

# MetILs: A FAMILY OF METAL IONIC LIQUIDS FOR REDOX FLOW BATTERIES

Travis M. Anderson,<sup>1</sup> Harry D. Pratt III,<sup>1</sup> Jonathan C. Leonard,<sup>1</sup>  
Chad L. Staiger,<sup>2</sup> and David Ingersoll<sup>1</sup>

<sup>1</sup>Advanced Power Sources Research and Development,  
Sandia National Laboratories, Albuquerque NM, USA

<sup>2</sup>Materials, Devices, and Energy Technologies,  
Sandia National Laboratories, Albuquerque NM, USA

## ABSTRACT

We present a new family of metal ionic liquids that are synthesized in a single-step reaction from low-cost precursors. The compounds consist of either manganese, iron, cobalt, nickel, copper, zinc, or cerium coordination cations and weakly coordinating anions such as 2-ethylhexanoate, triflate, triflimide, or tetrafluoroborate that may simultaneously act as a solvent and catholyte or anolyte. The results presented highlight the fundamental chemical concepts behind the formation of the materials as well as focus on our systematic improvements in viscosity, conductivity, and electrochemical reversibility.

**Keywords:** ionic liquid, flow battery, high energy density, low-cost energy storage

## INTRODUCTION

Global energy consumption is projected to significantly increase by mid-century, and this increased need will be partially met through the use of renewable energy sources. Due to the intermittent nature of these resources, compatible large-scale energy storage devices must likewise be invented. Simultaneously, the need for grid storage is also being driven by the evolving nature of the grid (green grid, smart grid, and the distributed nature of the grid) as well as by other technological developments including vehicle electrification. Redox flow batteries, a rechargeable system that uses the redox states of various species for charge/discharge purposes, represent a highly promising approach, provided higher energy densities and lower-cost materials can be developed [1].

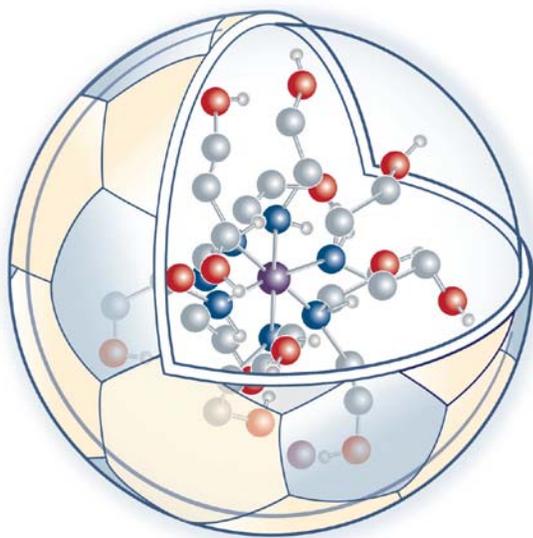
Work was therefore undertaken to advance state-of-the-art materials for flow battery energy storage. We have focused on non-aqueous systems because they potentially offer wider voltage windows, higher charge cycle efficiency, decreased temperature sensitivity, increased cycle life, and in some instances even favorable cost projections. Specifically, we have invented a method for synthesizing low-cost ionic liquids (ILs) with reducing-oxidizing (redox) transition metal species for incorporation into a flow cell configuration, relying on the difference in redox

potentials of two different ILs to establish the cell voltage. The ionically conductive ILs act as both electrolyte and active material, and, since they have no vapor pressure, ameliorate safety issues related to cell pressurization.

## DESCRIPTION

The transition-metal-based ionic liquid (MetIL) electrolytes are prepared in a single step simply by heating metal salts with an appropriate combination of ligands (typically aminoalcohols). The synthesis is highly scalable and facilitates molecular-level engineering of many of the physicochemical properties of the MetILs. To date we have examined over 100 possible metal salt/ligand combinations, of which approximately 20 look promising.

Our focus has primarily been on large asymmetric cations to help lower the melting point. By modifying the symmetry of transition-metal-based coordination cations with polarizable amine and hydroxyl groups, we have created an electronically asymmetric secondary coordination sphere illustrated in Figure 1 that perturbs ion pairing. The partial positive and negative charges are sufficiently distributed to limit interaction with an anion while simultaneously keeping electrons sufficiently mobile to either add charge to or remove charge from the metal ion at the center of the complex.



**Fig. 1.** Three-dimensional ball-and-stick notation of a representative MetIL cation illustrating the partial positive and negative charge distribution in the secondary coordination sphere.

### PERFORMANCE DATA

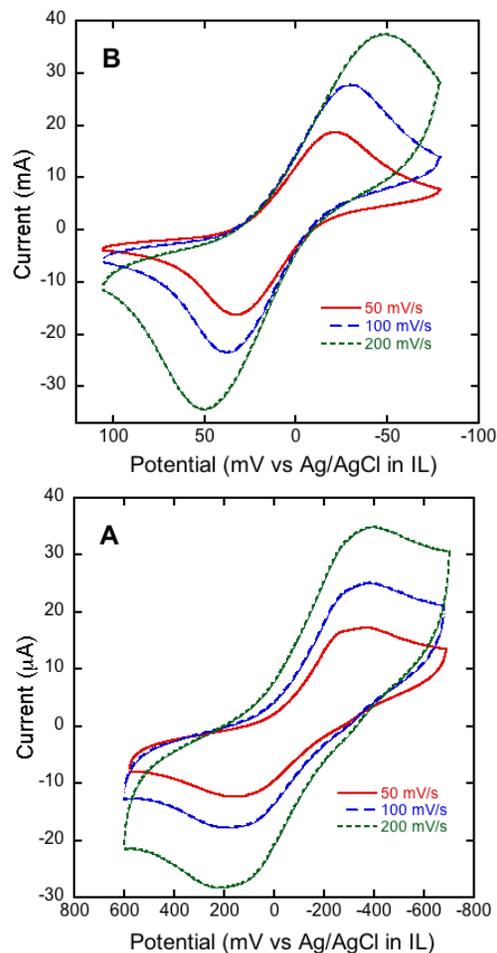
Table 1 gives the complete molecular formulas for 10 representative MetILs. In 2010, we published a proof-of-concept paper focusing on one MetIL, Fe{NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>}<sub>6</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub> [2]. Cyclic voltammograms (at varying scan rates) for this compound are illustrated in Figure 2A. The high viscosity and low conductivity of this compound prevented the direct acquisition of electrochemical data. As a result, measurements were performed by dissolving the iron IL in another more conductive (and conventional) IL. The complex displays several quasi-reversible waves attributed to Fe(III)/Fe(II) reduction and re-oxidation.

**Table 1.** Molecular formulas of 10 representative MetILs.

|   |
|---|
| Ce{NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH} <sub>8</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>3</sub>   |
| Cu{NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH} <sub>6</sub> [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )CO <sub>2</sub> ] <sub>2</sub>   |
| Cu{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )CO <sub>2</sub> ] <sub>2</sub> |
| Cu{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub>   |
| Cu{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sub>2</sub>  |
| Cu{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [BF <sub>4</sub> ] <sub>2</sub>   |
| Co{NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH} <sub>6</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub>   |
| Fe{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>3</sub>   |
| Mn{NH(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> } <sub>6</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub>   |
| Ni{NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH} <sub>8</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>3</sub>   |
| Zn{NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH} <sub>6</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub>   |

In contrast to the iron IL, a manganese compound, Mn{NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>}<sub>6</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>, was

prepared that displays fully reversible Mn(II)/Mn(III) oxidation and re-reduction (Figure 2B, at 50 mV/s scan rate and dissolved in the more conductive IL) [3]. This compound also displays improved conductivity over the iron IL, but the viscosity (~12000 cP) is not practical for a flow cell. Although both the manganese and iron ILs consist of dihydroxyamine ligands and triflate anions, infrared data indicate that the iron preferentially coordinates through the hydroxyl groups whereas manganese coordinates through the amine.

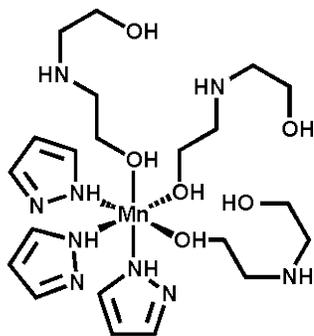


**Fig. 2.** Cyclic voltammograms of the iron (A) and manganese (B) ILs dissolved in a more conductive IL at various scan rates; the working electrode is glassy carbon and the counter electrode is platinum.

A number of copper ionic liquids have also been synthesized. The low symmetry of the tetragonally distorted d<sup>9</sup> Cu(II) cation makes it particularly amenable to the modification of select physicochemical properties (including viscosity and conductivity). However, reduction of Cu(II) to Cu(I)

results in an energy-consuming geometry change that makes it challenging to obtain reversible electrochemistry.

We have also recently prepared compounds containing either Co(II), Ni(II), Zn(II), or Ce(III). By far the most promising compound in terms of viscosity and conductivity was the cerium IL,  $\text{Ce}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_8[\text{CF}_3\text{SO}_3]_3$ . This is most likely attributed in part to the expanded coordination number of cerium (eight-coordinate) in contrast to the six-coordinate iron or manganese, for example. In addition, the Shannon-Prewitt ionic radius of eight-coordinate Ce(III) is 114 picometers, nearly double that of most first-row transition metals [4]. However, the high cost of cerium and the poor reversibility of the Ce(III)/Ce(IV) redox couple has prompted us to return focus to first-row metals with the caveat that emphasis be placed on expanded coordination and larger/bulkier ligands (including some aromatics) that can effectively increase the net radius of the coordination complex. The structure of one such representative compound is shown in Figure 3.



**Fig. 3. Representative MetIL cation containing bulkier aromatic and hydroxamine ligands.**

## SUMMARY

A new family of redox-active ionic liquids for flow battery applications has been developed by Sandia National Laboratories. Most compounds are quite inexpensive to produce and some show promising viscosity, conductivity, or electrochemical reversibility. New compounds are continuing to be developed and tested, and cell test data are forthcoming.

## REFERENCES

- [1] M. Skyllas-Kazacos, M.H. Chakrabarti, S.A. Hajimolana, F.S. Mjalli, and M. Saleem, "Progress in Flow Battery Research and Development," *J. Electrochem. Soc.* **158**, Issue 8, 2011, pp. R55-R7.
- [2] T.M. Anderson, D. Ingersoll, A.J. Rose, C.L. Staiger, and J. C. Leonard, "Synthesis of an ionic liquid with an iron coordination cation," *Dalton Trans.* **39**, Issue 37, 2010, pp. 8609-8612.
- [3] H.D. Pratt III, A.J. Rose, C.L. Staiger, D. Ingersoll, and T.M. Anderson, "Synthesis and characterization of ionic liquids containing copper, manganese, or zinc coordination cations," *Dalton Trans.* 2011.
- [4] R.D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.* **A32**, 1976, pp. 751-767.

## BIOGRAPHICAL NOTE



**Conference presenter:** Travis M. Anderson (Ph.D., Emory University, 2002) is a staff member in Sandia National Laboratories' Advanced Power Sources Research and Development group. His research interests focus around the synthesis and characterization of redox-active coordination complexes, flow batteries, and thermal battery aging.

