

NARI Seedling Fund – Phase II Final Technical Report

Enabling Electric Aviation with Ultra High Energy Lithium Metal Batteries

John Lawson (ARC-TSM), Thomas Miller (GRC-LEX0), James Wu (GRC-LEX0), William Bennett (GRC-LEX0), Dionne Hernandez (GRC-LEX0), Brianne DeMattia (GRC-LEX0), Justin Haskins (ARC,AMA), Charles Bauschlicher (ARC-TS), Vadim Lvovich (GRC-LEX0)

Introduction

Green aviation's goals of high energy efficiency, low emissions and reduced noise can be achieved with electric aircraft. A principal barrier to electric aviation is limitation of currently available high capacity energy storage. Li-ion batteries (LIB) with metal oxide cathodes, graphite anodes, and organic liquid electrolytes represent the state-of-the-art. However, LIBs have issues in terms of safety and thermal stability. In addition, LIBs fall well short of meeting the power and energy requirements for electric aircraft¹. Breakthroughs beyond the current state-of-the-art in battery technology are necessary to fully realize green aviation.

New electrode materials can provide the breakthroughs required to reach the next level in battery technology. Li metal anodes combined with advanced cathode materials such as Li-Air or Li-Sulfur offer substantial weight reduction and the promise of 5X improvements in specific energies, e.g. 1000 Wh/kg (Li-Air) compared to 200 Wh/kg for LIB². The *fundamental* obstacle to the use of Li metal anodes in advanced, rechargeable, high energy batteries is poor charge/discharge cycling efficiency and safety concerns due to dendrite formation at the anode-electrolyte interface which can cause internal short circuits.

Alternative electrolytes based on non-flammable, thermally and electrochemically stable ionic liquids (mixtures of cation and anion molecules) have the potential to solve these problems. For example, recent work has shown certain ionic liquids (IL) electrolytes may suppress the formation of dendrites and show improved cycling capabilities relative to traditional organic electrolytes³. The number of possible ionic liquids and other similar electrolytes is vast, and while some ILs show dendrite suppression, others do not. Identifying the fundamental factors controlling the performance of these ultra-high energy Lithium metal batteries (LMB) as well as developing tools for rapid screening and selection of optimal components for fabrication is required to assess fully their potential.

The global objective of this Seedling project is to develop *an integrated experimental/computational infrastructure* to accelerate fundamental understanding, screening and design of novel IL electrolytes for advanced ultra-high energy LMBs. *The novelty of our approach results from the combination of validated computational modeling with experimental screening to produce a reliable predictive capability* for the selection of optimal components, their fabrication parameters, and the design of ultra-high energy LMB that can meet energy storage challenges of current and future NASA missions and many terrestrial transportation application such as electric vehicles and aircraft.

Approach

We performed an integrated computational-experimental investigation of the impact of novel ionic liquid electrolytes on performance characteristics, such as cycle life and dendrite growth/suppression, on Li metal electrodes in LMB. We have assembled a cross-cutting and cross-Center team of experts to tackle this problem.

Computational studies, led by ARC, consisted of molecular dynamics simulations and *ab initio* computations of several promising IL electrolytes. Molecular dynamics (MD) simulations are atomic level modeling tools to investigate the structure, dynamics and thermodynamics as a function of temperature and voltage of large collections of molecules. Two major computational tool development tasks were performed; a high fidelity “polarizable force field” (PFF)⁴ was implemented into our simulation codes and the capability to treat electrode/electrolyte interfaces under an applied voltage was developed. These simulations were validated against experimental measurements and will support future experimental electrolyte optimization and screening efforts. *Ab initio* methods are well-established quantum chemistry tools for accurately modeling reactive processes. These techniques were used to determine basic structural and electronic properties of the specific IL molecular species and also to identify interfacial chemical reactions both with and without an applied voltage.

Experimental studies, led by GRC, characterized fundamental properties of electrolytes including ionic conductivity to evaluate the performance of each electrolyte in laboratory LMBs. Electrolyte compatibility with electrode materials were performed via cyclic voltammetry (CV). CV helps identify the presence of undesirable decomposition reactions, as well as the required Li plating and stripping processes which are essential for a viable LMB. Electrochemical impedance spectroscopy (EIS) helped further characterize the performance of the electrolytes in LMBs. EIS scans, performed over the lifetime of a cell, identify sources of performance loss (loss of ionic conductivity, surface area development, and resistive film growth). After cycling, cell components were examined for evidence of morphology changes and visual evidence of decomposition of the electrolyte. Scanning electron microscopy (SEM) was used to characterize morphology changes, including dendritic growth, of the cycled electrodes. Optical microscopy was performed to visually characterize the nature of the electrode surface deposits. Energy dispersive X-ray spectroscopy (EDS) provided evidence of elemental compositions of the morphological features. This task revealed the physical changes of the Li electrodes after cycling, and identified possible

decomposition products on the surface. These analyses helped explain why the cell did or did not perform as expected. Properties and performance were assessed and compared to the computational analysis results and traditional battery metrics.

In this project, three ILs were considered: 1-butyl-1-methylpyrrolidinium bis(fluoro-sulfonyl)imide ([pyr14][TFSI]), 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM][BF₄]) and 1-propyl-1-methylpyrrolidinium bis(trifluoro-methanesulfonyl)imide ([pyr13][FSI]). The IL [pyr14][TFSI] has shown significant dendrite suppression and Li anode cycling ability on the order of 1000 cycles in laboratory systems whereas [EMIM][BF₄] has shown little or no dendrite suppression and very poor cycle life⁵. On the other hand, [pyr14][TFSI] has low ionic conductivity compared to [EMIM][BF₄] which has higher values. The third IL [pyr13][FSI] is perhaps the most promising, displaying both electrochemical stability and relatively high ionic conductivity⁶. Understanding why one IL performs so well whereas other, related systems do not is an important step towards discovering electrolyte design rules for these advanced electrochemical systems. Chemical structures for the IL considered are shown in Figure 1.



Figure 1: Chemical structure for ionic pairs of [pyr14][TFSI] (left) and [pyr13][FSI] (middle) and [EMIM][BF₄] (right)

Published Results

For the above ILs, we performed an extensive computational/experimental analysis as outlined above. This detailed analysis has resulted in a series of reports, journal articles and conference presentations. We provide here pointers to that considerable documentation.

Preliminary results for [pyr14][TFSI] and [EMIM][BF₄] can be found in our Phase I report:

-- Lawson, Miller, Wu, Bennett, Bauschlicher, Haskins and Scheidegger, "ARMD Seedling Fund – Phase I Final Technical Report: Enabling Electric Aviation with Ultra High Lithium Metal Anode Batteries", (2012), http://nari.arc.nasa.gov/sites/default/files/Lawson_Seedling-2012-Phase-I-Final-Report-AdvBatteries.pdf

The first complete series of studies were related to fundamental properties of isolated, bulk ILs important for

battery operation. Very good agreement between simulation and experiment was found. Detailed results were reported in the following article:

-- Haskins, Bennett, Wu, Hernandez, Borodin, Monk, Bauschlicher and Lawson, "Computational and experimental investigation of Li doped ionic liquids: [pyr14][TFSI], [EMIM][BF₄] and [pyr13][FSI]", J. Phys. Chem. B 118, (2014) p. 11295

The experimental studies were focused initially on evaluating performance of separate battery components such as Li anodes in symmetric lithium coin cells, with the purpose of future complete impedance analysis of full cells with Li anode and dedicated cathodes. A detailed experimental electrochemical and surface science study monitoring of LMB cells and investigating the impact of novel ionic liquid electrolytes on cycle life and dendrite growth/suppression on Li anodes was presented in the ECS Transactions paper:

-- Lvovich, Wu, Bennett, Demattia, and Miller, "Applications of AC Impedance Spectroscopy as Characterization and Diagnostic Tool in Li-Metal Battery Cells." ECS Transactions 58, no. 22 (2014) p. 1-14.

An exhaustive computational chemistry study providing theoretical validation for the polarizable force field used in the bulk molecular dynamics studies was reported in:

-- Bauschlicher, Bucholz, Haskins, Lawson and Borodin, "Structure and energetics of Li⁺-(BF₄)_n, Li⁺-(FSI)_n, and Li⁺-(TFSI)_n: ab initio methods and polarizable force field approaches", J. Phys. Chem. B 118, (2014) p. 10785

Further studies of bulk ionic liquid properties using highly accurate, ab initio methods were reported in:

-- Haskins, Bauschlicher and Lawson, "Ab initio simulations and electronic structure of Lithium solvated ionic liquids: structure, transport and electrochemical stability", J. Phys. Chem. B, (2015), accepted

The second series of studies consisted of computational analysis and predictions about the structure and properties of the ILs in the presence of an electrode interface; interaction of the ILs with the electrode surface affects the local molecular ordering of the IL as well as its properties. The interfacial structure also sets the stage for subsequent chemical decomposition processes. In addition, we predicted using simulations and measured experimentally the electrochemical double layer capacitance (EDLC) of the IL electrolyte-electrode interface as a function of voltage. EDLC of the electrochemical interface is an important battery parameter and is also important for supercapacitor applications. Results of these studies can be found in:

-- Haskins, Wu, Hernandez, Bennett and Lawson, "Computational and experimental study of Li-doped ionic

NARI Seedling Fund – Phase II Final Technical Report

liquids at electrified interfaces”, J Phys. Chem. B (2015), submitted

Standard computational methods were extended and refined in order to perform simulations with confidence and accuracy. New methodological developments were reported:

-- Haskins and Lawson, “*Computational methods for molecular dynamics simulations of ionic liquids at electrified interfaces*”, J. Phys. Chem. (2015), submitted

The third series of studies considered chemical reactions between the IL electrolyte and the Li metal anode surface. We identified important interfacial chemical reactions as a function of applied voltage. Identifying which reactions occur and what products are produced at a fixed voltage is critical in understanding the factors that drive stable cycling and subsequently in devising dendrite growth suppression strategies and designing new, stable electrolytes. Results of these investigations will be reported in:

-- Haskins, Bauschlicher and Lawson, “*Computational chemistry of ionic liquid decomposition at electrochemical interfaces*”, J. Phys. Chem. (2015), in preparation

The final series of experimental studies included building and characterization of the performance of laboratory LMBs using the three ILs. Strong correlations were found between computations and experimental battery characterizations. Properties of the surface layer were identified as the source of the difference in cycle life using the different IL electrolytes. In addition, a full Li-O₂ cell was built and characterized using the best performing IL electrolytes. Li-O₂ have the highest theoretical storage capacity possible; however, practical realizations have been plagued with severe difficulties arising from the aggressive decomposition of the electrolyte at the highly reactive electrode surfaces. Cycle life for these cells using IL electrolytes was superior to that found to date in the literature. Results of these studies were reported in the ECS Transaction journal publication as well as in several conference presentations.

Conference Presentations

Results from this Seeding project were reported in the following conference presentations:

-- “Study of Stable Cathodes and Electrolytes for High Specific Density Lithium-Air Battery”, D. M. Hernández-Lugo, J. Wu, W. Bennett, Y. Ming, Y. Zhu - *Electrochemical Society Meeting*, Chicago, IL, 2015

-- “Development of Novel Li-metal battery cell chemistries at NASA Glenn Research Center”, V. F. Lvovich, *Space Power Workshop*, Manhattan Beach, CA, May 13, 2015..

-- “Development of Li-metal battery cell chemistries at NASA Glenn Research Center”, V. F. Lvovich, J. Wu, W. R. Bennett, P. Loyselle, D. Hernandez-Lugo, F. Dynys, T.

Miller, *65st Annual Meeting of the International Society of Electrochemistry*, Lausanne, Switzerland, September 2014.

-- “An advance physical and electrochemical study of Li-metal battery components”, D. Hernandez-Lugo, J. Wu, W. Bennett, B. Demattia, V. Lvovich, *Beyond Li-ion*, Chicago, IL, June 4, 2014.

-- “Applications of AC Impedance Spectroscopy as Characterization and Diagnostic Tool in Rechargeable Energy Storage Devices”, V. F. Lvovich, J. J. Wu, W. Bennett, B. Scheidegger, P. Loyselle, K. Burke, M. Hoberecht, I. Jakupca, *224 Meeting of The Electrochemical Society*, San Francisco, CA, October 29, 2013.

-- “Investigation of Structure and Transport in Li-doped Ionic Liquid Electrolytes: [pyr14][TFSI],[pyr13][FSI], and [EMIM][BF4]”, J. B. Haskins, W. R. Bennett, D. M. Hernandez-Lugo, J. J. Wu, O. Borodin, J. D. Monk, C. W. Bauschlicher, *American Chemical Society Annual Meeting*, San Francisco, CA, August 10, 2014

-- “Investigation of Structure and Transport in Li-doped Ionic Liquid Electrolytes: [pyr14][TFSI], [pyr13][FSI], and [EMIM][BF4]”, J. B. Haskins, W. R. Bennett, D. M. Hernandez-Lugo, J. J. Wu, O. Borodin, J. D. Monk, C. W. Bauschlicher, *American Institute of Chemical Engineers Annual Meeting*, Atlanta, GA, November 16, 2014

-- (Invited Talk) "Structural and Chemical Properties of Ionic Liquids at Electrochemical Interfaces: Computations and Experiment", J. B. Haskins, W. R. Bennett, D. M. Hernandez-Lugo, J. J. Wu, O. Borodin, C. W. Bauschlicher, *American Chemical Society Annual Meeting*, San Diego, CA, March 13-17, 2016

References

¹ NASA/CR–2011-216847, *Subsonic Ultra Green Aircraft Research (SUGAR): Phase I Final Report*, Boeing, (2011)

² Galiński, Lewandowski, and Stepniak. “*Ionic liquids as electrolytes.*” *Electrochimica Acta* 51, no. 26 (2006): 5567-5580

³ Schweikert, Hofmann, Schulz, Scheuermann, Boles, Hanemann, Hahn, and Indris. “*Suppressed lithium dendrite growth in lithium batteries using ionic liquid electrolytes: Investigation by electrochemical impedance spectroscopy, scanning electron microscopy, and in situ 7 Li nuclear magnetic resonance spectroscopy.*” *Journal of Power Sources* 228 (2013): 237-243.

⁴ Borodin, Smith, and Henderson. “*Li⁺ cation environment, transport, and mechanical properties of the LiTFSI doped N-methyl-N-alkylpyrrolidinium⁺ TFSI ionic liquids.*” *The Journal of Physical Chemistry B* 110, no. 34 (2006): 16879-16886.

⁵ Howlett, MacFarlane, and Hollenkamp. “*High lithium metal cycling efficiency in a room-temperature ionic liquid.*” *Electrochemical and Solid-State Letters* 7, no. 5 (2004): A97-A101; Bhattacharyya, Key, Chen, Best,

Hollenkamp, and Grey. "*In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries.*" *Nature Materials* 9, no. 6 (2010): 504-510.

⁶ Best, Bhatt, and Hollenkamp. "*Ionic liquids with the bis (fluorosulfonyl) imide anion: electrochemical properties and applications in battery technology.*" *Journal of The Electrochemical Society* 157, no. 8 (2010): A903-A911.