Li-FSI Impurity Impact Study

Final CRADA Report

Energy Systems Division

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Final CRADA Report

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Participant Dollars: 87,000

Argonne PI: Gregory Krumdick

Participant(s):

<u>Boulder Ionics Corporation</u>	<u>87,000</u>
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Summary of Major Accomplishments:

There is growing interest in lithium bis(fluorosulfonyl)imide (LiFSI) as an alternative to LiPF₆ and as an additive to electrolytes used in lithium-ion cells. LiFSI has attracted attention because it is reported to have higher ionic conductivity, better high temperature stability, and enhanced stability toward hydrolysis. Also, LiFSI additive to electrolytes can bring benefits of improved storage properties and reduced gas evolution in the cells.

Different levels of different electrochemically active impurities could affect the performance of LiFSI as an electrolyte salt for Li-ion batteries, generating inconsistent and conflicting interpretations of the experimental data.

Summary of Major Accomplishments:

Argonne in collaboration with Boulder conducted comparative study of several commercial samples of LiFSI to assess effect of impurity profile on electrochemical performance of the materials. Additionally, we investigated the effects of added impurities on self-discharge current, cycle life and calendar life of the cells.

Ion chromatography (IC) was used for chemical analyses of trace impurities in the samples. We found that purity and impurity profile of commercial samples of LiFSI vary significantly both from vendor to vendor and from lot to lot.

To assess effect of impurity profile on self-discharge current the cells were charged from 3.5 to 5.0 V in 0.1 V steps and held for 5 h at each step. Self-discharge current is defined as a current observed by the end of each 5 h period. All experiments were carried out at 30 °C in Al Clad CR2032 NCM523//Graphite full cells using a Celgard 2325 separator. The electrolytes were formulated to contain 1.2 M LiFSI in EC/EMC 3/7 by weight. Self-discharge current shows some dependence on sample investigated. It was noticeably lower at 4.1V for electrolytes formulated from samples B and C. Samples from the two vendors both contain substantial amount of unknown impurity absent in any other samples. We believe that the impurity partially passivate metals thus lowering the self-discharge current associated with corrosion.

To investigate cycle life aging performance of various samples of the material the electrolytes were formulated to contain 1.2 M LiFSI in EC/EMC 3/7 by weight from each vendor. The cells were cycled between 3.0 and 4.1 V at C/2 rate for 100 cycles. All experiments were carried out at 30 °C in Al clad CR2032 NCM523//Graphite full cells using a Celgard 2325 separator.

The calendar life aging investigation utilized the same electrolyte formulations and experimental setting as cycle life aging study. The cells were charged and held at 4.1 V for 100 h at 30 °C while the current was observed. Although samples from vendor B and C performed slightly better on the calendar life aging test the experiment revealed substantial self-discharge current at 4.1 V for all six LiFSI samples. In a pouch cells series of experiment we used machine-made (Li-Fun) 200 mAh NCA//Gr pouch cells. The cells were cycled between 3.0 and 4.1 V at 1C rate in triplicate using electrolyte formulated from selected LiFSI samples.

The experiment revealed that electrolytes formulated from different LiFSI samples all perform similarly in pouch cells test.

Summary of Technology Transfer Benefits to Industry:

We conducted systematic study of LiFSI to determine how impurities affect its performance. The purpose of the project was to help industry develop material specification that will be used to standardize the material purity required for optimum performance. Without the standard manufacturers may be forced to make higher purity, more expensive material than necessary.

The study revealed that that purity and impurity profile of commercial samples of LiFSI vary significantly both from vendor to vendor and from lot to lot. We found that electrolytes formulated from different LiFSI samples all perform similarly in pouch cells test.

To evaluate impact of a particular impurity, we spiked commercial sample of LiFSI with various additives. We found that treatment of the electrolyte with lithium chloride has a detrimental effect on self-discharge current and the current increased with concentration of chlorine ion as measured by IC. On the other hand added moisture up to 500 ppm had no effect on electrochemical performance of the material.

Based on the results of the study we recommended that chlorine impurity should be removed to the single digit ppm level whereas high level of moisture can be tolerated without deleterious effect on cells

Summary of Technology Transfer Benefits to Industry:
performance.

Other Information/Results: (Papers, Inventions, Software, etc.)

Effect of Impurity Profile on Cycling Behavior of LiFSI Electrolytes
Krzysztof Pupek, Daniel Abraham, Trevor Dzwiniel, Gregory Krumdick
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