Enabling Electric Aviation with Ultra High Energy Lithium Metal Batteries

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NASA Aeronautics Research Mission Directorate (ARMD)
FY12 Seedling Phase I Technical Seminar
July 9-11, 2013
Electric Aviation

- **Green aviation**: high efficiency, low emissions, low noise
- **Solar Impulse**: largest technological limitation -- battery storage
- **Hybrid aircraft**: battery weight is significant limitation
- **Commercial aircraft**: battery powered onboard systems
- **Boeing 787 Dreamliner**: current battery electrolytes are flammable
- **Progress in electric aviation will depend on advances in ultra high energy, safe batteries**
Lithium Metal Anodes

- Potential for 5X increase in storage capacity
- **Safety** and **cycling** problems: issues for **Li-Air**, **Li-S**, etc
- **Holy Grail** of advanced battery technology

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F. Orsini et al., J. Power Sources 76, 19-29 (1998)
Two Ionic Liquids are similar but have very different cycling behavior - why?

Fundamental understanding will enable design of ultra high energy batteries
• **Innovation:** computational predictive tool tightly coupled to experiments to accelerate fundamental understanding, screening and design of novel electrolytes for advanced batteries

• **Application:** investigate *two* Ionic Liquid electrolytes (one good cycling and one poor) for Lithium metal anode batteries

• **Cross-Center, Multi-Disciplinary Team**

• **ARC Computational Materials Group:** modern computational material science methods

• **GRC Electrochemistry Branch:** wide-ranging experience in battery development experimental characterization

• **Benefit/Impact:** predictive tool for accelerated development of ultra high energy, safe batteries

• **Aggressive Work Plan** (12 milestones) -- all met or exceeded
Technical Approach

I. Isolated Ionic Liquids
- Transport simulations
- Experimental validation

II. Experimental Cell Characterization
- Build cells
- Electrochemical characterization
- Surface layer identification

III. Ionic Liquid-Electrode interface
- Interface simulations with voltage
- Electric double layer structure

IV. Interfacial chemistry
- Electrolyte surface decomposition
- Chemical pathways
- Surface layer formation

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I. Isolated Ionic Liquids
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
IV. Interfacial Chemistry
V. Summary/Future Directions
Molecular Dynamics Simulations

- Newton’s law $F=ma$ for atoms
  \[ F = -\nabla E \]
- Bonded interactions:
  \[ E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} \]
- Non-bonded interactions:
  \[ E_{\text{vdw}} + E_{\text{qq}} \]
- “Polarizable” interactions
  \[ E_{\mu q} + E_{\mu\mu} \]
- New polarizable software module for Ionic Liquid simulations developed
- Massive datasets for analysis
Thermodynamics

Well-established theoretical foundation (statistical mechanics)

Heat Capacity

\[ C_P = \frac{(H + PV)}{T} \bigg|_P = \frac{\left\langle (H + PV)^2 \right\rangle_{NPT}}{k_B T^2} \]

Isothermal Compressibility

\[ T = \frac{1}{V} \frac{V}{P} \bigg|_T = \frac{\left\langle V^2 \right\rangle_{NPT}}{\langle V \rangle k_B T} \]

Thermal Expansion Coefficient

\[ P = \frac{1}{V} \frac{V}{T} \bigg|_P = \frac{\left\langle V (H + PV) \right\rangle_{NPT}}{\langle V \rangle k_B T^2} \]

Thermal Pressure Coefficient

\[ V = \frac{P}{T} \bigg|_V = \frac{P}{T} \]
Non-equilibrium transport coefficients (fluctuation-dissipation theorems)

**Diffusion**

\[ D \mu \quad dt \langle v(t)v(0) \rangle \]

**Viscosity**

\[ xy \mu \quad dt \langle p_{xy}(t)p_{xy}(0) \rangle \]

**Ionic Conductivity**

\[ IC \mu \quad \frac{d}{dt} \langle (qr(t) \quad qr(0))^2 \rangle \]
Example: Li$^+$ Ion Solvation Shell

Li-TSFI anion

Li-BF$_4$ anion

Detailed molecular structure

Anion distribution about Li ions

[Li]-[TFSI]

[Li]-[BF$_4$]
Density

Neat Ionic Liquids

Lithiated Ionic Liquids

Excellent agreement with GRC experiments
Viscosity

Good agreement with GRC results
Diffusion coefficient

[pyr14][TFSI]

[EMIM][BF₄]

Diffusion data from GRC in progress
Ionic Conductivity

Good agreement with GRC results

Conclusion: good agreement on broad range of electrolyte properties
Phase I Seedling

I. Isolated Ionic Liquids
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
IV. Interfacial Chemistry
V. Summary/Future Directions
Lithium Coin Cell

- Laboratory cells – easily constructed
- Focus characterization of the Li metal electrode
Cell Cycling

- [EMIM][BF₄] cell fails after 150 cycles
- [pyr14][TFSI] cell cycles successful up to 1750 cycles
Impedance Spectroscopy

- [EMIM][BF₄] cell has **increasing** resistance
- [pyr14][TFSI] cell has **decreasing** resistance (increasing Li surface area)
Cyclic Voltammetry

- [pyr14][TFSI] cell: Li plating/stripping
- [EMIM][BF$_4$] cell: no Li stripping
- [EMIM][BF$_4$] cell: decomposition
- Consistent with impedance data
- [EMIM][BF$_4$] cell with VC additive improves Li plating/stripping
- Decomposition explored in Phase II
- Additives to be explored in Phase II
Surface Morphology: \([\text{pyr14}][\text{TFSI}]\)

- Li electrode after 1780 cycles
- "Mossy" Li deposits rich in electrolyte elements \((O, S, F)\)
- Smooth Li surface visible where mossy layer flaked off
- Mossy layer source of increased surface area
- *Consistent with reduction in impedance*

Conductive mossy surface layer facilitates good cycling
Surface Morphology: [EMIM][BF₄]

- Li electrode after 130 cycles
- “Waxy” film covers ~75% of Li surface (rich in F and C)
- Film consists of electrolyte decomposition products
- Li under film appears bright and un-utilized
- Reduction in active area
- Consistent with increase in impedance

Insulating waxy surface layer results in poor cycling

Fundamental question: Why does one electrolyte give favorable surface layer and the other does not?
Phase I Seedling

I.  Isolated Ionic Liquids
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
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V. Summary/Future Directions
Electrolyte-Electrode Interface

**Question:** How does Ionic Liquid organize itself at electrode interface?

- Interface simulations with applied voltage (not milestone)
- *Produced new (second) software module to be distributed*
- Full interface properties as function of voltage in Phase II
Electric Double Layer: [pyr14][TFSI]

TFSI Anion buildup at Cathode

Pyr14 Cation buildup at Anode

Charge Density (e/Å³)

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Ion Density: [pyr14][TFSI]

- Molecular layering near interface
- Classical theory predicts exponential decay

**Conclusion:** Molecular ordering near interface sets stage for interfacial reactions
I. Isolated Ionic Liquids
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
IV. Interfacial Chemistry
V. Summary/Future Directions
Question: What are the chemical reactions and products between Li electrode and Ionic Liquid electrolyte?

Ab Initio Molecular Dynamics
- High fidelity modeling
- Zero voltage
- Ions bound to surface
- No decomposition of ions
Ab Initio Molecular Dynamics
- High fidelity modeling
- Zero voltage
- Ions bound to surface
- Immediate decomposition of TSFI anion
- Screening tool for electrolytes(?)

Conclusion: At zero voltage, very different anion decomposition behavior and products. Suggests that different surface layers will result (preliminary).

Phase II will consider surface reactions with applied voltage
I. Isolated Ionic Liquids
II. Ionic Liquid-Electrode Interfaces
III. Interfacial Chemistry
IV. Experimental Cell Characterization
V. Summary/Future Directions
Summary

- **Phase I Major Accomplishments:**
  - Determined *transport properties* (computation/experiment) of two ILs
  - Built and characterized Li cells (cycling, impedance, voltammetry, SEM/EDAX)
  - Identified different surface layers for different electrolytes
  - Determined *interface double layer properties* (computation)
  - Identified *initial surface reactions* from simulations (computation)

- **Cross-Center, Multi-Disciplinary Team: ARC/GRC**

- **Benefit/Impact:** predictive tool tightly coupled to experiment for accelerated development of ultra high energy, safe batteries

- **Milestones:** We have met or exceeded all 12 milestones

- **Products:** two software modules to be distributed to community

- **Dissemination:** 3-4 journal articles plus conference presentations

- **Interest in Our Work:** DOE/ORNL, ARL, IBM Almaden Research

- **Spin-off Applications:** Ionic Liquids for Tribology, EPSCoR proposal
Future Directions

I. Interfaces under Bias
- Full interfacial properties vs voltage
- Measure interface capacitance

II. Surface Reactions under Bias
- Surface reactions vs voltage
- Compare to CV data

III. SEI growth simulations
- Surface layer formation simulations
- Compare to SEM/EDAX data

IV. Electrolyte Optimization
- Additives and alternative ILs
- Modeling support of optimization

V. Full Cells: Cathode and Anode
- Build and characterize full cells
- **Optional:** Li-Air cell with IL electrolyte
- **Optional:** Oxidative stability modeling
Seedling Team

• **GRC Electrochemistry Team**
  • Bill Bennett
  • James Wu
  • Tom Miller
  • Brianne Scheidegger

• **ARC Computational Modeling Team**
  • John Lawson
  • Justin Haskins
  • Charlie Bauschlicher
  • Josh Monk
  • Eric Bucholz

• **External Collaborators**
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Thank you for funding!