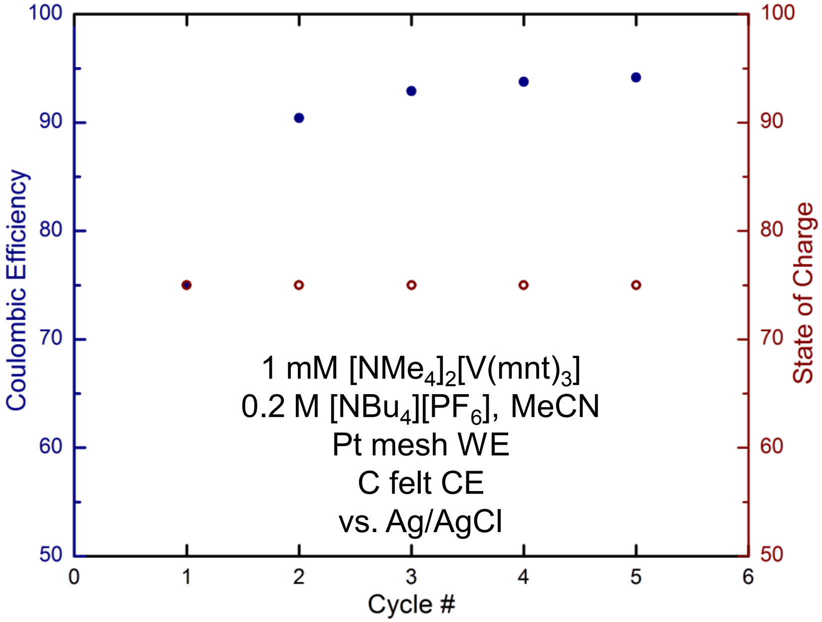
- Coulombic Efficiency reaches ~90% after 15 cycles (membrane and cell conditioning)
- Faradaic Efficiency drops quickly after the first few cycles (high internal resistances, full discharge is not being reached)



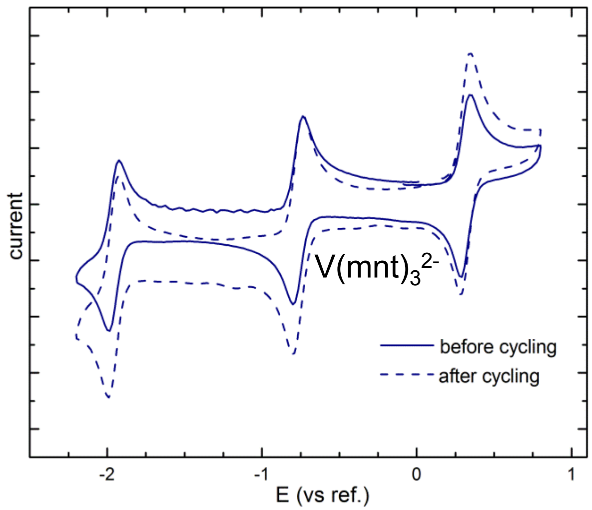


Half Cell Reactions ($V(mnt)_3^{2-} \leftarrow\rightarrow V(mnt)_3^{1-}$)

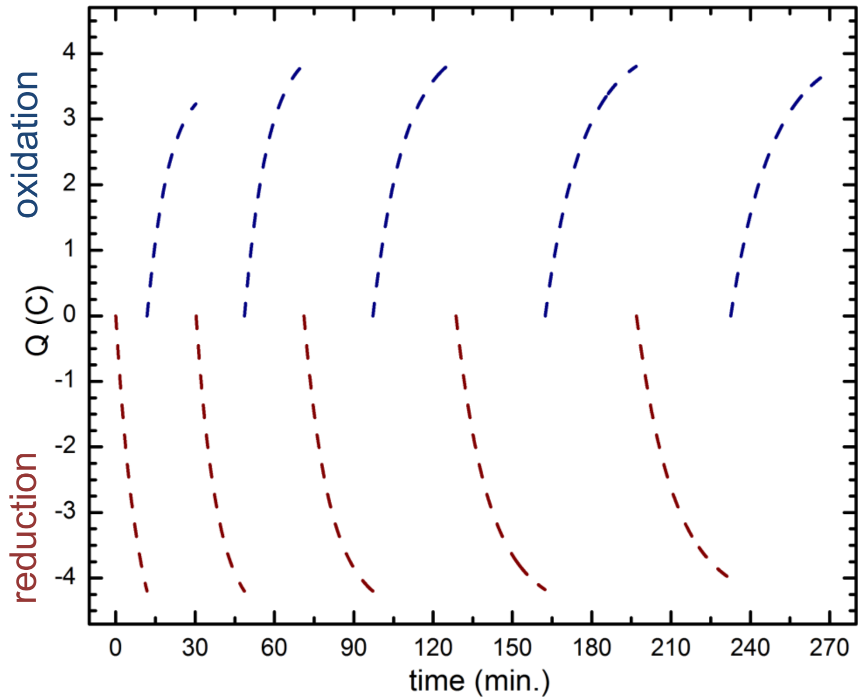


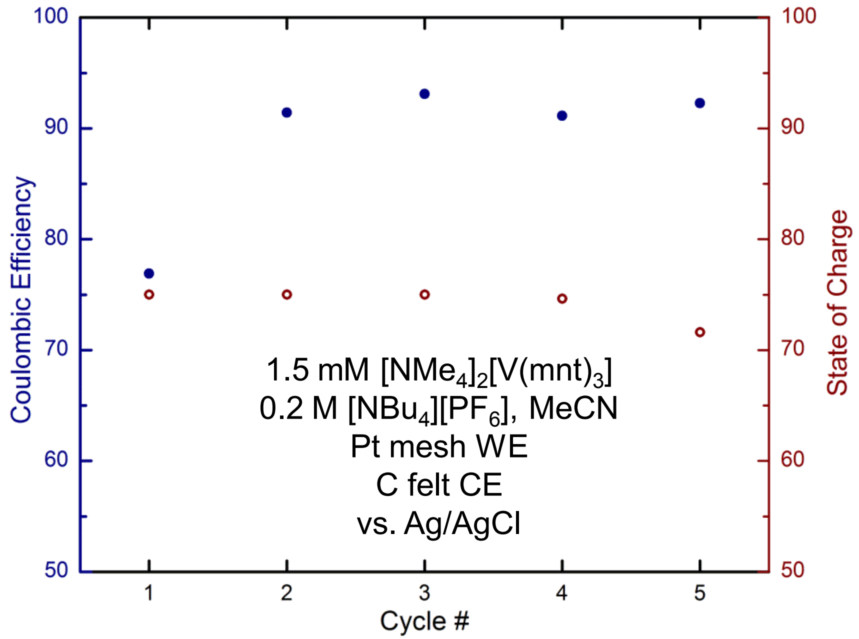


- E_{WE} = 0.5 V, bulk oxidation
- E_{WE} = -0.5 V, bulk reduction
- 75% SOC, 5 cycles
- Approaches 95% CE
- No decomposition observed

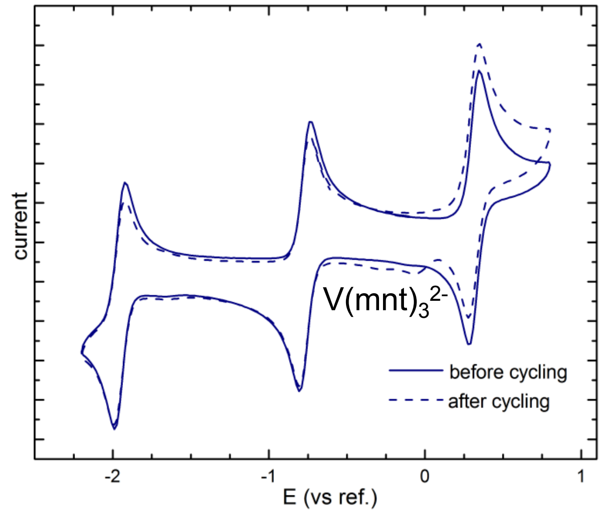


Half Cell Reactions ($V(mnt)_3^{2-} \leftrightarrow V(mnt)_3^{3-}$)

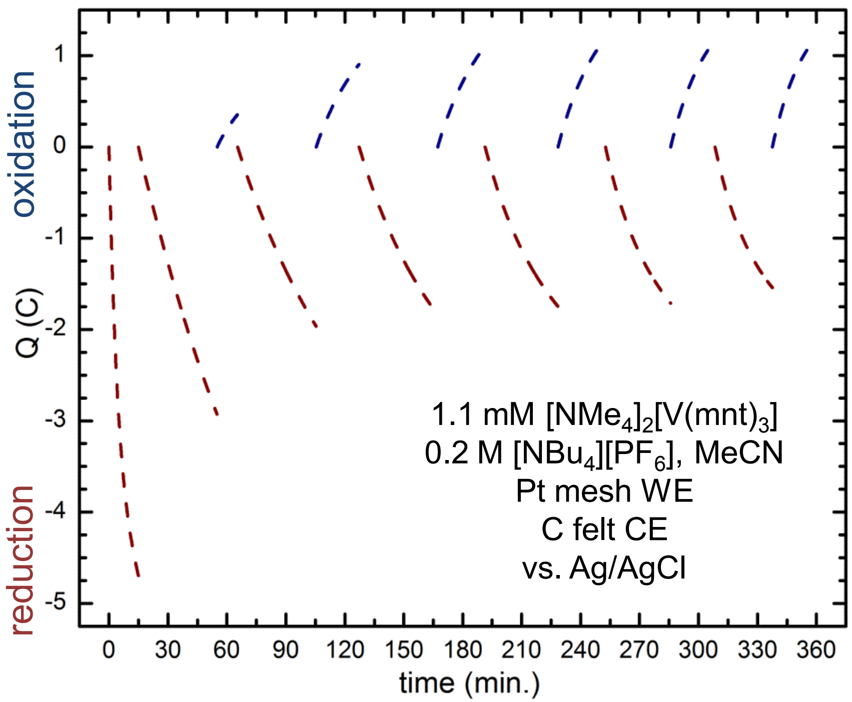


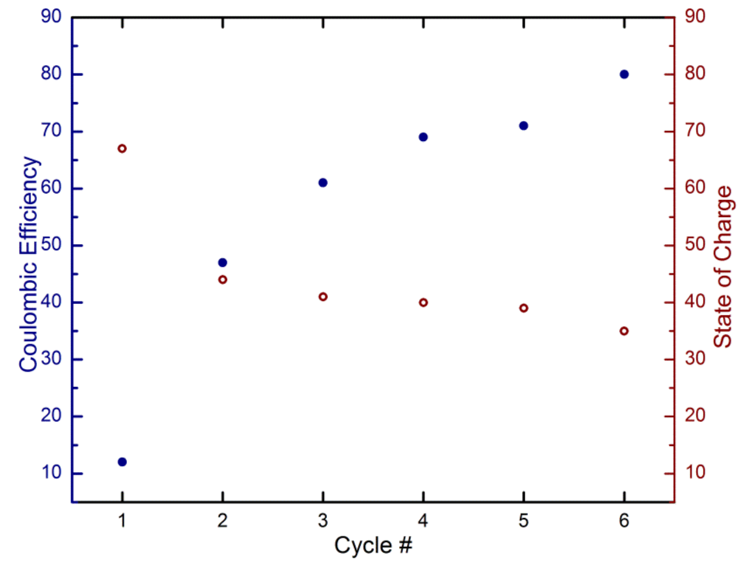


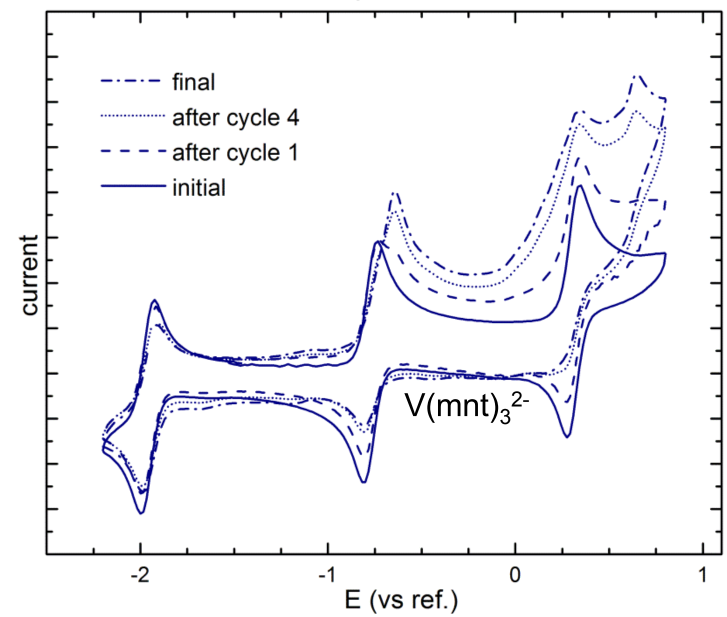
- E_{WE} = -1.2 V, bulk reduction
- E_{WE} = -0.2 V, bulk oxidation
- 75% SOC, 5 cycles
- Approaches >90% CE
- No decomposition observed



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



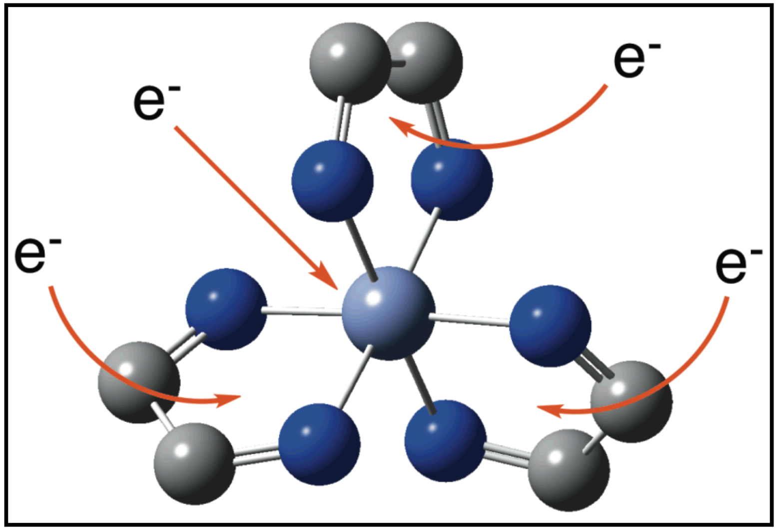




- E_{WE} = -2.2 V, bulk reduction
- E_{WE} = -1.4 V, bulk oxidation
- Lower SOC attained
- Low CE, gradually improves
- decomposition observed

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 $3^-/2^-$ are reversible, efficient
- Some decomposition occurs in cycling $3^-/4^-$ half reaction
- Focus now on cause of irreversibility and elucidating other promising electrolytes



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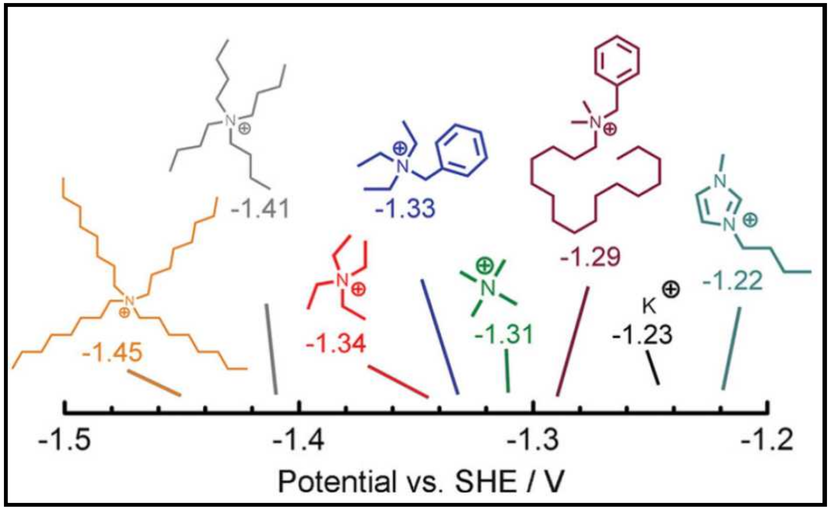

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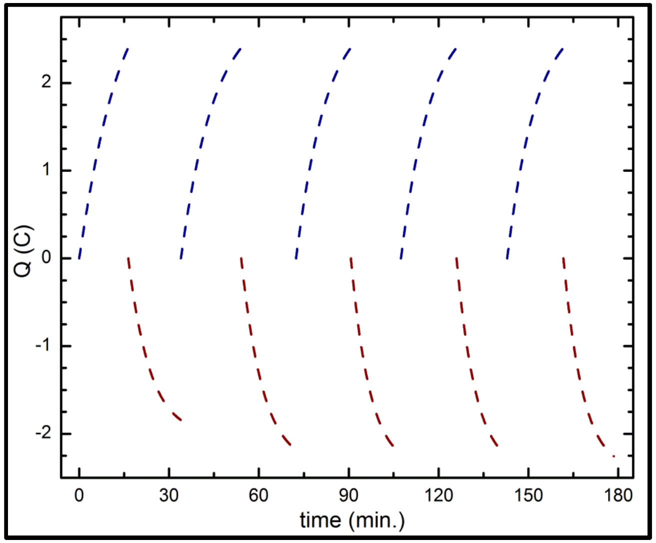

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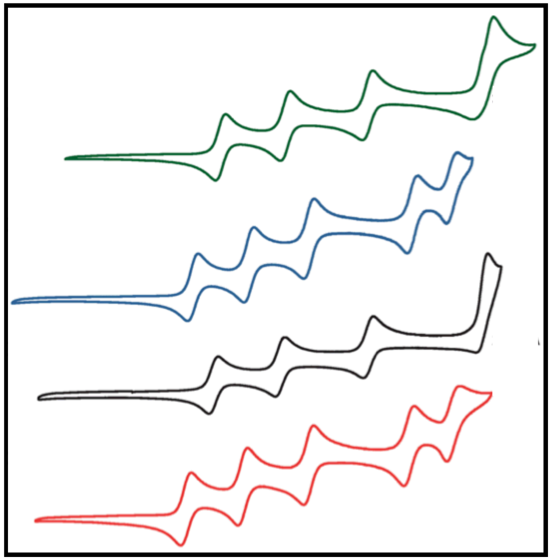

Acknowledgements

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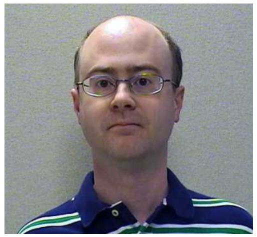
Project PIs:

Mitch Anstey



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