

Ionic Liquid Flow Battery Materials and Prototyping

T. M. Anderson* and H. D. Pratt III*

*Power Sources R&D, Sandia National Laboratories,
Albuquerque, NM, USA, tmander@sandia.gov

ABSTRACT

SNL has developed a series of ionic-liquid electrolytes with accompanying non-aqueous compatible membranes and flow cell designs for improved energy density redox flow batteries targeted to support increasing demands for stationary energy storage. The new electrolytes yield a higher energy density by chemically incorporating an electro-active transition metal element into the solvent's molecular formula. Although ionic liquids have higher viscosities than conventional non-aqueous electrolytes, they are promising for higher energy densities due to higher metal concentrations and wider voltage windows. We have addressed high viscosity by developing new materials through careful ligand and anion selection. We have also developed tunable membranes for non-aqueous compatibility and rapid laboratory-scale prototyping to quickly screen materials and cell designs. We are projecting a four-fold improvement in energy density over the next two years.

Keywords: ionic liquids, redox flow batteries, energy density

1 INTRODUCTION

Worldwide energy demand is projected to significantly increase by 2050, and this increased need will be met, at least in part, through the use of renewable energy sources such as solar and wind [1]. However, the intermittent output of these sources requires the development of large-scale stationary energy storage systems. Among the most promising technologies are redox flow batteries (RFBs) that utilize the oxidation and reduction reactions of redox couples to perform reversible charging and discharging [2, 3]. RFBs can have long lifetimes due to the fact that their electrode reactions do not involve the mechanical stresses associated with the insertion or removal of the active species. In addition, because the energy-bearing complexes are stored externally rather than in the electrode compartment, the energy capacity can be tailored independently from the power output.

Despite many compelling attributes, work is needed to increase energy density and decrease costs [4]. As part of our own efforts to address energy density, we previously reported proof-of-concept work on the synthesis of a family of low-cost metal ionic liquids (MetILs) that contain a first-row transition metal coordination cation and weakly pairing

monovalent anion(s) [5–8]. The advantage is the higher concentrations of active metal that can be achieved relative to dissolution of a salt into a solution.

This paper highlights the cell testing capabilities developed at SNL for flow battery R&D. It also discusses the synthetic processes required to produce MetILs and the variables that can be exploited to fine tune their properties with emphasis on lower viscosity and higher electrochemical reversibility. Finally, we end with a brief discussion of the performance of MetILs in laboratory-scale test fixtures.

2 EXPERIMENTAL

All starting materials were purchased from either Alfa Aesar or Sigma-Aldrich. The stabilities of the compounds were monitored using a Thermo Nicolet iS5 FT-IR equipped with a Smart Orbit (Diamond) ATR accessory. Electrochemical experiments on half-cells were performed at room temperature under Ar using a BASi Epsilon potentiostat. All solutions were freshly prepared and degassed prior to electrochemical testing. Cyclic voltammograms (CVs) were collected using a three-electrode setup with a freshly polished 3 mm diameter glassy carbon working electrode, Ag/AgCl (in 3 M KCl) reference electrode, and a platinum wire counter electrode.

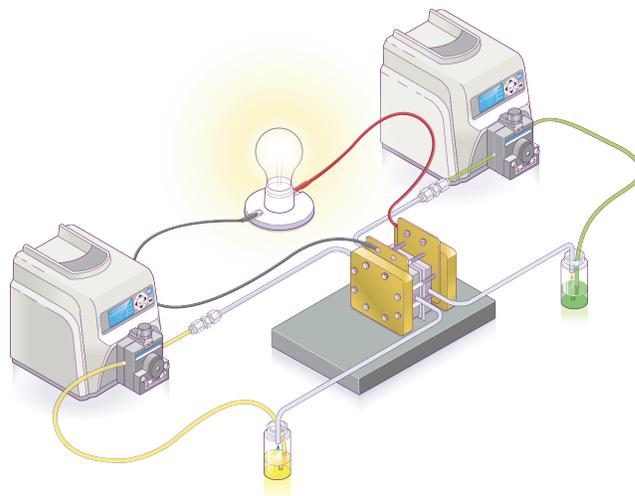


Figure 1: Schematic of a laboratory-scale flow battery test setup illustrating the peristaltic pumps, reservoirs, and electrochemical cell.

3 CELL TESTING CAPABILITIES

In a typical flow cell experiment (Figure 1), the cells consist of carbon-felt electrodes, current collectors, flow fields, gaskets, and a membrane. The flow cell testing system consists of a single cell, peristaltic pumps, polypropylene reservoirs, and chemically compatible tubing. A Solartron 1287 potentiostat/galvanostat is used to control the charging and discharging of the cell at variable temperatures and flow rates.

3.1 Pump Heads and Tubing

The test apparatus consisted of drive assemblies, head assemblies, tubing, and flow cell geometries. For all testing, we utilized Masterflex L/S series drives and various drive compatible pump heads were employed, depending on viscosities and desired flow rates. As an initial starting point, the 60 series Easy Load II was chosen because it features an adjustable occlusion to fine tune for the compression to allow higher pressure and suction lift for more viscous fluids and lower pressure for less viscous fluids. In addition, the four-roller rotor reduces the flow pulsation, which delivers fluids at a more consistent rate and provides more uniform wetting of the cell. For the Easy Load II pump head, Cole-Parmer provides an array of materials in Masterflex tubing that are compatible with the Easy Load II; the tubing was chosen based on compatibility charts provided by Masterflex/Cole-Parmer. It is important to note that solvent compatibility alone is inadequate in determining long-term performance, since friction created by potential nanoparticulates can degrade the material over time. We have made this assessment based on the fact that we notice perforations at the tubing roller interface. Hose size inner diameter and outer diameter (ID/OD) is generally based upon viscosity for the Easy Load II with increasing viscosity necessitating greater tubing size. In addition to the Easy Load II, we have utilized the PTFE tubing head. The PTFE tubing head utilizes six rollers and can pump fluids at even higher pressures than the Easy Load II (up to 100 psi). The PTFE tubing head utilizes Masterflex tubing sets; these sets come in either 2 mm ID by 4 mm OD or 4 mm ID by 6 mm OD. We utilize Swagelok stainless steel reducing unions to transition between metric size tubing sets and SAE size PTFE tubing, generally feeding in flow with eighth-inch OD tubing with quarter-inch OD outflow. This variation in ID/OD is employed to reduce bottleneaking at the exit pathway and reduce overall back pressure in the system/membrane.

3.2 Flow Cell Design

The basis of our redox flow cell was based on the classic methanol fuel cells that are commercially available. In particular, we utilized several designs from Fuel Cell Technologies. This design provides for separate positive and negative half-cells and it provides a compression

mechanism for the membrane, flow fields, and current collectors. It is common for these materials to be made out of graphite to resist harsh chemical conditions. However, the relatively benign nature of our MetILs compounds allowed for other materials to be used including stainless steel (304). This can potentially allow some cost savings over machining graphite materials. The stainless steel designs allow the viscous MetIL solutions to flow with more fluid turns, in contrast to sharp angles generally present in methanol fuel cells. Our stainless steel assemblies could be put together using their own bolt circles, and they were also designed to fit into the Fuel Cell Technologies hardware assemblies. The latter design also provided a cost effective means of making iterations to the flow path. Sample geometries that were tested include a straight trough (eighth-inch in width and depth with radial ends), serpentine patterns, and circular flow fields. In addition, all of these geometries could be oriented in either the vertical or horizontal feed orientation. Fluids with viscosity values between 500 and 700 cP (at 25 °C) generally require larger flow paths than those provided by the classic methanol fuel cells. When assembling a cell, a compression of twenty percent to the carbon felt was generally achieved. In addition, plasma treating the membranes, carbon felt, or both prior to cell assembly was beneficial to performance. Finally, it is important to note that machined graphite is available as either Poco or pyrosealed Poco. However in most of our experiments more favorable results were obtained with pyrosealed Poco. In summary, these are the tools that we have on hand to construct a MetIL based redox flow battery.

Table 1: Summary of cupric ionic liquids as a function of chemical constitution.

Ligand ¹	Anion 1 ²	Anion 2 ²	State at 25 °C	ΔE^3 [mV]
EA	EHN	EHN	Liquid	244
EA	OTf	OTf	Solid	158
EA	EHN	OTf	Solid	158
EA	BF ₄	BF ₄	Liquid	102
EA	BF ₄	OTf	Solid	256
EA	BF ₄	EHN	Liquid	187
EN	BF ₄	BF ₄	Liquid	112
DEA	EHN	EHN	Liquid	522
DEA	OTf	OTf	Liquid	566
DEA	EHN	OTf	Solid	507
DEA	BF ₄	BF ₄	Liquid	150
DEA	BF ₄	OTf	Liquid	159
DEA	BF ₄	EHN	Liquid	201

¹EA = ethanolamine, EN = ethylenediamine DEA = diethanolamine; ²BF₄ = tetrafluoroborate, EHN = 2-ethylhexanoate, OTf = CF₃SO₃; ³0.1 M solutions in 1-butyl-3-methyl-imidazolium hexafluoro-phosphate with a glassy carbon (working) electrode (scan rate 50 mV s⁻¹).

4 SYNTHESIS AND CHARACTERIZATION

A series of copper-based MetILs were prepared with varying ligands and anions in order to elucidate trends for lower viscosity (<1000 cP) and higher electrochemical reversibility (i.e. peak separations less than 200 mV), and the results are summarized in Table 1. The results showed the most promising compounds are those containing either EA or EN ligands and BF_4^- anions. In addition, several of the compounds have electrochemical reversibility values that were comparable or even better than ferrocene (~150 mV) under identical conditions (i.e. in an ionic liquid). The cyclic voltammograms (CVs) of $\text{Cu}(\text{DEA})_6(\text{CF}_3\text{SO}_3)_2$, $\text{Cu}(\text{EA})_6(\text{BF}_4)_2$, and $\text{Cu}(\text{DEA})_6(\text{BF}_4)_2$, performed at a 100 mV s^{-1} scan rate with a glassy carbon working electrode, are shown in Figure 2. The open circuit potential was around 3.0 V in all three compounds (i.e. the fully oxidized species was present at the start of the experiment). The CV for $\text{Cu}(\text{EA})_6(\text{BF}_4)_2$ indicated that electrodeposition and stripping of the bulk metal on the working electrode occurred at 0.5 V and 2.4 V, respectively, with the $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ redox pair centered at 2.5 V. The redox processes at 1.1 V, 1.4 V, and 2.0 V were attributed to the ethanolamine ligand, and this assignment was verified by comparing the CV with that of a pure sample. Compounds $\text{Cu}(\text{DEA})_6(\text{BF}_4)_2$ and $\text{Cu}(\text{DEA})_6(\text{CF}_3\text{SO}_3)_2$ underwent $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ reductions at 2.3 V and 2.1 V, respectively, which was consistent with the differences in the ion pairing

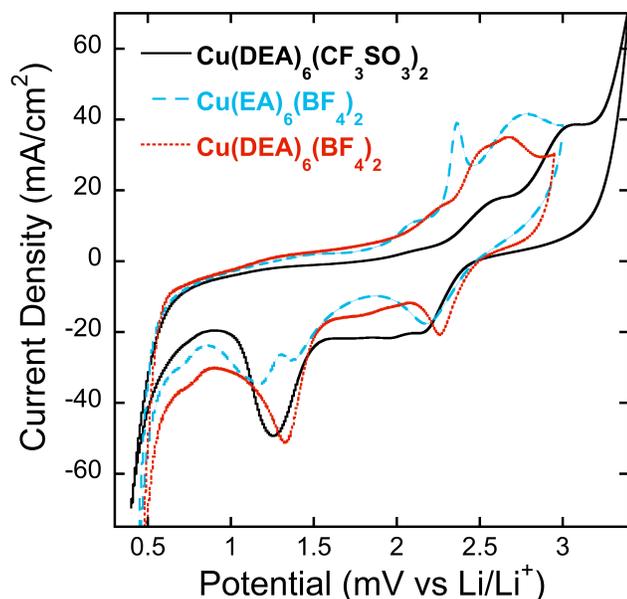


Figure 2: Cyclic voltammograms of $\text{Cu}(\text{DEA})_6(\text{CF}_3\text{SO}_3)_2$, $\text{Cu}(\text{EA})_6(\text{BF}_4)_2$, and $\text{Cu}(\text{DEA})_6(\text{BF}_4)_2$ with a scan rate of 100 mV s^{-1} and a glassy carbon working electrode.

of BF_4^- and CF_3SO_3^- . In contrast to $\text{Cu}(\text{EA})_6(\text{BF}_4)_2$, neither $\text{Cu}(\text{DEA})_6(\text{BF}_4)_2$ nor $\text{Cu}(\text{DEA})_6(\text{CF}_3\text{SO}_3)_2$ had any evidence of stripping although copper deposition was slightly more facile (i.e. a slightly higher potential) in

$\text{Cu}(\text{DEA})_6(\text{BF}_4)_2$. Given that DEA is a more strongly coordinating ligand, the results suggested that DEA hindered stripping. Finally, static cell testing of a cell containing $\text{Cu}(\text{EA})_6(\text{BF}_4)_2$ and $\text{Fe}(\text{C}_{20}\text{H}_{27}\text{N}_2)(\text{PF}_6)$ in separated compartments showed significantly improved discharge profiles that were consistent with more reversible plating and stripping of copper. In addition, the coulombic efficiency increased from 50 to 65%. Additional efforts to further improve copper plating and stripping reversibility are currently underway, and flow cell testing of these compounds has commenced.

5 FLOW CELL TESTING

Flow cell testing in a serpentine flow field was performed using copper- and iron-based MetILs with a 1.5 V separation. A number of commercial membranes were examined but Neosepta AHA gave the best results. The Coulombic efficiency as a function of cycle number is shown in Figure 3 for two different active material concentrations. The increased concentration gave more scatter in the data, but a higher energy density was achieved. We are currently looking at tunable SNL-made membranes to increase performance.

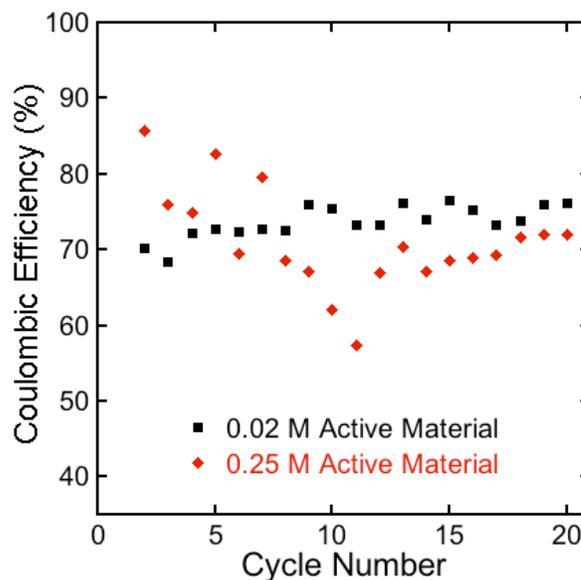


Figure 3: Coulombic efficiency of a copper- and iron-based MetIL redox flow battery as a function of cycle.

6 ACKNOWLEDGEMENT

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