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Copper Ionic Liquids: A New Approach to Stationary Energy Storage Through Tunable Ion Pairing

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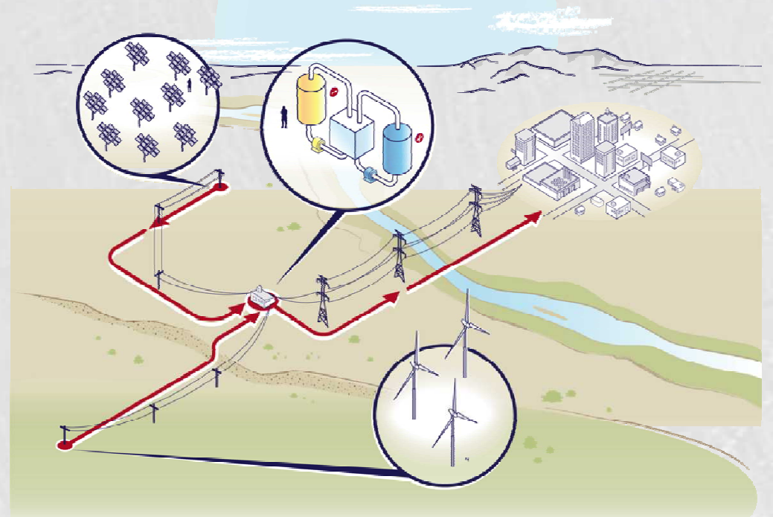
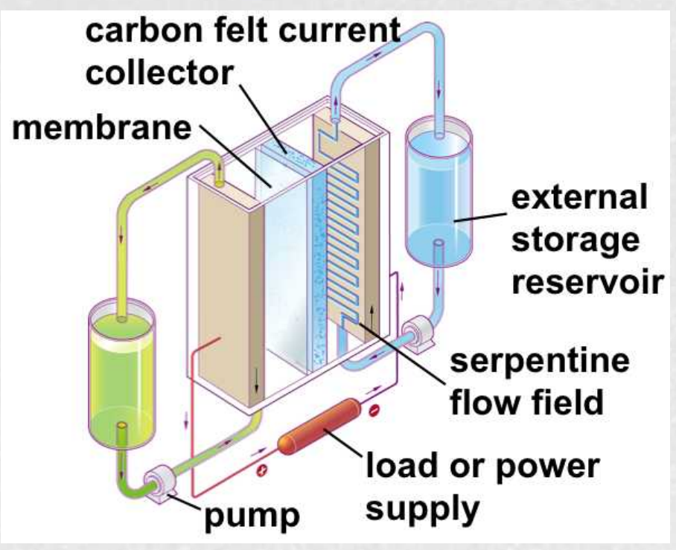
Introduction

The integration of renewable energy sources into the current electricity grid is crucial for a sustainable energy future. However, the intermittent nature of these resources requires the development of large-scale energy storage devices. Redox flow batteries (RFBs) are a promising technology for energy storage that utilize the oxidation and reduction reactions of two redox couples to perform reversible charging and discharging. We are working specifically to create new cathode and anode solutions to increase energy density in RFBs. Current aqueous RFBs show great promise, however these systems are limited by low energy densities. Non-aqueous systems should allow for improved energy density due to the accessibility of wider potential windows. Ionic liquids, including metal-containing compounds (MetILs), are a subset of these solvents that add further value through higher thermal stabilities and negligible vapor pressures.





MetILs

It is well established that the ligand can have a considerable affect on the physicochemical properties (viscosity, conductivity, and electrochemical reversibility), but we recently reported the role of the anion in fine tailoring the chemistry of copper (II)-based MetILs.

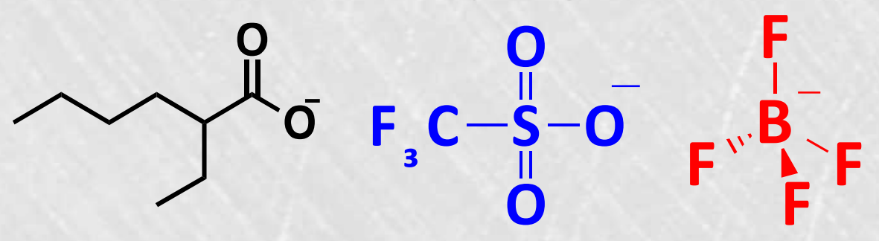
Role of the Anion

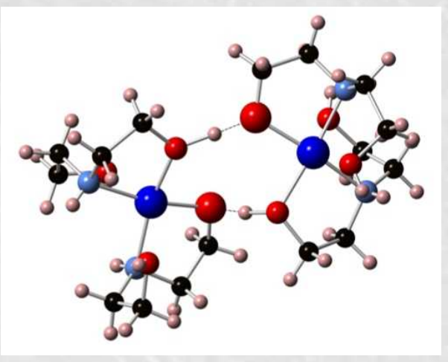
In order to identify the influence of ion pairing more closely, we have synthesized a family of copper(II)-based materials containing various combinations of 2-ethylhexanoate, tetrafluoroborate, and/or triflate. The complexes that contained tetrafluoroborate displayed the best physicochemical properties to date. Interestingly, the triflate anion pairs the strongest and shows less reversible electrochemistry and higher viscosity.

Ligands

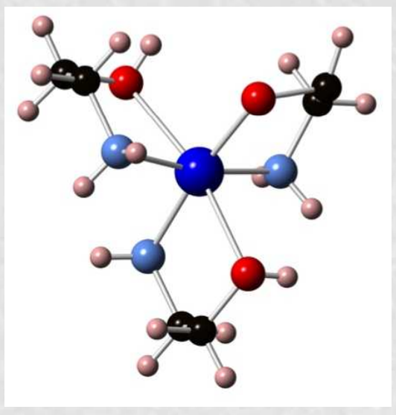
EA ethanolamine
DEA diethanolamine

Anions





Cu(DEA)$_2$



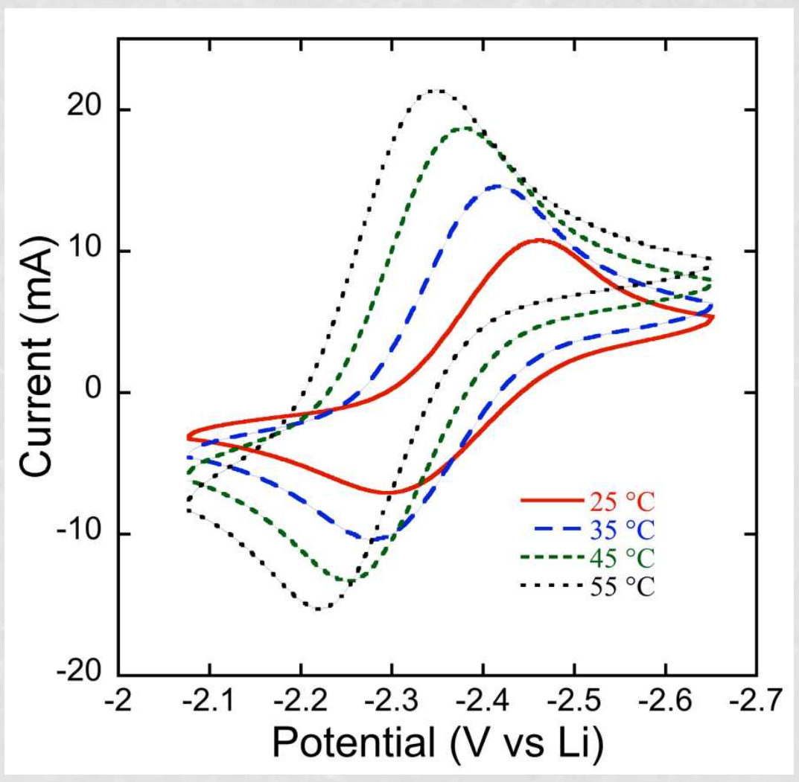
Cu(EA)$_3$

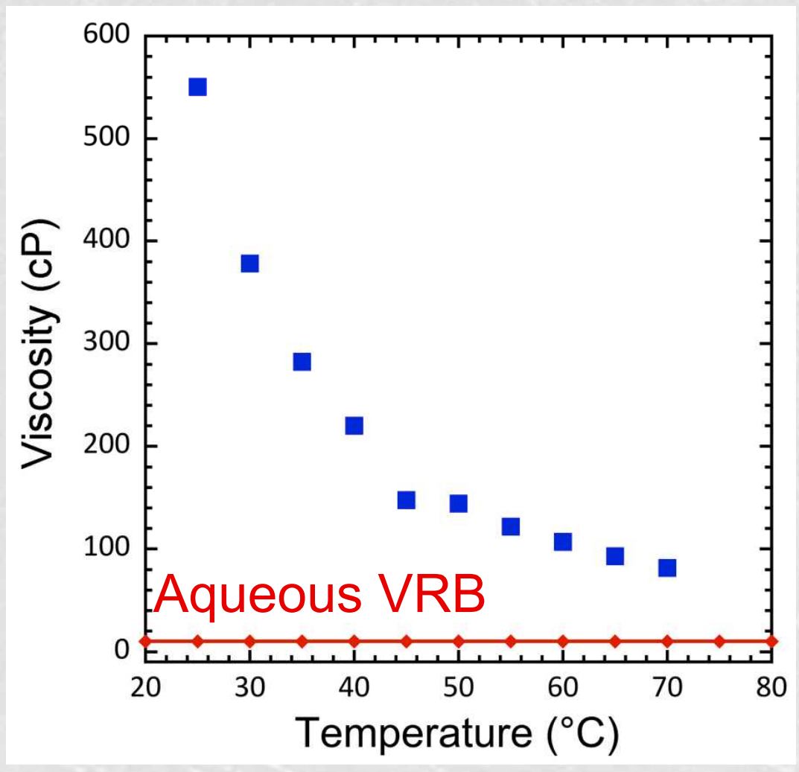
Ligand	Anion 1	Anion 2	State at 25 °C	σ [mS/cm]	ΔE [mV]
EA	⬛	⬛	Liquid	0.207	244
EA	🟦	🟦	Solid	---	158
EA	⬛	🟦	Solid	---	158
EA	🟥	🟥	Liquid	6.80	102
EA	🟥	🟦	Solid	---	256
EA	🟥	⬛	Liquid	0.586	187
DEA	⬛	⬛	Liquid	0.014	522
DEA	🟦	🟦	Liquid	0.067	566
DEA	⬛	🟦	Solid	---	507
DEA	🟥	🟥	Liquid	1.05	150
DEA	🟥	🟦	Liquid	0.210	159
DEA	🟥	⬛	Liquid	0.142	201

Pratt, Leonard, Steele, Staiger, and Anderson, *Inorg. Chim. Acta.* **2013**, 78.

Temperature Dependence

Due to the high viscosity of these particular compounds, variable temperature studies were conducted to see if slightly higher temperatures would improve their properties. A slight increase in reversibility is observed with increasing temperature, but there is notably improved viscosity.

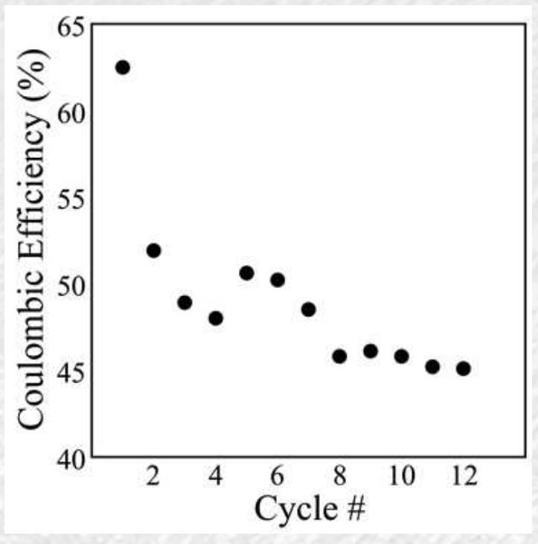


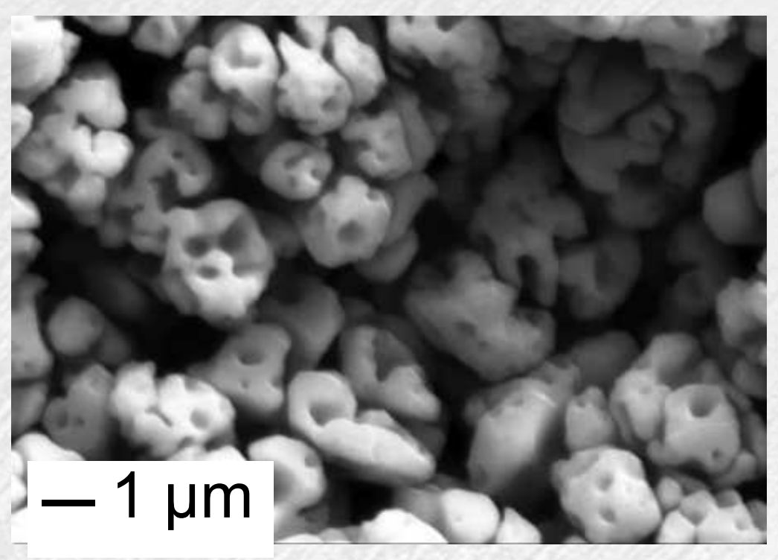


Electrochemical Results

Static Cell Testing

Given the promising reversibility of some of these compounds, an H-Cell consisting of a ferrocene ionic liquid and a copper MetIL was constructed. Copper plating was observed due to the significant over potentials caused by the cell design despite the fact that the intent was only to cycle between copper(I) and (II).



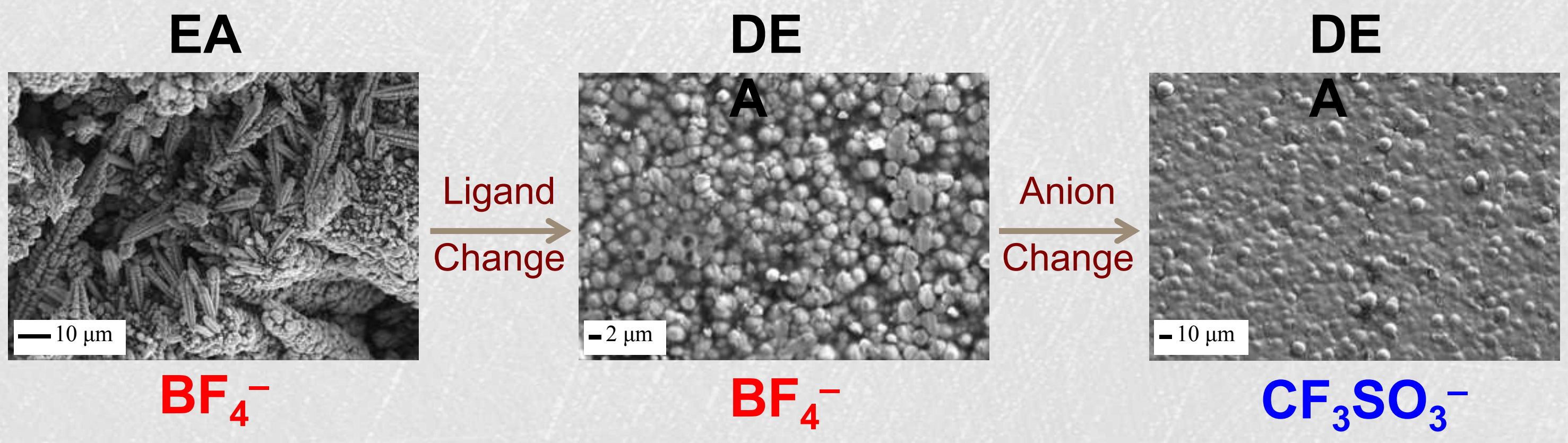


Scanning Electron Microscopy (SEM) of the anode shows copper particles with pitting that suggests partially reversible copper plating and stripping.

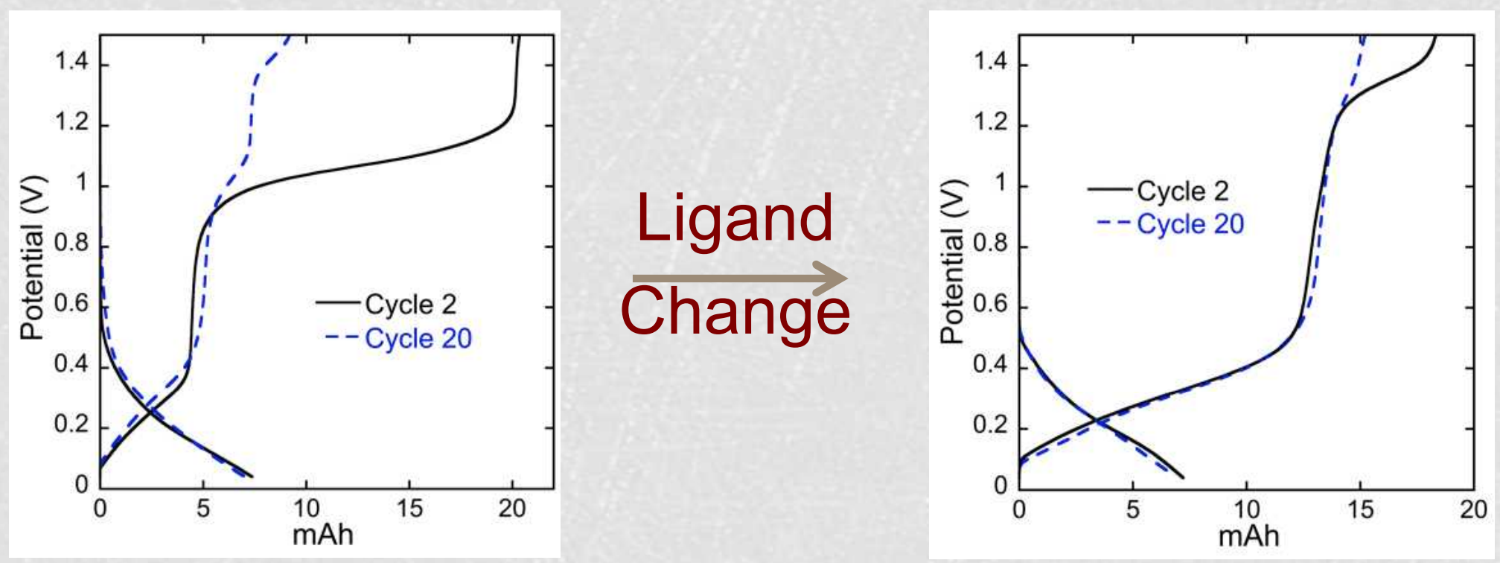
Pratt, Ingersoll, Hudak, McKenzie, and Anderson, *J. Electroanal. Chem.* **2013**, 153.

Electrodeposition Studies

This prompted a reinvestigation of the electrochemistry of the copper MetILs, focusing on the plating and stripping properties of these materials. The resulting SEM studies presented here show that copper plating, as well as dendrite growth, is dependent on the nature of the ligands associated with the metal center and that the anions influence the deposited particle size.



BF_4^- BF_4^- $CF_3SO_3^-$



Significant improvements in the battery performance were achieved by optimizing the ligand and anion choice for the static cell, and three oxidation states of copper have now been utilized.

Conclusions

- A new family of transition metal containing ionic liquids (MetILs) have been synthesized and characterized.
- Ionic liquids containing transition metal elements offer the unique opportunity to have high concentrations of active metal in non-aqueous environments.
- The compounds have been characterized via infrared and UV-vis spectroscopies, and the electrochemical properties have been evaluated using cyclic voltammetry and galvanostatic cycling.
- Static cell testing shows that improvements in performance can be achieved through the judicious choice of ligands and anions.
- Current efforts are focusing on cell engineering to accommodate viscous materials.

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