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MetILs^3: A Strategy for Maximizing Energy Density in Flow Battery Electrolytes

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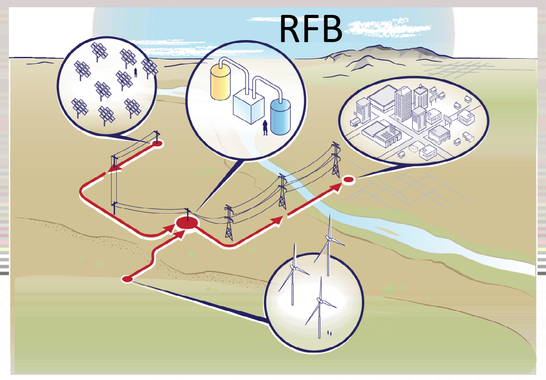
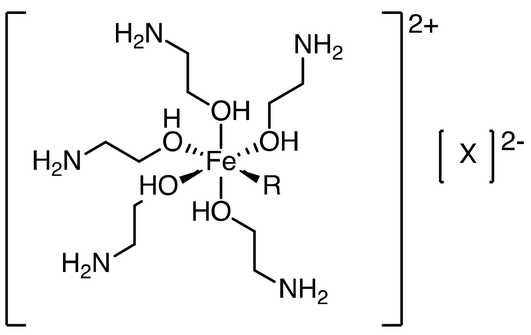
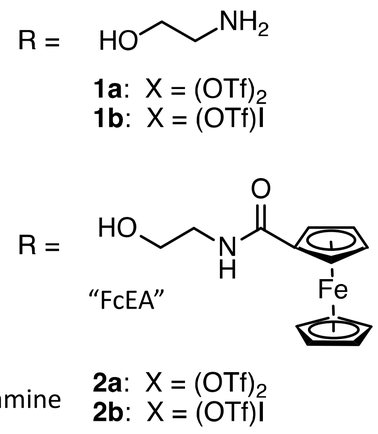
Redox flow batteries (RFBs) offer a readily scalable solution to grid scale energy storage. Nonaqueous RFB chemistries enable higher cell potentials as compared to aqueous systems, but are often limited to solubilities <1 M. To increase the concentration of redox active species, we argue that ***RFB electrolytes should be thought of as electrochemical fuel,*** where as much of the electrolyte as possible is incorporated into the charge storing process.



Our Approach: Start with an inexpensive, redox-active metal ionic liquid (MetIL) and introduce redox activity everywhere: the ion core, ligands, and anions, creating an energy dense MetIL^3.



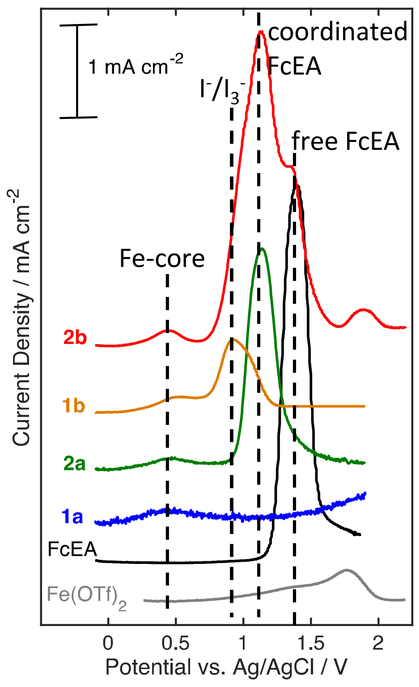
Stoichiometric quantities of iron salts and ethanolamine are simply mixed, then briefly heated to 150 °C.



Composition	Density (g cm^{-3})	RAE (mol L^{-1})	T_{melt} / °C	Conductivity at 25 °C (mS cm^{-1})
1a	1.29	1.79	16.4	0.315
2a	1.37	2.94	70.5	(solid)
1b	1.28	3.07	0.9	0.210
2b	1.42	4.16	85.4	(solid)

MetILs^3 with up to **4.16 mol L^{-1}** redox active electrons (RAE) have been synthesized.

Electrochemical Characterization



25 °C , 10 µm carbon fiber working electrode
10 mM active species in 0.5 M LiTFSI in propylene carbonate

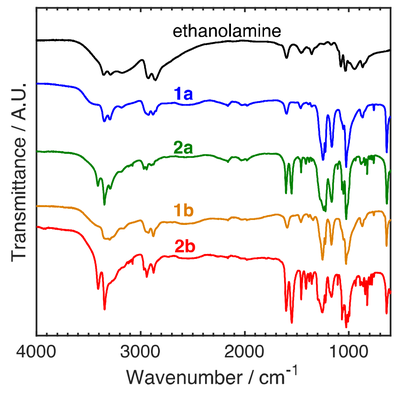
Square wave voltammetry identifies unique redox activity at

Fe-core (all MetILs^3): $Fe^{2+} \rightarrow Fe^{3+} + e^-$
uncoordinated, "free" $Fe(OTf)_2$ E = 1.768 V
coordinated in MetIL^3, E = 0.418 V

Ferrocene ligands FcEA (MetILs **2a**, **2b**) : $Fc \rightarrow Fc^+ + e^-$
uncoordinated, free Fc: E = 1.392 V
Fc coordinated in MetIL^3: E = 1.132 V

Iodide anions (MetILs **1b**, **2b**): $3I^- \rightarrow I_3^- + 2e^-$
E = 0.924 V

IR Spectroscopy



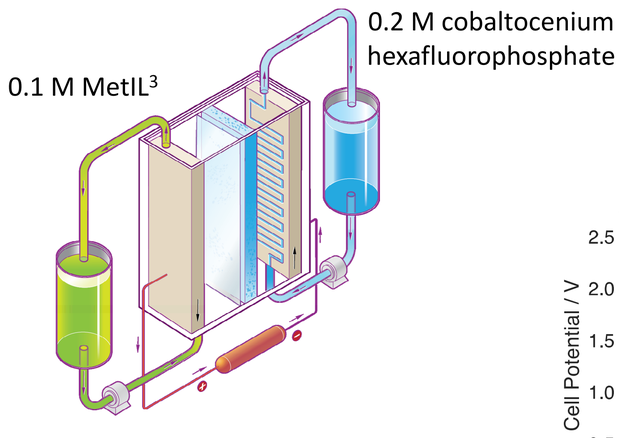
Larger shifts in O-H stretches near 2860 cm^{-1} than N-H stretches near 3354 cm^{-1} suggest coordination of ligand O-H groups to the Fe^{2+} metal center .

Composition	O-H / cm^{-1}	N-H / cm^{-1}
1a	+20	-7
2a	+16	-7
1b	+18	-7
2b	+15	-8

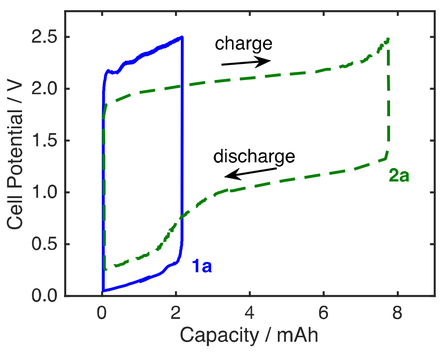
IR peak shifts vs. ethanolamine

Flow Battery Testing

The performance of the original MetIL (**1a**) and the MetIL^3 with ferrocene-containing ligands (**2a**) were compared in a lab-scale flow battery with a cobaltocene anode.

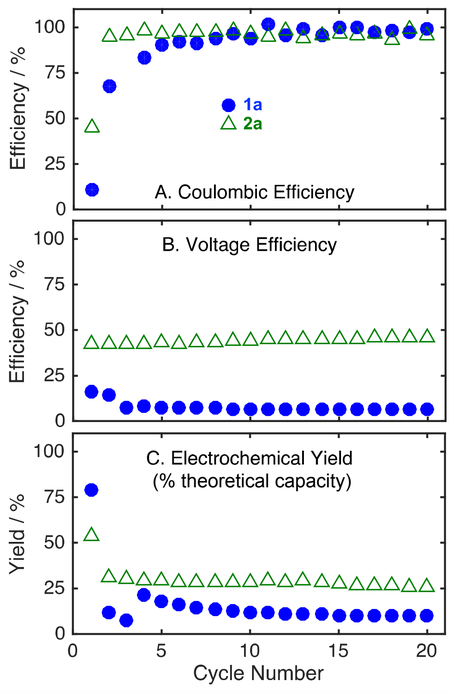


propylene carbonate + 0.5 M TFSI
Fumasep FAP-PK anion exchange membrane
5 mA cm^{-2} using SGD carbon felt electrodes
25 °C



MetIL^3 **2a** increased capacity 4x compared to the original MetIL (**1a**).

MetIL^3 **2a** enabled significantly higher voltage efficiencies and electrochemical yields vs. the original MetIL (**1a**).



MetILs^3 offer the potential to be the solvent, supporting salt, and redox-active species, all in one energy-dense fuel for redox flow batteries.

Acknowledgments
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NNSA National Nuclear Security Administration

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