

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

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We present a new family of metal based ionic liquids (MetILs) for use in flow battery applications. These materials are synthesized in a single step by simply heating a metal salt in the presence of a ligand containing multiple polarizable functional groups. The utility of this reaction has allowed a wide range of metal cation, anion and ligand combinations to be prepared and electrochemically characterized. Compounds consisting of manganese, iron, cobalt, nickel, copper, zinc, or cerium coordination cations and weakly coordinating anions such as 2-ethylhexanoate, triflate, triflimide have been combined with alkanolamines to give room temperature ionic liquids. These ionically conductive materials act as both electrolyte and as the electroactive, charge storing, species. The results presented highlight the fundamental chemical concepts behind the formation of the materials as well as focus on physical and electrochemical properties.

**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 met through the construction of new power generation facilities. Many of these new facilities around the world will produce power from traditional energy resources such as coal, natural gas and nuclear. However, regulatory factors and environmental concerns will also increase the percentage of power generation from renewable resources including wind and solar.

With the increasing penetration of renewable energy into the grid, the effects of evolving an electrical grid from one of large plants producing constant quantities of power to a distributed grid that integrates power generation at many different scales, efficiencies and intermittencies is only beginning to be understood. A general consensus has emerged that some form of energy storage will be required to maintain grid efficiency, reliability and security.

Energy storage for renewable energy sources allows the storage of energy for times when demand is high (peak shaving) or to lessen the impact changing light and/or weather conditions (load leveling). A number of technologies based on electrical, chemical, electrochemical, and mechanical processes have been proposed to address the energy storage needs of an electrical grid with a high percentage of renewable energy sources.[1, 2]

Among the many types of energy storage systems, reducing-oxidizing (redox) flow batteries have emerged as a promising approach to fill the technology gap.[3, 4] Redox flow batteries are a type of rechargeable electrochemical system that relies on the redox states of various species for the purposes of storing energy. A schematic representation of a flow battery is depicted in Fig. 1. The electroactive species, anolyte and catholyte, are liquids held in tanks. Charging and discharging of this battery happens through a redox process in the cell. An appealing property of this type of battery, in addition to its rapid charge/discharge ability, is its scalability. To increase the energy stored in this system requires one to simply increase the size of the anolyte and catholyte tanks. Likewise, increasing the power output of

the flow battery only necessitates the addition of more cells. While redox flow batteries have many positive attributes, widespread deployment of the technology has not occurred. Concerns over charge cycle efficiencies, low energy densities, raw material costs, cross contamination of anolyte and catholyte and corrosiveness/safety issues have contributed to an unacceptably high cost per kWh.

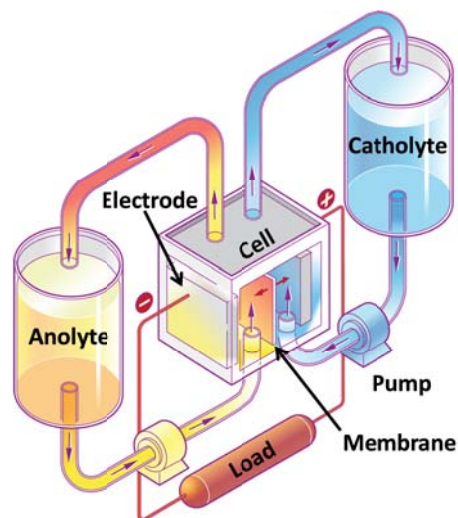


Fig. 1. Schematic of a redox flow battery.

A small, but growing area of research in redox flow batteries is directed toward developing non-aqueous electrolytes. Non-aqueous electrolytes address the shortcomings of current systems by potentially offering wider voltage windows, higher charge cycle efficiency, decreased temperature sensitivity, and increased cycle life. Metal (Cr, Mn, Ru, U, V)  $\beta$ -diketonates with an tetraalkylammonium salt in an organic solvent (namely acetonitrile, MeCN) have been investigated for use as electrolytes in a flow battery system.[5-9] Cell potentials ( $E_{\text{cell}}$ ) greater than 1.3 V ( $E_{\text{cell}}$  value for aqueous vanadium redox battery) were obtained in the non-aqueous Cr, Ru and V systems. Rubrene, an organic molecule that can have multiple oxidation states, in

MeCN was briefly investigated.[5] Despite a favorable cell potential and good electrochemical reversibility, its poor solubility in MeCN and material costs will likely limit its utility. Coordination compounds containing a metal salt complexed to a nitrogen containing ligand (i.e. 2,2'-bipyridine, alkyldiamine, etc.) were recently examined for use in a redox flow battery applications.[10-13] Cell potentials up to 2.4 V in an organic solvent (MeCN or propylene carbonate) with a supporting electrolyte were obtained. Charge/discharge efficiencies of some batteries after repeated cycling were above 80%, however energy capacity decreased with cycling.[13]

## DESCRIPTION

We have focused on research and development efforts on non-aqueous systems as well because of the aforementioned operational advantages and potential for reduced cost. Specifically, we have invented a method for synthesizing low-cost ionic liquids (ILs) with 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 very low vapor pressure, ameliorate safety issues related to cell pressurization.

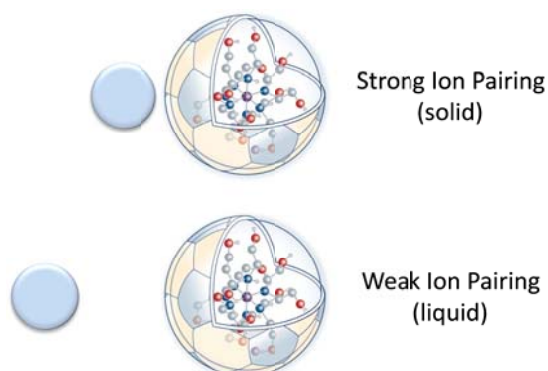


Fig. 2. Effects of ion pairing on material properties. The MetIL cation is represented by a three dimensional ball-and-stick notation illustrating the partial positive and negative charge distribution in the secondary coordination sphere. The light blue sphere represents the anion.

Our focus has primarily been on large asymmetric cations to help depress 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 Fig. 2 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.

An iron based MetIL was initially prepared and characterized to demonstrate the concept.[14] To prepare this MetIL, iron (III) triflate  $[\text{Fe}(\text{OTf})_3]$  was heated with six equivalents of diethanolamine (DEA) to give a pure viscous liquid,  $\text{Fe}(\text{DEA})_6(\text{OTf})_3$ . Electrochemical studies revealed several quasi-reversible waves attributed to  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  reduction and re-oxidation of  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$ . However the

high viscosity and poor conductivity of this material prevent the direct use of this material in a flow battery.

The promising results obtained from  $\text{Fe}(\text{DEA})_6(\text{OTf})_3$  prompted an investigation into other cation/anion/ligand combinations for improved electrochemical reversibility, improved conductivity and lower viscosity.[15] Copper, manganese and zinc containing MetILs were prepared and characterized for use in a flow battery application.  $\text{Cu}(\text{DEA})_6(\text{NTf}_2)_2$  ( $\text{NTf}_2$  = triflimide) and  $\text{Mn}(\text{DEA})_6(\text{OTf})_2$  displayed orders of magnitude better conductivity than  $\text{Fe}(\text{DEA})_6(\text{OTf})_3$ . The  $\text{Cu}(\text{II})/\text{Cu}(\text{I})$  redox couple for  $\text{Cu}(\text{DEA})_6(\text{NTf}_2)_2$  was shown to be quasi reversible using cyclic voltammetry (CV). The  $\text{Mn}(\text{III})/\text{Mn}(\text{II})$  redox couple for  $\text{Mn}(\text{DEA})_6(\text{OTf})_2$  was found to be fully reversible. The improved electrochemical properties of the MetIL compounds, however, were offset by undesirably high viscosities ( $> 1000$  cP at  $25^\circ\text{C}$ ).

## MATERIALS & METHODS

All starting materials were purchased from Aldrich, Strem or Alfa Aesar and used as received. Viscosity measurements were performed on a Brookfield DV-II +Pro viscometer. Cyclic voltammograms (CVs) were collected in a glove box under Ar using a BAS100B potentiostat in a three-electrode cell. The working electrode was a freshly polished 3 mm diameter glassy carbon, 1.6 mm diameter Au or 1.6 mm diameter Pt. A Pt wire was used as a counter electrode and the reference electrode was  $\text{Ag}/\text{AgCl}$  in 1-ethyl-3-methyl-imidazolium chloride (EMIC) in 1, 2-dimethyl-3-propyl-imidazolium bis(trifluoromethylsulfonyl) imide (DMPI-Im). Conductivity measurements were made using a Solartron 1255B frequency analyzer with a SI 1287 electrochemical potentiostat. The custom sample cell had a ~5 mm in diameter Pt working and Pt counter electrodes in a co-facial arrangement. This cell had a cell constant of ~10, as determined by measuring a solution of known specific conductance. A Tenney environmental chamber was used to maintain precise control over the sample and cell temperatures.

## PERFORMANCE DATA

### Synthesis and Cost

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 alkanolamines). The synthesis is highly scalable and facilitates molecular-level engineering of many of the physicochemical properties of the MetILs. To date we have examined close to two hundred possible metal salt/ligand combinations. Table 1 gives a representative sample of MetILs prepared to date.

Table 1. Molecular formulas of ten representative MetILs. (EA = ethanolamine, EHN = 2-ethylhexanoate,  $\text{NTf}_2$  = triflimide, OAc = acetate, OTf = triflate)

$\text{Ce}(\text{EA})_8(\text{OTf})_3$	$\text{Co}(\text{EA})_6(\text{OTf})_2$
$\text{Cu}(\text{DEA})_6(\text{EHN})_2$	$\text{Fe}(\text{DEA})_6(\text{OTf})_3$
$\text{Cu}(\text{DEA})_6(\text{OAc})_2$	$\text{Mn}(\text{DEA})_6(\text{OTf})_2$
$\text{Cu}(\text{DEA})_6(\text{OTf})_2$	$\text{Ni}(\text{EA})_8(\text{OTf})_3$
$\text{Cu}(\text{DEA})_6(\text{NTf}_2)_2$	$\text{Zn}(\text{EA})_6(\text{OTf})_2$

Since the MetIL compound represents both electrolyte and the energy storing (electroactive) species, the opportunity to achieve high energy densities is possible. Currently, MetIL compounds in our library have electroactive species (metal) concentrations on the order of 1.6 M. These concentrations are low compared to what is currently achievable in aqueous vanadium redox battery chemistries, which is up to 2.5 M vanadium.[16] However, higher energy densities are achievable by decreasing the molar volume of the MetIL through the use of smaller ligands, anions, and/or cations. Calculations of some theoretical MetIL compounds have shown metal concentrations up to 6.5 M are possible. Utilization of metals that can accommodate multi-electron processes (i.e. Mn, V, Cr, etc.) is also a path forward to high energy densities.

Increases in energy density should directly translate to lower capital costs. A MetIL based flow battery is attractive technology to achieve aggressive capital cost goals of \$100 /kWh. Ligands such as ethanolamine and diethanolamine are readily available in multi-ton quantities because of current applications in gas treatment, personal care and agricultural industries.[17] Most metal salts, particularly copper ones, are also readily available and low cost.

## Electrochemistry

Initially the most promising compound in terms of viscosity and conductivity was the cerium IL,  $\text{Ce}(\text{EA})_6(\text{OTf})_3$ . 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  $\text{Ce}(\text{III})$  is 114 picometers, nearly double that of most first-row transition metals.[18] However, the high cost of cerium and the poor reversibility of the  $\text{Ce}(\text{III})/\text{Ce}(\text{IV})$  redox couple ( $\sim 600$  mV) prompted us to return focus to first-row metals.

One of the more productive families of MetIL materials are those based on copper. The low symmetry of the tetragonally-distorted  $d^9$   $\text{Cu}(\text{II})$  cation makes it particularly amenable to the modification of select physicochemical properties (including viscosity and conductivity). The reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$  can result in an energy consuming change from octahedral to tetrahedral geometry. Despite this however, several copper MetILs have shown good electrochemical reversibility and conductivity.

For electrochemical studies the typically high viscosities of MetILs necessitate their dilution in 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $\text{BMIM-PF}_6$ ).  $\text{BMIM-PF}_6$  was chosen so as to minimize solvent/coordination effects. The absence of vibrational frequency shifts in the FTIR when  $\text{BMIM-PF}_6$  was used as a MetIL solvent confirmed its non-interfering nature. A CV of  $\text{Cu}(\text{DEA})_6(\text{EHN})_2$ , shown in Fig 3a, demonstrates the utility of MetILs in electrochemical processes. The peak currents increase approximately with the square root of the scan rate, suggesting a diffusion limited electrochemical redox process. Table 2 summarizes the anodic and cathodic peak separation for  $\text{Cu}(\text{DEA})_6(\text{EHN})_2$  at various scan rates. The electrochemical reversibility of  $\text{Cu}(\text{DEA})_6(\text{EHN})_2$  is poor with  $\text{Cu}(\text{I})/\text{Cu}(\text{II})$  peaks separated by more than 500 mV. The 500+ mV peak separation is likely due in part to the high viscosity and low conductivity of the system.

To determine the effects of the electrode and solvent on our electrochemical system, a ferrocene standard was run. The ferrocene/ferrocenium redox couple is known to be fully

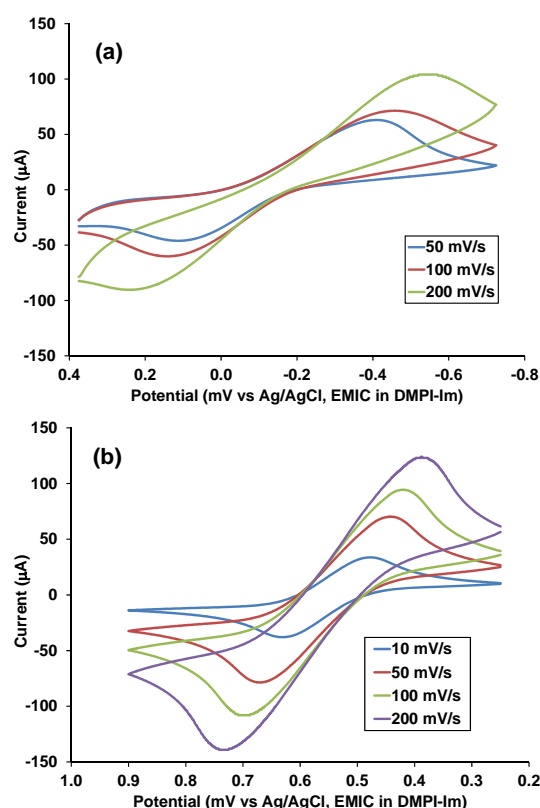


Fig. 3. CVs of  $\text{Cu}(\text{DEA})_6(\text{EHN})_2$  (a) and ferrocene (b). Both compounds were diluted in  $\text{BMIM-PF}_6$  prior to analysis and the CVs were collected using a glassy carbon working electrode.

reversible, but the degree of anodic and cathodic peak separation can vary depending on the working electrode and solvent system.[19] Ferrocene in  $\text{BMIM-PF}_6$  with a glassy carbon working electrode, platinum counter and IL based reference electrode had reversibilities ranging from 72 to 263 mV depending on the scan rate (Table 2). Peak currents for ferrocene also increased with the square root of scan rate. To date we have identified several compounds with electrochemical reversibility better than ferrocene, including  $\text{Mn}(\text{DEA})_6(\text{OTf})_2$  reported recently.[15]

Table 2. Electrochemical reversibility, the difference between anodic and cathodic peak potentials, of a Cu MetIL and ferrocene at various scan rates.

Scan Rate (mV/s)	Reversibility (mV)	
	$\text{Cu}(\text{DEA})_6(\text{EHN})_2$	Ferrocene
10		72
50	523	149
100	689	203
200	724	263

## Viscosity

It is well known that ILs suffer from high viscosities due to intermolecular forces associated with ion pairing, and MetILs are no different. The temperature dependence on viscosity for MetILs is important since a redox flow battery is likely operate under variety of environmental conditions. Figure 4 shows a plot of temperature versus viscosity for  $\text{Cu}(\text{DEA})_6(\text{EHN})_2$  and its DEA precursor. Viscosities are

$$\mu = Ae^{b/T} \quad (1)$$

greater than 3500 cP at temperatures below 30 °C. This is an order of magnitude greater than the DEA precursor. Both compounds are first order fluids that follow an exponential model (Eqn. 1) where A and b are constants,  $\mu$  is viscosity and T is temperature. We have previously shown that the nature of the cation and anion in the MetIL can have a dramatic effect on viscosity, compounds with viscosities ranging from 1300 to 14000 cP at 25 °C have been prepared.[15]

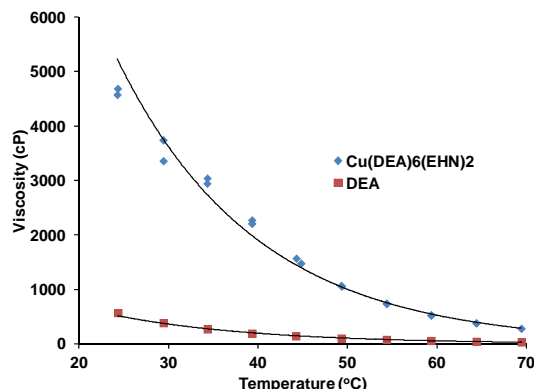


Fig. 4. Viscosity versus temperature for Cu(DEA)<sub>6</sub>(EHN)<sub>2</sub> and DEA.

## SUMMARY

A new family of redox-active ionic liquids for flow battery applications has been developed. The simplicity of the MetIL synthesis has allowed a rapid exploration of cation, anion and ligand combinations. Most compounds are inexpensive to produce and some show promising viscosity, conductivity, and/or electrochemical reversibility. New compounds are continuing to be developed. Future studies include static and flow based electrochemical cell testing to establish the viability of these compounds in a flow battery regime.

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