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Enabling Electric Aircraft with Ultra-High Energy Batteries

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NASA Aeronautics Research Mission Directorate (ARMD)

2015 Seedling Technical Seminar

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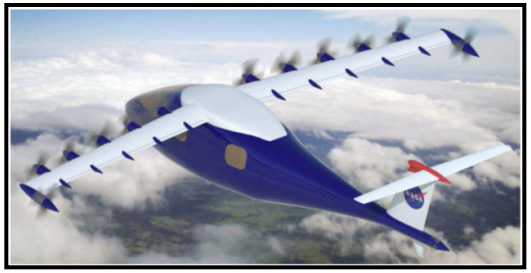
Electric Aircraft Requirements

- **Energy Density:**
  - *400 Wh/kg* – general aviation threshold
  - *500 Wh/kg* – typical general aviation
  - *600-700 Wh/kg* – commercial threshold
  - *750+ Wh/kg* – commercial service
- **Specific Power**: 300 W/kg
- **Cycles:** *1000s* of recharges
- **Recharge time:** ~40 minutes at high rate ~2C
- **Safety:** stable, non-flammable materials

No one is currently working on developing high energy, rechargeable, safe batteries for electric aircraft



NASA Electric Aircraft

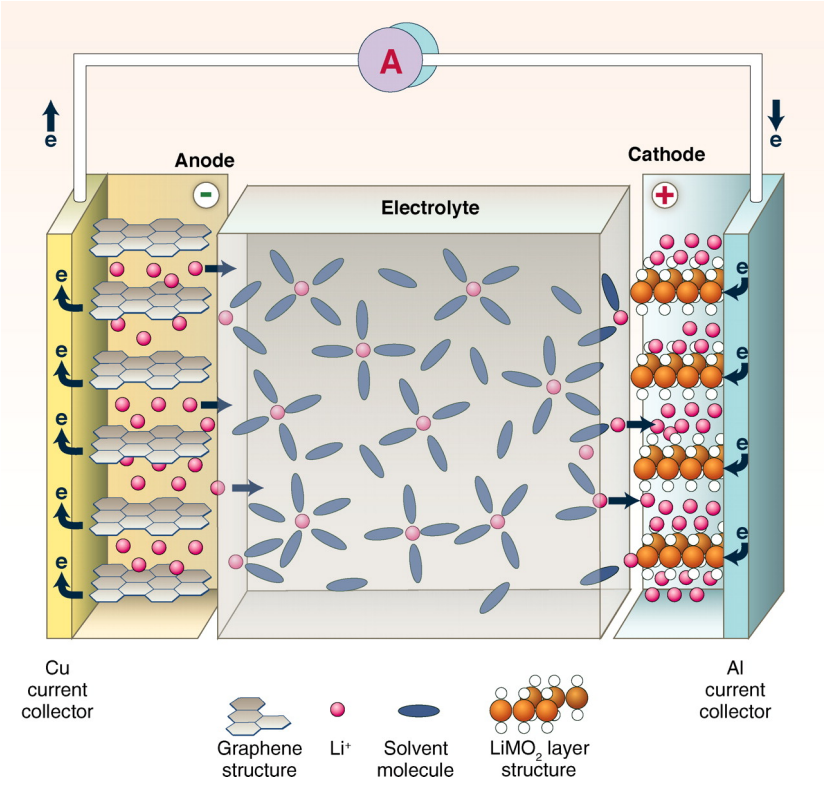
Boeing SUGAR Volt

Failed Dreamliner Battery

MD Moore and B Fredericks, AIAA Scitech, (2014)

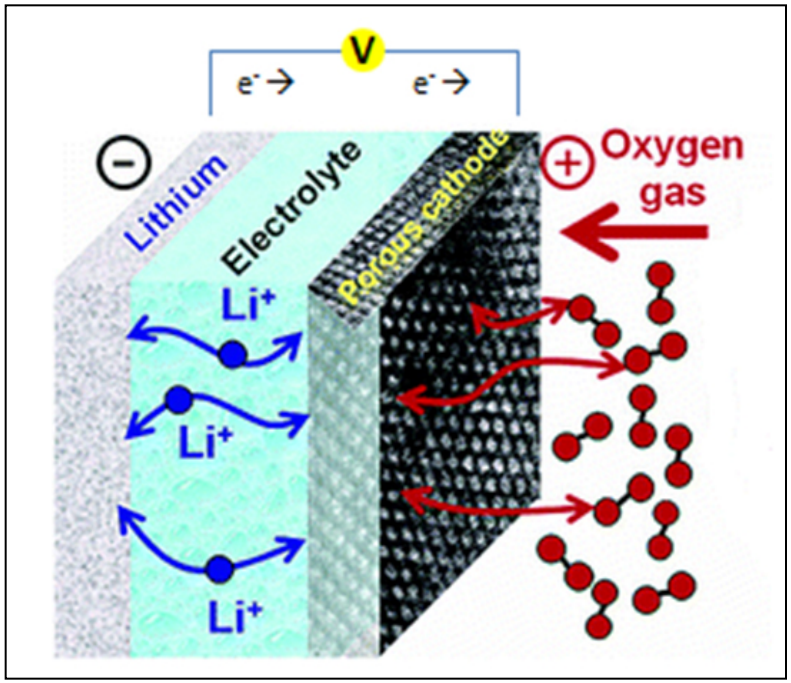
SOA: Lithium-Ion Batteries

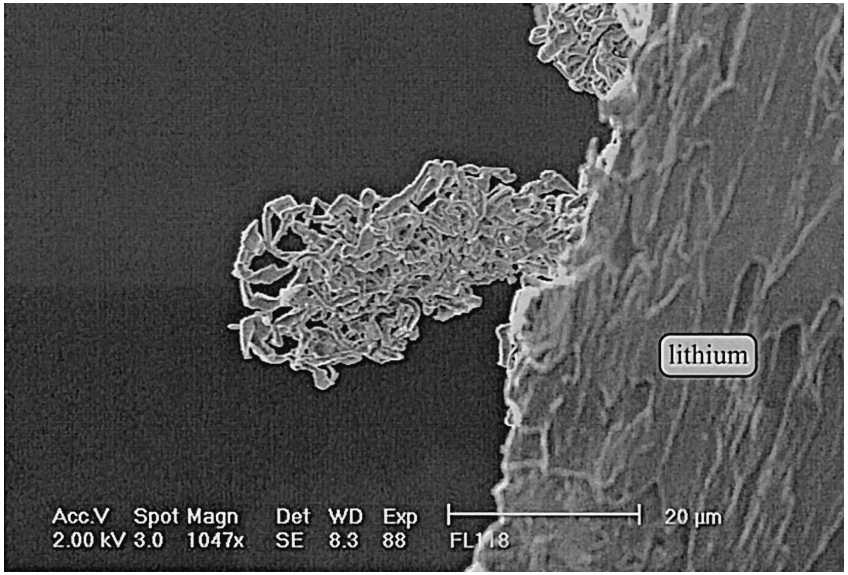
- **LIB Materials**
  - *Anode*: Graphite
  - *Cathode*: Metal Oxide
  - *Electrolyte*: Organic Carbonate Liquids
- **LIB Specs**
  - *Specific energy*: **240 Wh/kg** (*Cell level*)
  - *Specific power*: **300 W/kg**
  - *Cycles*: **1000s (Excellent!)**
  - *Recharge time*: **~10 hrs**
  - *Safety*: **flammable electrolyte**
  - *Temperature range*: **-20C to +40C**
- **LIB has excellent <u>rechargeability</u>**
- **LIB has problems with <u>energy density</u>, <u>recharge time</u> and <u>safety</u> for electric aircraft**



New battery "<u>chemistries</u>" (electrodes/electrolytes) needed for <u>high specific energy</u>, <u>highly rechargeable</u>, <u>safe</u> batteries required for electric aircraft

New Anode: Lithium Metal





Battery failure due to dendrites (*electrolyte decomposition*)

- **Advantage:** Lithium metal anode has ***5X*** increase in energy density relative to LIB
- **Disadvantage:** *safety* and *cycling* worse than LIB due to electrolyte decomposition!
- Solution to "Li metal problem" is the *Holy Grail* of advanced battery technology

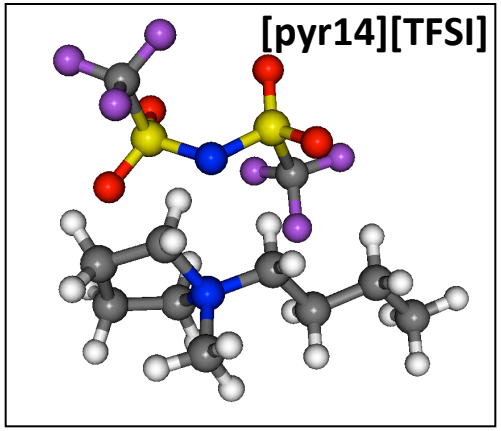
Rechargeable **batteries with high energy, Li metal anodes are not currently possible due to** ***electrolyte decomposition*** **of standard/LIB electrolytes**

New Electrolyte: Ionic Liquids

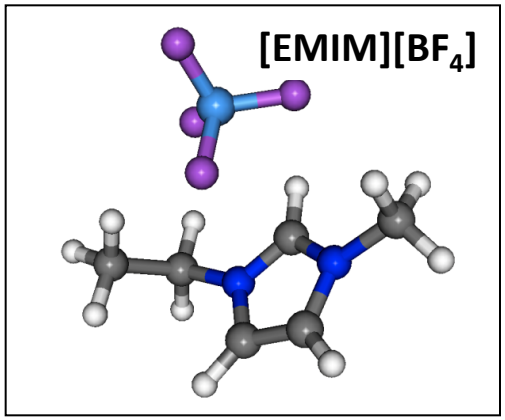
- **Electrolyte selection is the key to Li metal problem**
- *Ionic liquids* consist of molecular anion/cation pairs
- Highly stable and non-flammable (safe)
- **Some ILs are stable against Li metal decomposition; however, others are not. *Why*?**
- Stability of two ILs against Li metal investigated:
  - **[pyr14][TSFI]** – *good* stability
  - **[EMIM][BF_4]** – *poor* stability
- ***Stability* is critical for battery rechargeability**
- Many *other* properties required for viable electrolyte
- Vast number of ILs possible ~10^{18}
- **Chemical design/synthesis of new ILs with tailored properties possible**

Ultimate goal: determine *electrolyte design rules* for high energy, safe, rechargeable batteries

Good Stability



Poor Stability



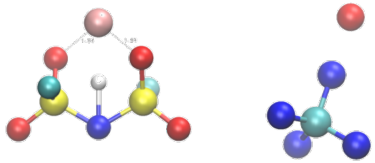
Bhattacharyya et al., Nat. Mat. 9, (2010), p 504

Technical Goals

- **Technical Questions:**
  - Is IL ionic conductivity too low for batteries?
  - What is detailed interaction between IL electrolyte and Li metal anode?
  - What is the cell performance with ILs and Li metal electrodes?
  - What is detailed interaction between IL electrolyte and cathode materials? (future)
  - What is the optimal electrolyte for electric aircraft requirements? (future)
  - N.B., understanding of all these issues is incomplete for SOA LIB after 20 years
- **Cross-Center, Multi-Disciplinary Team**
- **ARC Computational Materials Group**: modern computational material science and computational chemistry
- **GRC Electrochemistry Branch:** wide-ranging experience in battery development and experimental characterization
- **Innovation:** *develop unique set of computational tools tightly coupled to experiments to accelerate fundamental understanding, screening and design of novel electrolytes for complex, advanced batteries*
- **Benefit/Impact:** accelerated development of high energy, safe, rechargeable batteries to enable electric aircraft. Integrated approach will revolutionize the battery industry and air transportation

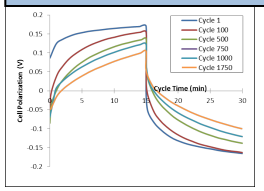
Technical Approach

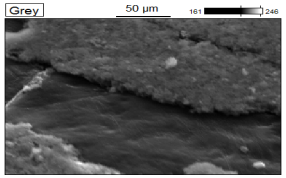
I. Isolated Ionic Liquids



- Conductivity simulations
- Experimental validation

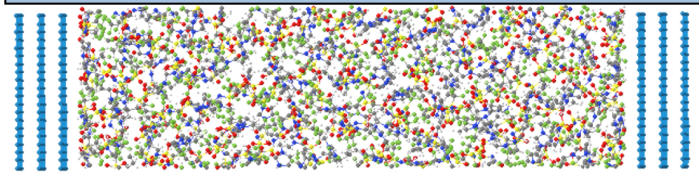
II. Experimental Cell Characterization





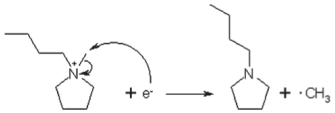
- Build cells
- Electrochemical characterization
- Surface layer identification

III. Ionic Liquid-Electrode interface



- Interface simulations with voltage
- Electric double layer structure

IV. Interfacial chemistry



- Electrolyte surface decomposition
- Chemical pathways
- Surface layer formation

Seedling Project

I. **Isolated Ionic Liquids**
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
IV. Interfacial Chemistry
V. Extra Funding: Li-Air Cells
VI. Summary

Molecular Dynamics Simulations

- Newton's law *F=ma* for each atom

$$F = -\nabla E$$

- Bonded interactions:

$$E^{bond} + E^{angle} + E^{torsion}$$

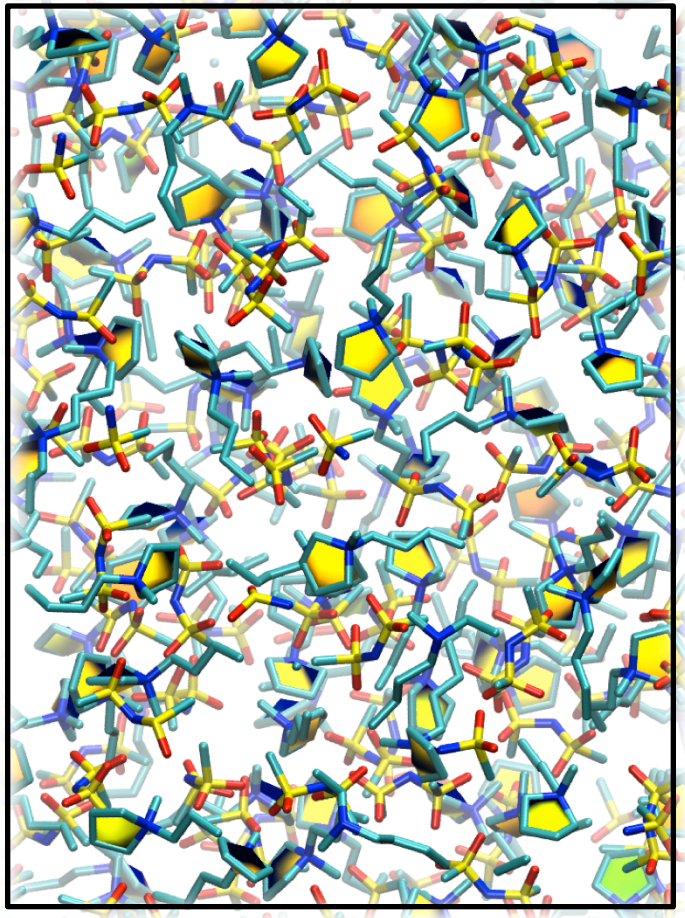
- Non-bonded interactions:

$$E^{vdw} + E^{qq}$$

- "Polarizable" interactions

$$E^{\mu q} + E^{\mu\mu}$$

- ***New polarizable software module for Ionic Liquid simulations developed***
- Massive trajectory datasets for analysis



[pyr14][TFSI]

Thermodynamics

Well-established theoretical foundation (statistical mechanics)

Heat Capacity

$$C_P = \left.\frac{\partial(H+PV)}{\partial T}\right|_P = \frac{\left\langle \delta\left(H+PV\right)^2 \right\rangle_{NPT}}{k_B T^2}$$

Isothermal Compressibility

$$\beta_T = \left.\frac{1}{V}\frac{\partial V}{\partial P}\right|_T = \frac{\left\langle \delta V^2 \right\rangle_{NPT}}{\left\langle V \right\rangle k_B T}$$

Thermal Expansion Coefficient

$$\alpha_P = \left.\frac{1}{V}\frac{\partial V}{\partial T}\right|_P = \frac{\left\langle \delta V \delta\left(H+PV\right) \right\rangle_{NPT}}{\left\langle V \right\rangle k_B T^2}$$

Thermal Pressure Coefficient

$$\gamma_V = \left.\frac{\partial P}{\partial T}\right|_V = \frac{\alpha_P}{\beta_T}$$

Transport Properties

Non-equilibrium transport coefficients (fluctuation-dissipation theorems)

Diffusion

$$D \propto \int dt \left\langle v(t) v(0) \right\rangle$$

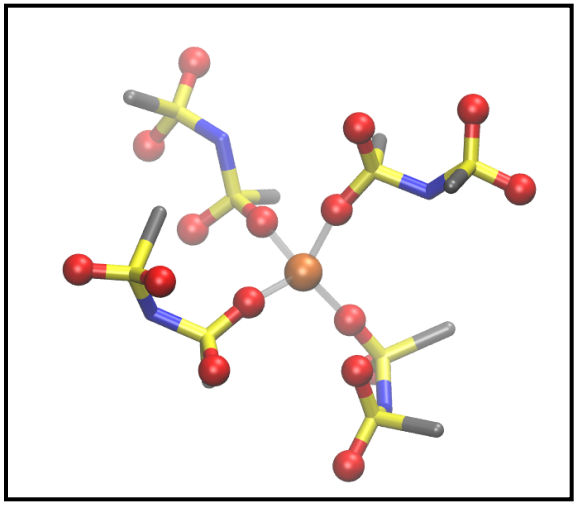
Viscosity

$$\eta_{xy} \propto \int dt \left\langle p_{xy}(t) p_{xy}(0) \right\rangle$$

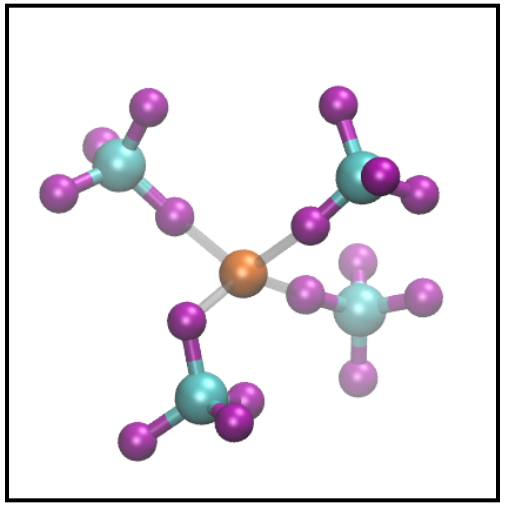
Ionic Conductivity

$$\gamma_{IC} \propto \frac{d}{dt} \left\langle \left(qr(t) - qr(0) \right)^2 \right\rangle$$

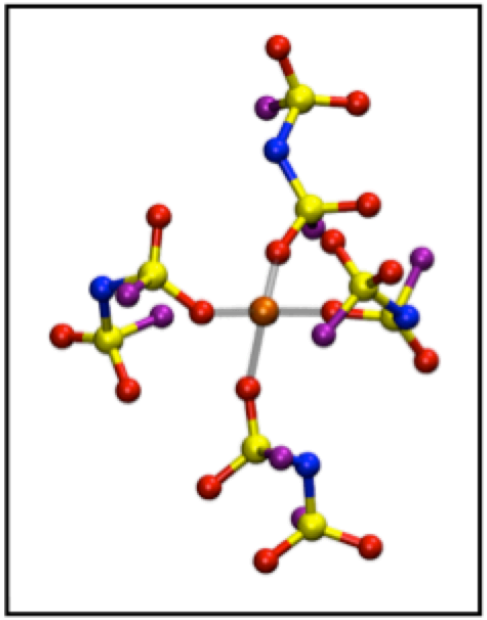
Li Ion Solvation Shell



Li-TSFI shell



Li-BF_4 shell



Li-FSI shell
(<u>new for Phase II</u>)

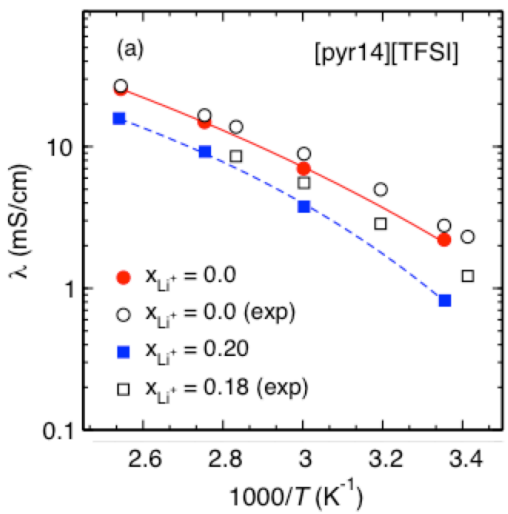
Detailed information on how ionic liquid electrolyte organizes itself around Li ion

Important for electrolyte properties and battery performance

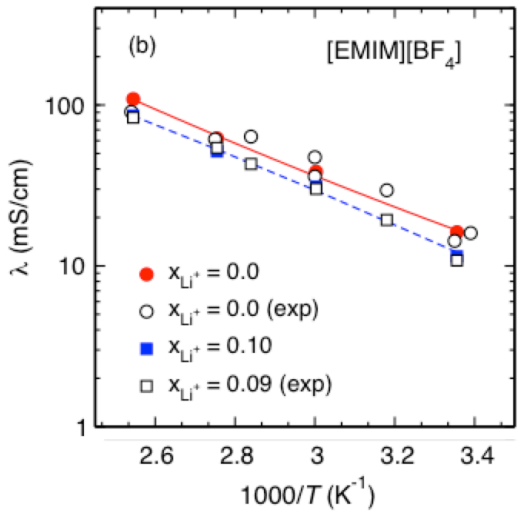
Best, Bhatt and Hollenkamp, JECS 157 (2010), A903

Ionic Conductivity

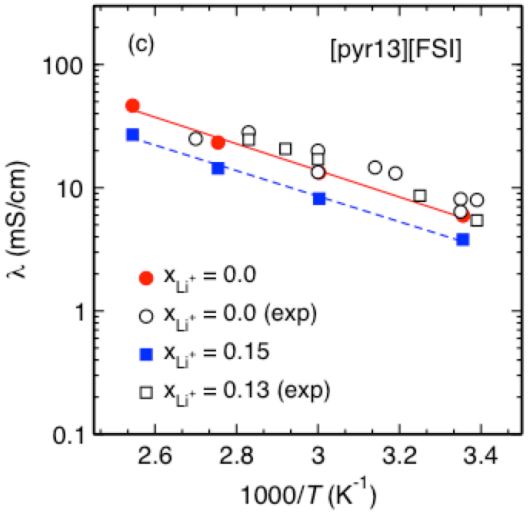
Low Conductivity



High Conductivity



High Conductivity



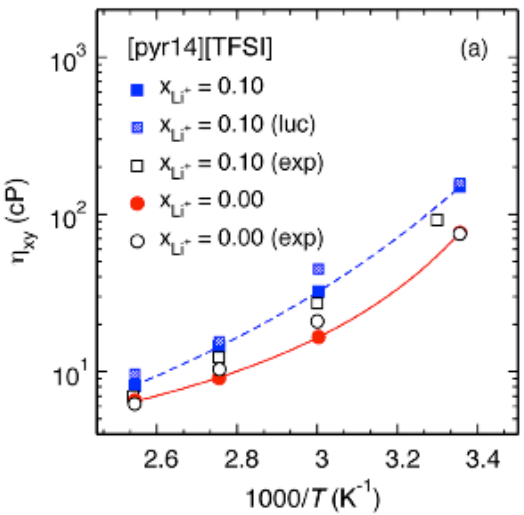
Excellent agreement with GRC experiments

New Ionic Liquid [pyr13][FSI] has significantly higher conductivity than [pyr14][TFSI]

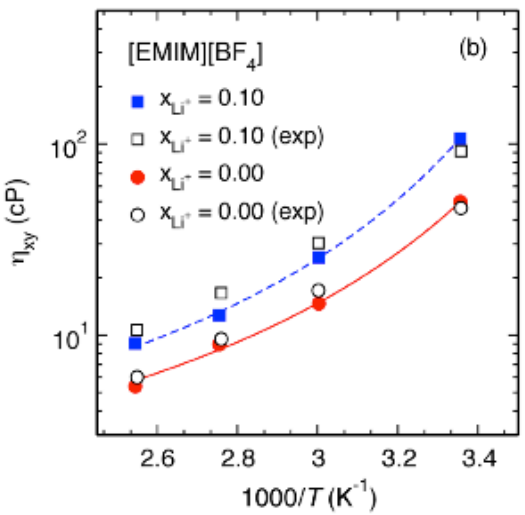
Conduction mechanisms examined in detail suggesting further improvements possible

Viscosity

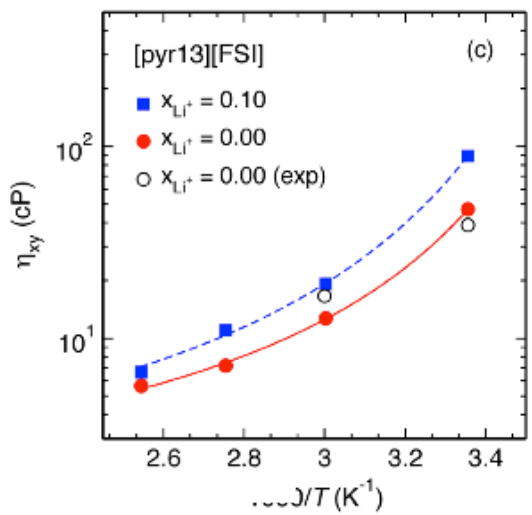
High Viscosity



Low Viscosity



Low Viscosity



Broad agreement between modeling and experiments for a range of properties
New IL system has superior transport properties to others considered

Journal Publications

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Computational and Experimental Investigation of Li-Doped Ionic Liquid Electrolytes: [pyr14][TFSI], [pyr13][FSI], and [EMIM][BF_4]

Justin B. Haskins,[†] William R. Bennett,[∥] James J. Wu,[∥] Dionne M. Hernández,[∥] Oleg Borodin,[⊥] Joshua D. Monk,[†] Charles W. Bauschlicher, Jr.,[‡] and John W. Lawson*,[§]

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Nominated for 2014 NASA paper of the year

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Structure and Energetics of $Li^+-(BF_4^-)_n$, $Li^+-(FSI^-)_n$, and $Li^+-(TFSI^-)_n$: Ab Initio and Polarizable Force Field Approaches

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Oleg Borodin

Electrochemistry Branch, Sensor & Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland 20783, United States

Detailed computational chemistry study (not in proposal)

Seedling Project

I. Isolated Ionic Liquids

II. Experimental Cell Characterization

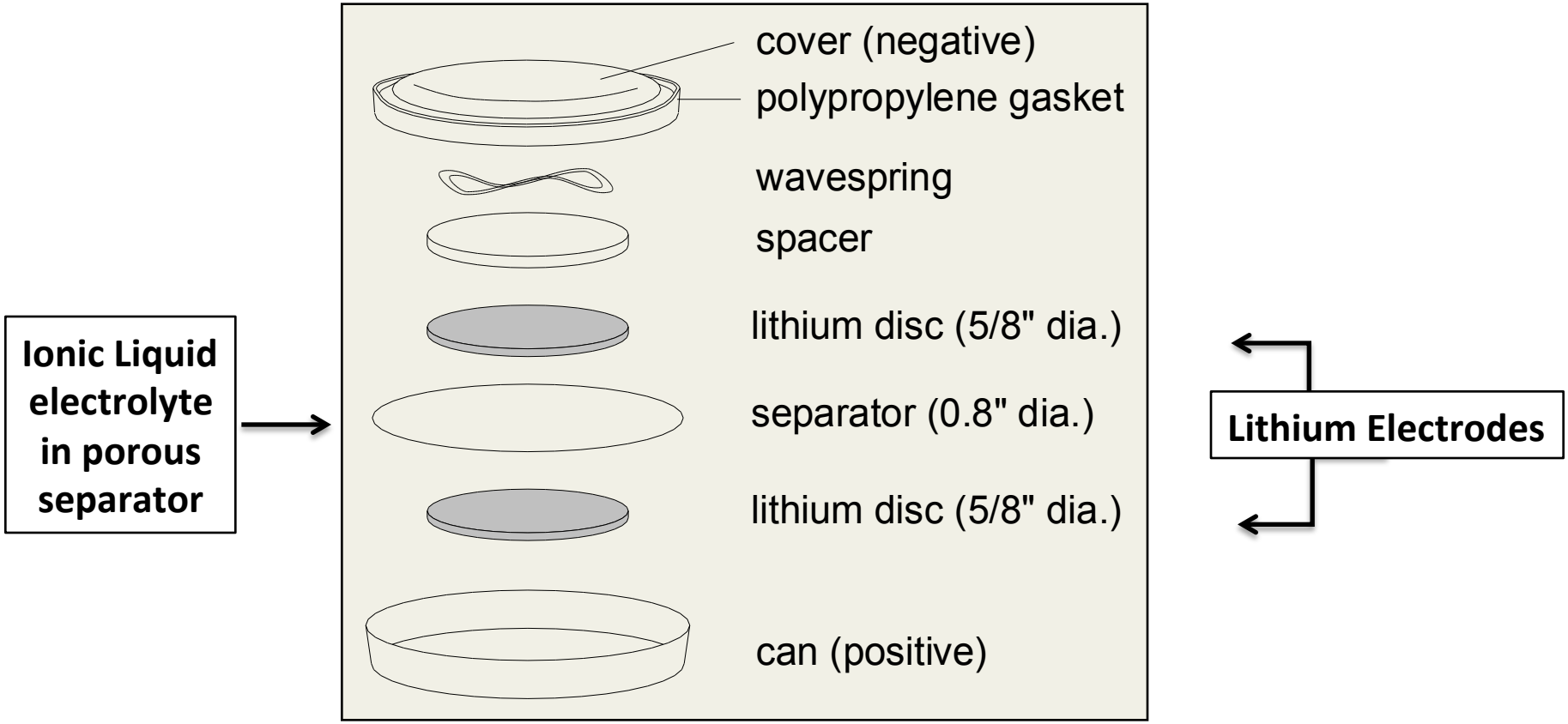
III. Ionic Liquid-Electrode Interfaces

IV. Interfacial Chemistry

V. Extra Funding: Li-Air Cells

VI. Summary

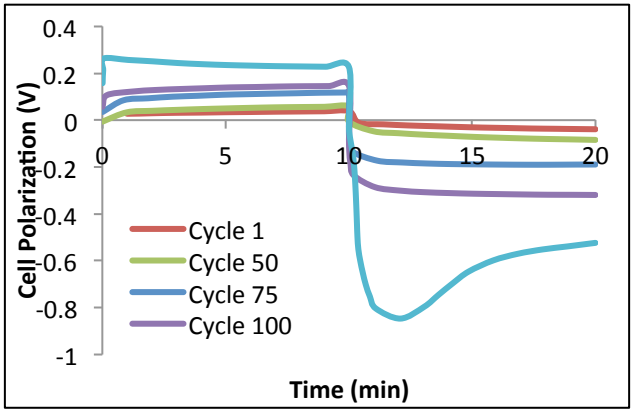
Lithium Coin Cell



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

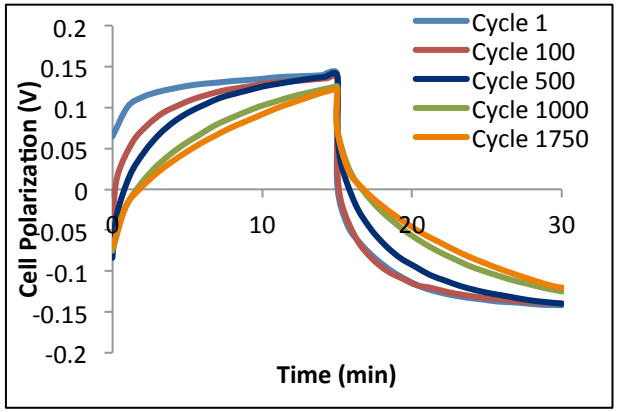
Cell Cycling

[EMIM][BF_4] fails after <u>100</u> cycles



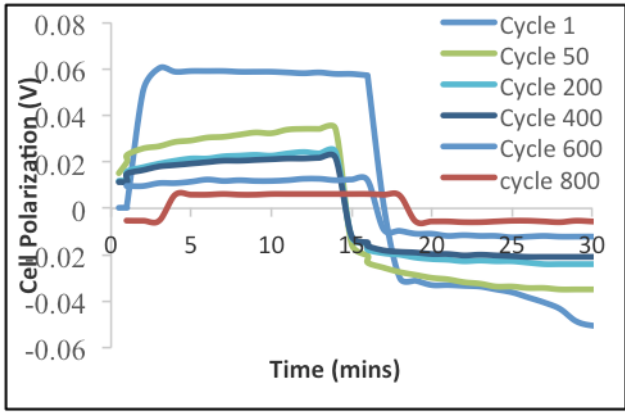
High Conductivity

[pyr14][TFSI] cycles up to <u>1750</u> cycles



Low Conductivity

[pyr13][FSI] cycles up to <u>800</u> cycles

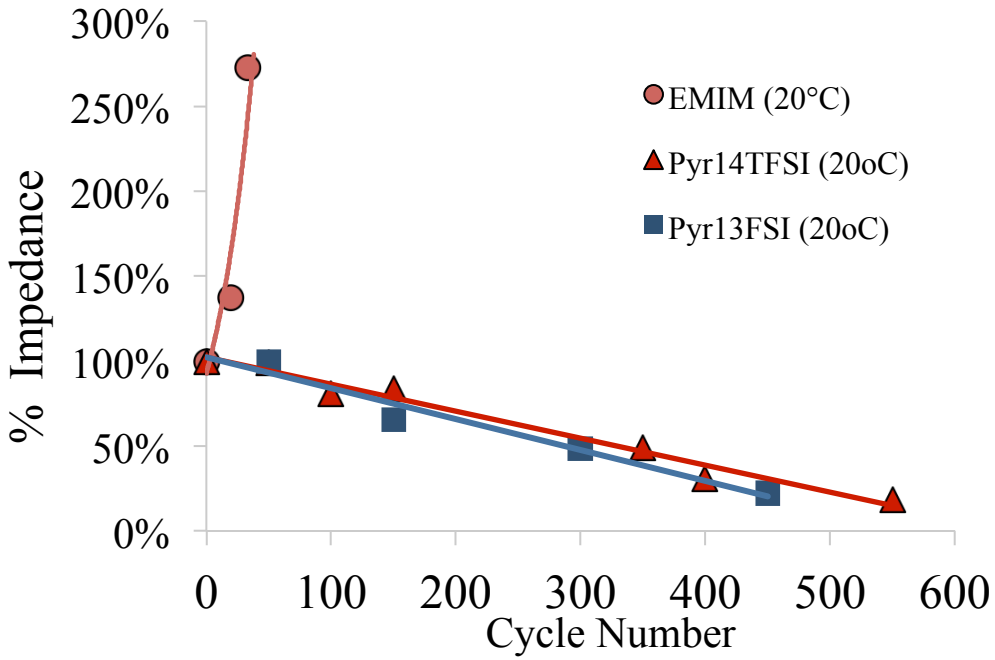


High Conductivity

[pyr14][TFSI] and [pyr13][FSI] exhibits stable, extended cycling

[EMIM][BF_4] fails after 100 cycles

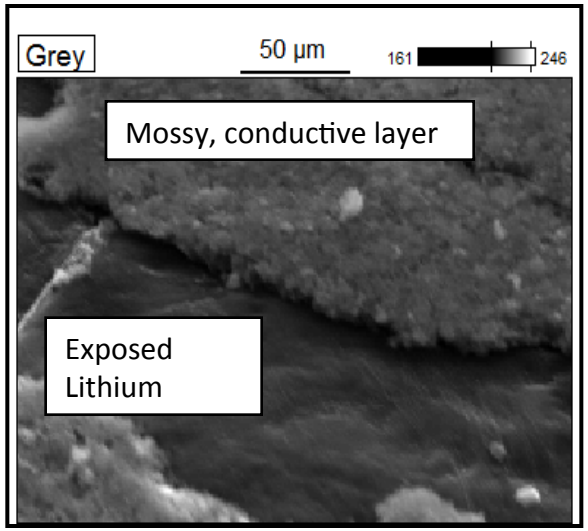
Impedance Spectroscopy



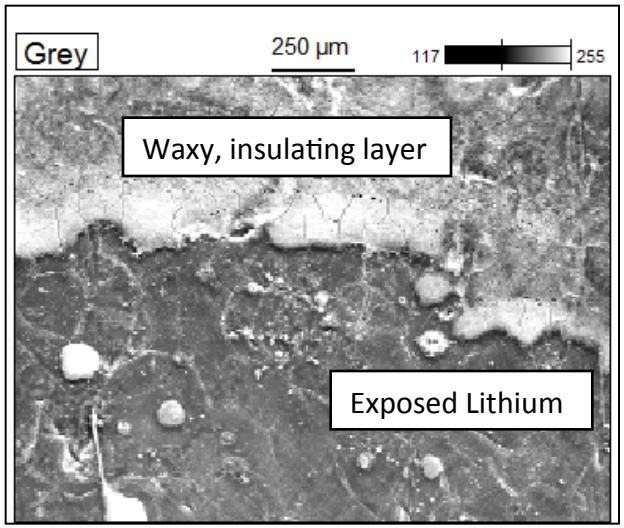
[EMIM][BF_4] has <u>increasing</u> surface layer resistance
[pyr14][TFSI] and [pyr13][FSI] have <u>decreasing</u> surface layer resistance

Surface Morphology

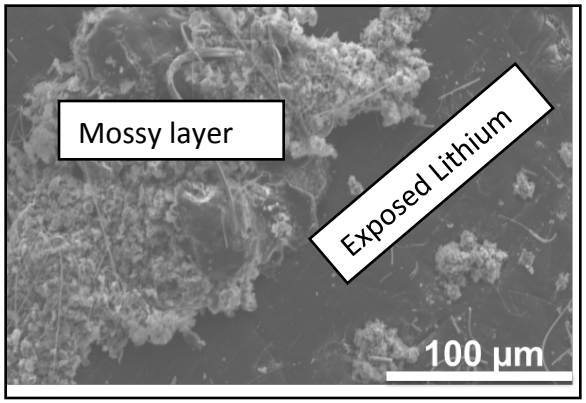
[pyr14][TFSI]



[EMIM][BF4]



[pyr13][FSI]



Surface layers (*mossy* vs *waxy*) have dramatic effect on cycling performance

Essential to understand formation chemistry to select/design optimal, stable electrolytes

Computational modeling to investigate properties and formation of complex surface layers

Seedling Project

I. Isolated Ionic Liquids

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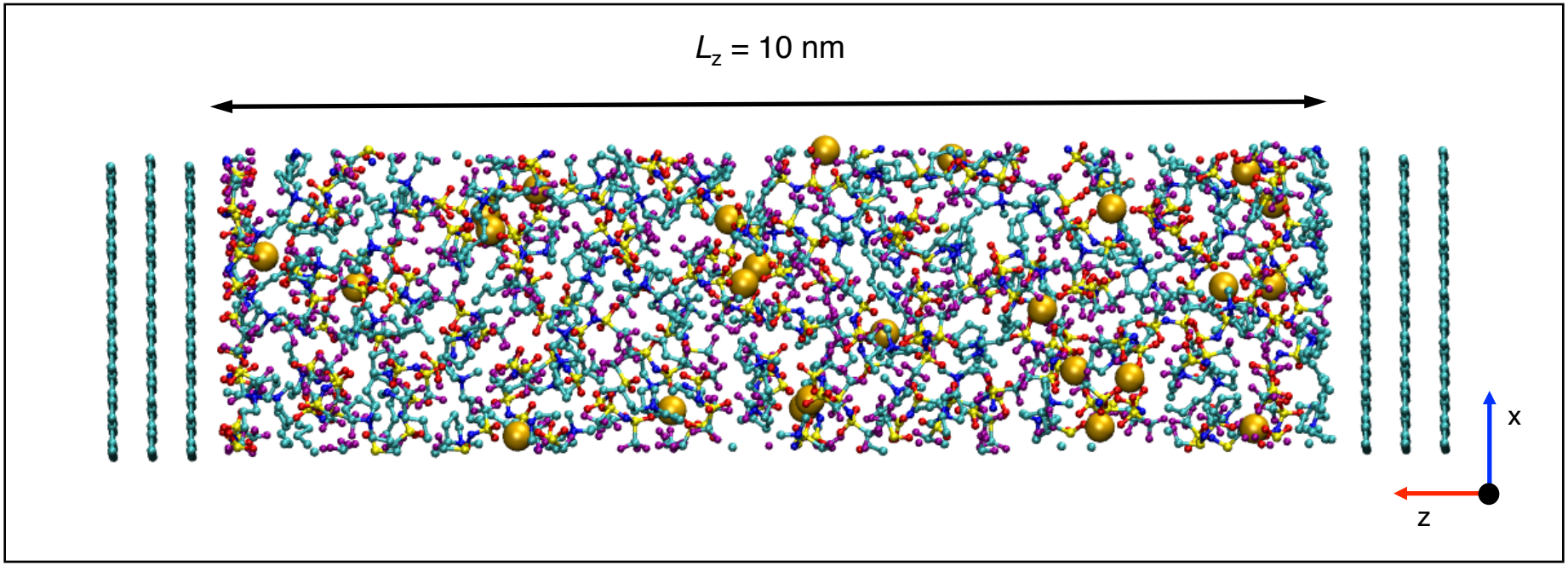
III. Ionic Liquid-Electrode Interfaces

IV. Interfacial Chemistry

V. Extra Funding: Li-Air Cells

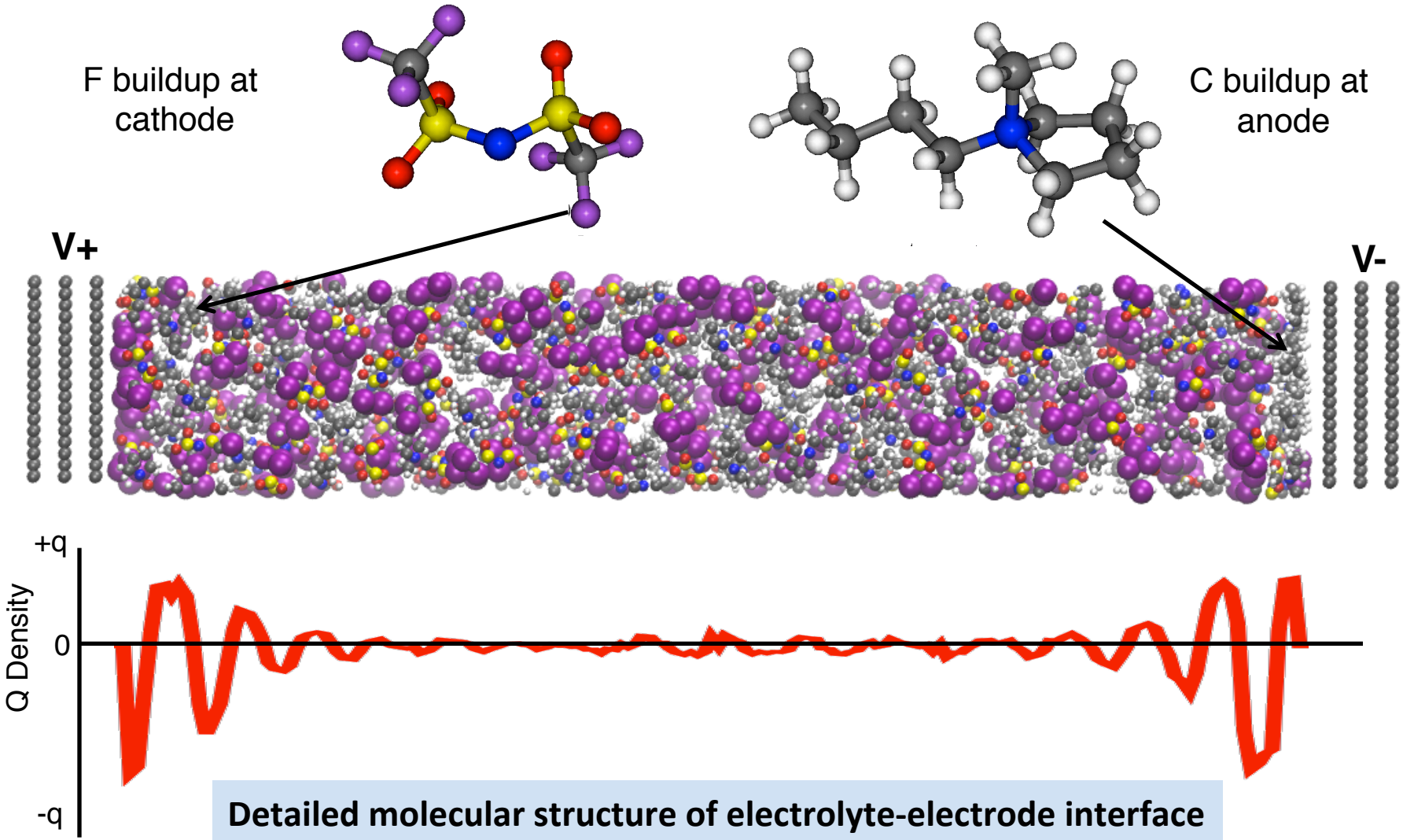
VI. Summary

Electrolyte-Electrode Modeling



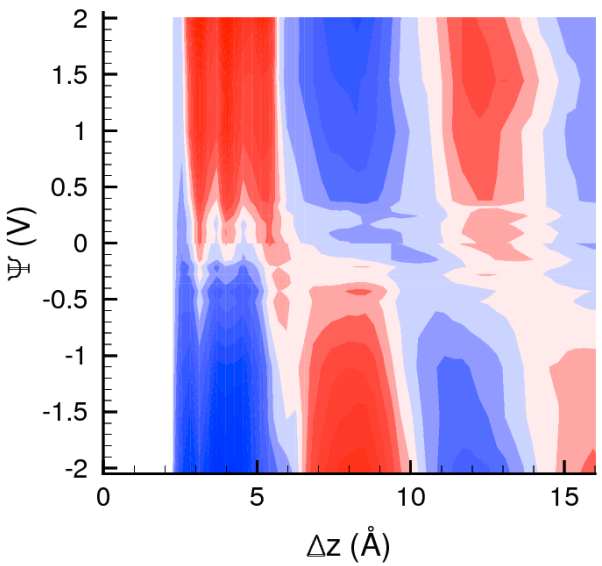
- **Structure and properties of interfacial electric double layer**
- Interface structure sets the stage for electrolyte decomposition
- Advanced simulation techniques implemented
- Neat systems and Li-doped systems
- **<u>Application to batteries and supercapacitors! (CAS proposal)</u>**

Interfacial Double Layer

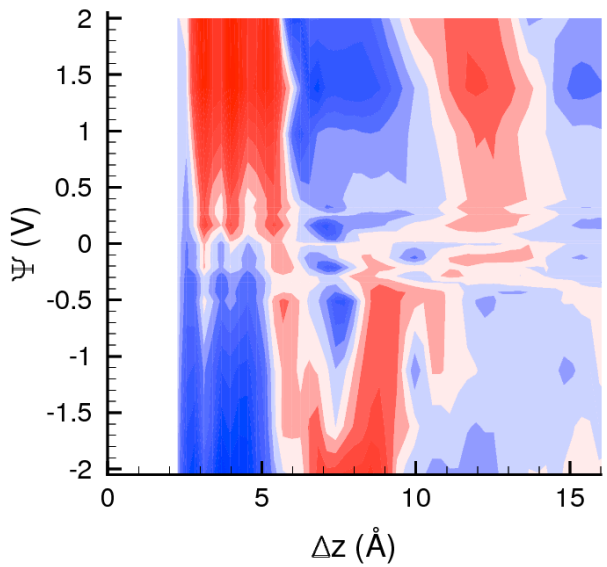


Detailed molecular structure of electrolyte-electrode interface

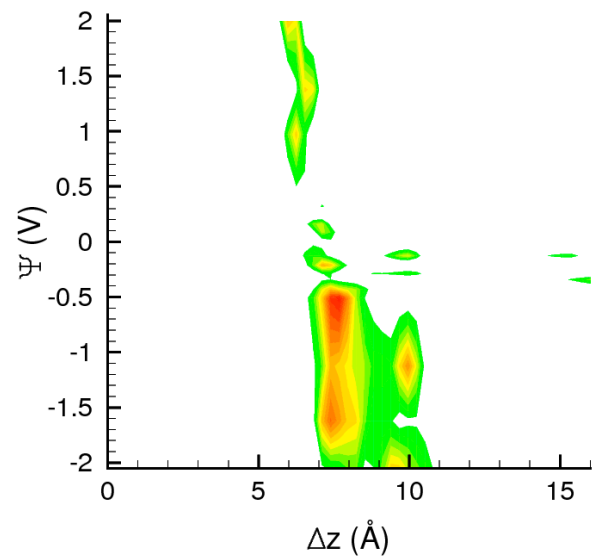
Interface Voltage Maps



Pure [pyr14][TFSI]



20% Li[TFSI]

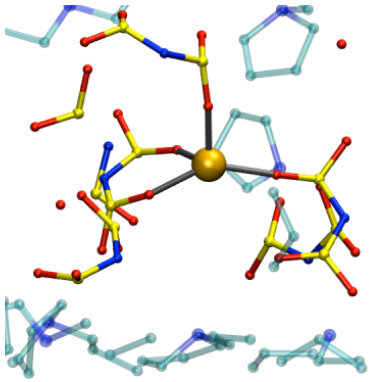


Li-only

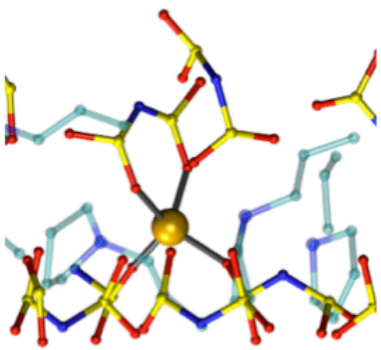
- *Alternating layers of anions (red) and cations (blue)*
- **Interface changes as a function of voltage and Li ion concentration**
- Li-doping *disrupts* well ordered double layer at the interface
- Li^+ strongly *localized* in anode layer 5-10 Ang. from electrode

Li-Ion Interface Distribution

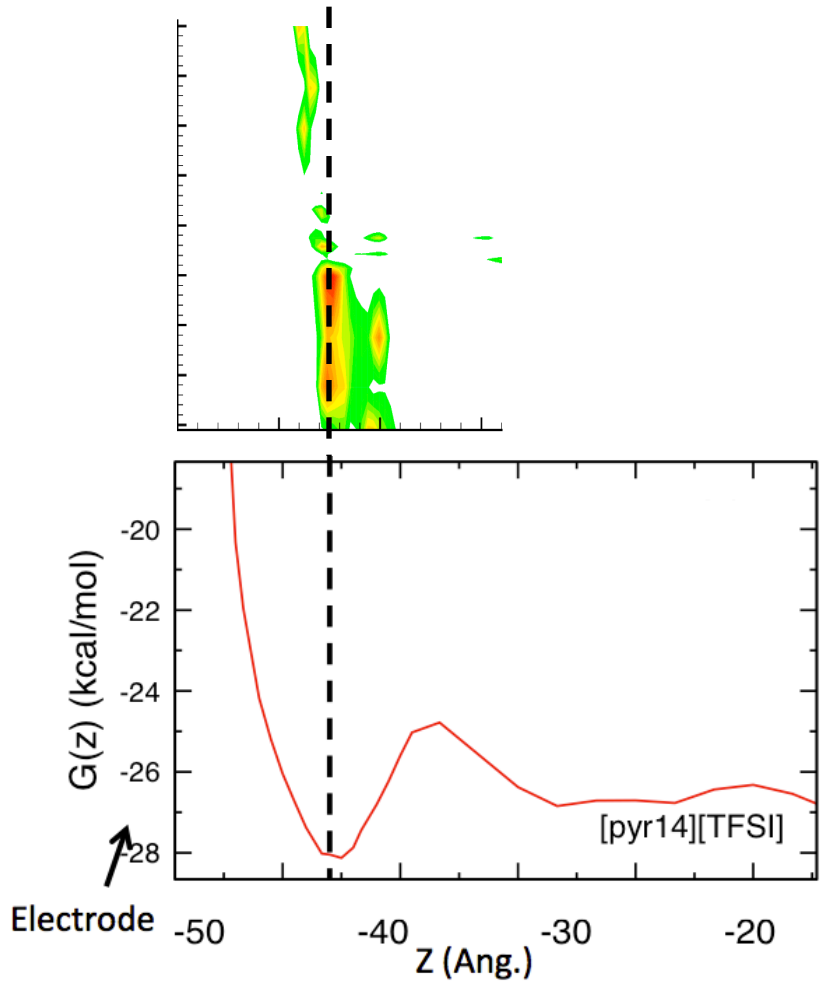
Anode



Cathode



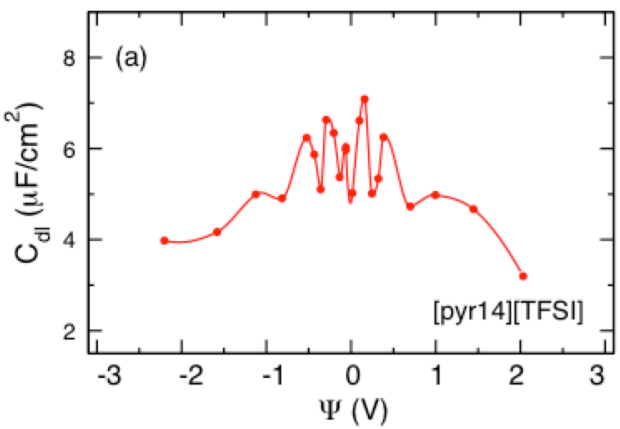
Li ions embedded in anion layers



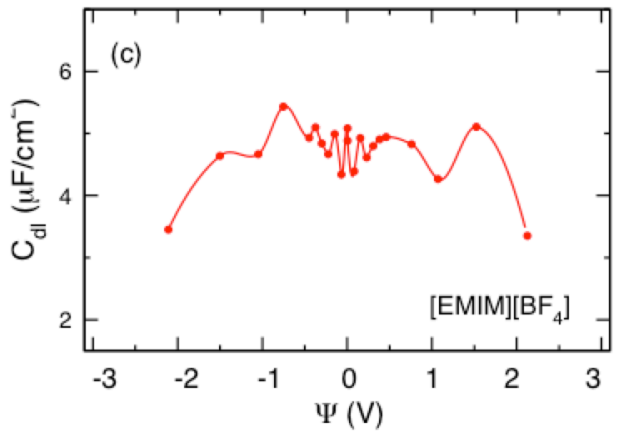
Energy barrier for Li ions to approach surface

Differential Capacitance

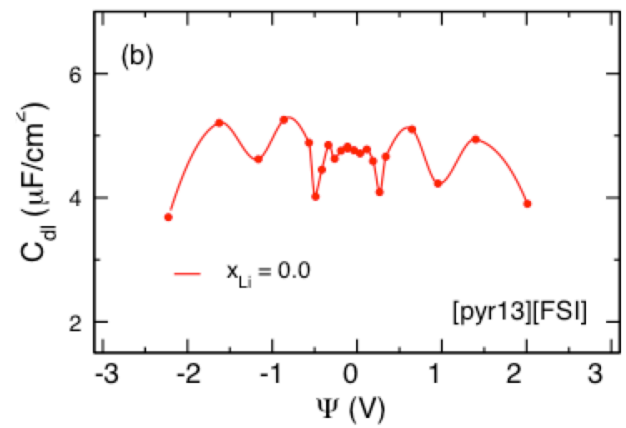
[pyr14][TFSI]



[EMIM][BF$_4$]



[pyr13][FSI]



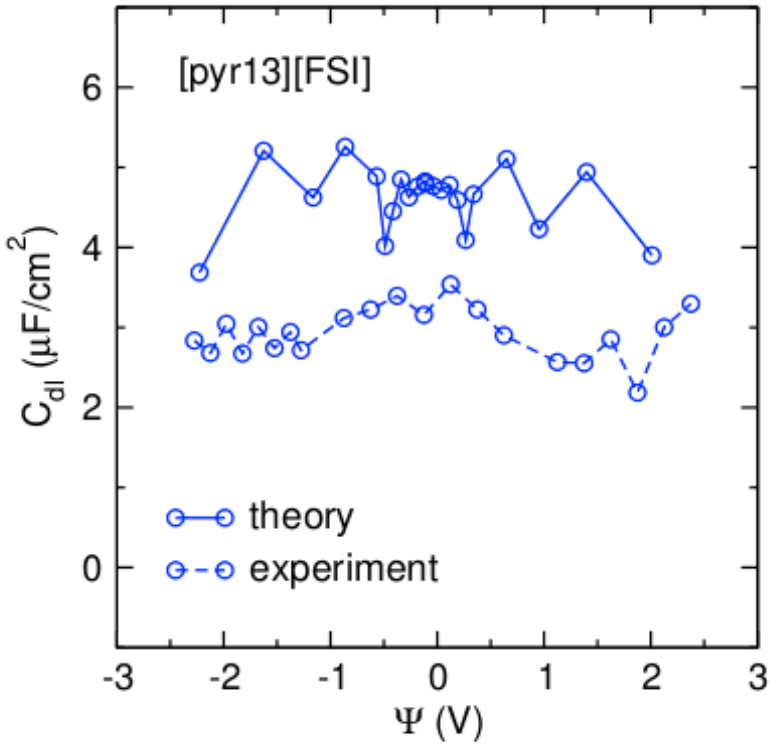
Interfacial double layer stores charge

Simulations correlate differential capacitance with detailed molecular interface structure

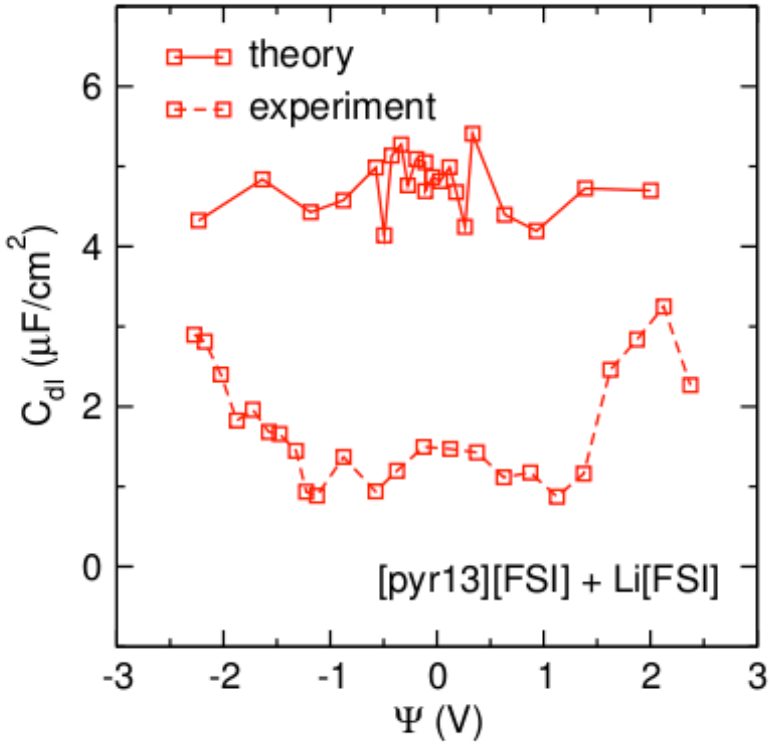
Simulations have application to <u>supercapacitors</u> (CAS)

Differential Capacitance

[pyr13][FSI]



[pyr13][FSI] + Li Salt



Reasonable agreement with experiment: data very sensitive to surface details

Very recent class of simulations - experimentation must catch up with this level of detail

Seedling Project

I. Isolated Ionic Liquids

II. Experimental Cell Characterization

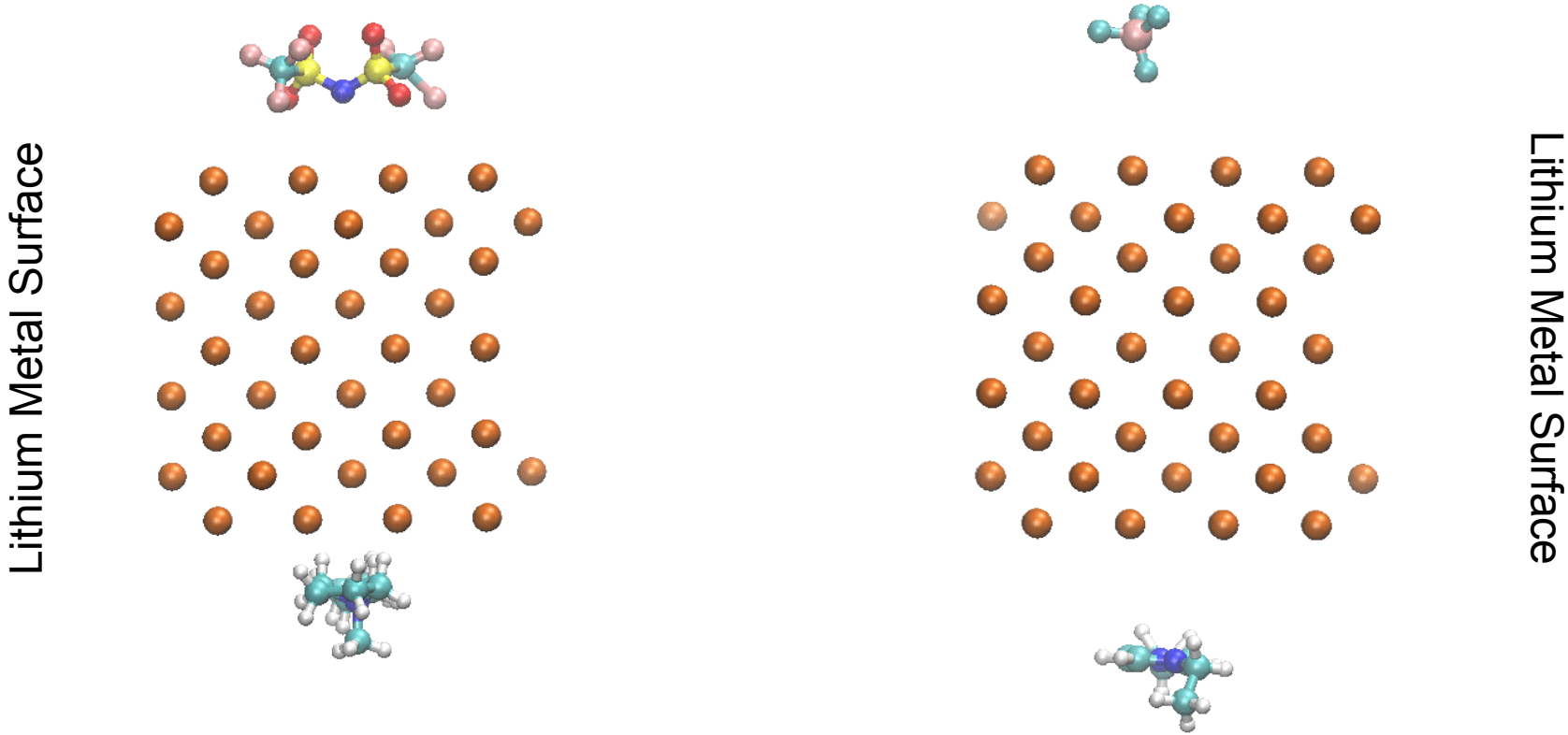
III. Li-Air Full Cells

IV. Ionic Liquid-Electrode Interfaces

V. Interfacial Chemistry

VI. Summary/Future Directions

Electrolyte Decomposition

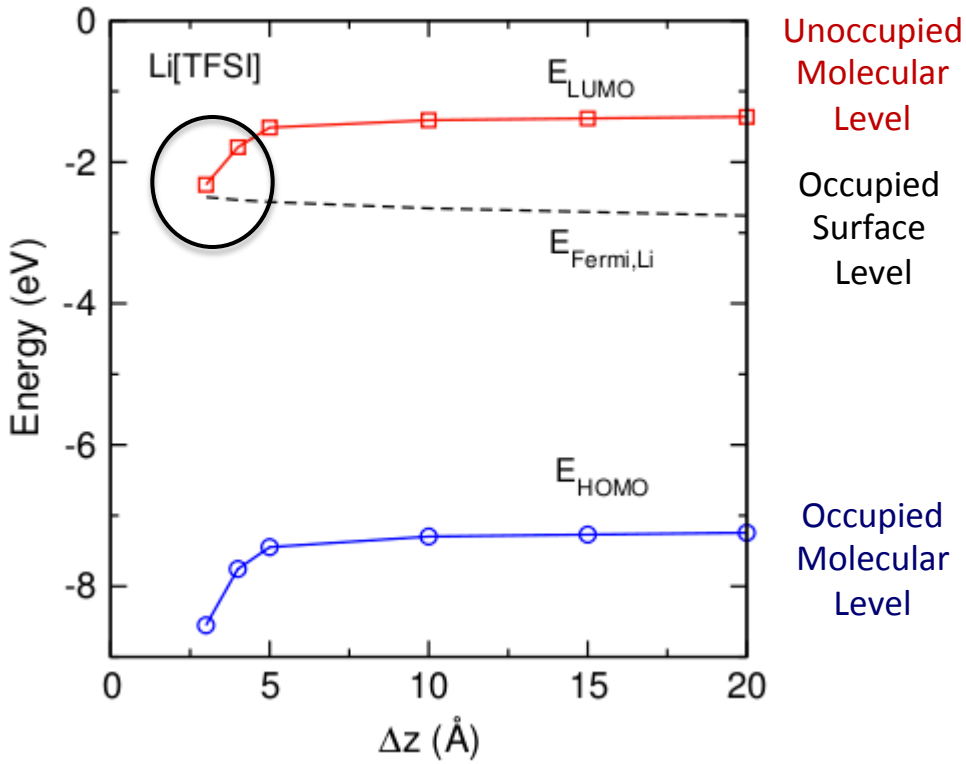


[pyr14]$^{+}$[TFSI]$^{-}$

[emim]$^{+}$[BF_4]$^{-}$

High accuracy, high expense, quantum simulations of electrolyte decomposition

Decomposition Conditions

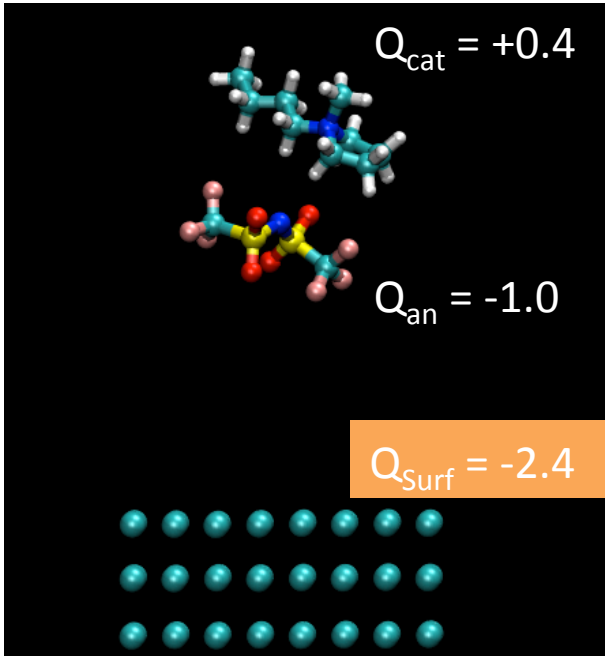


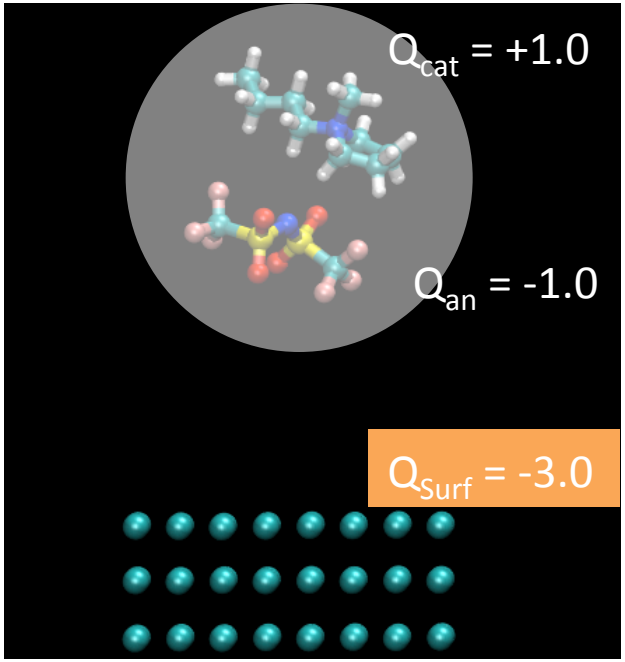
Distance of Molecule from Surface

Decomposition occurs when molecular and surface electronic levels cross

Explanation of behavior seen in simulations

Decomposition Voltage Dependence





First attempt to charge the surface

Problem: electrons jump!

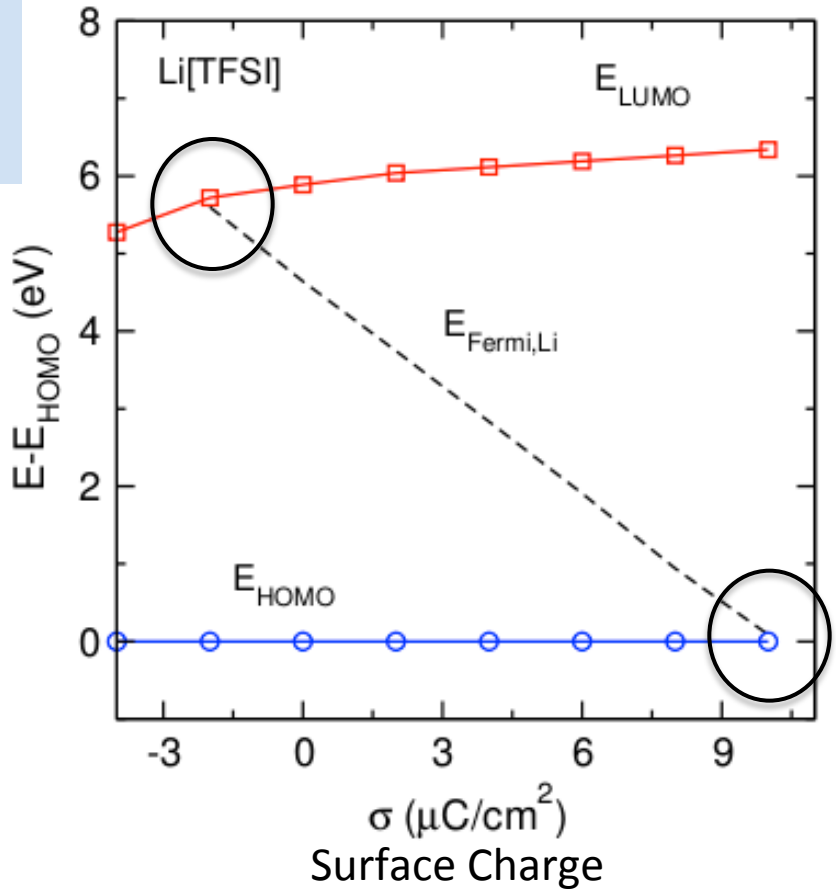
Constrained DFT to control electrons

New non-trivial implementation

Most electrolyte decomposition occurs under voltage conditions
Computations tools very primitive for this complex situation

Decomposition vs Voltage

Electron jumps to molecule



Unoccupied Molecular Level

Occupied Surface Level

Occupied Molecular Level

Electron jumps to surface

Easier to add electron to molecule than to remove one to surface

Predict conditions for electrolyte decomposition (preliminary results)

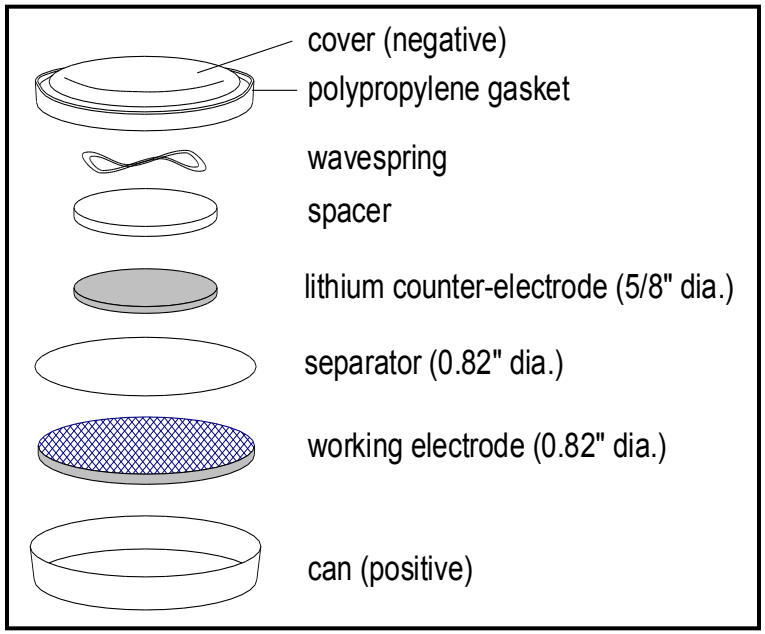
Seedling Project

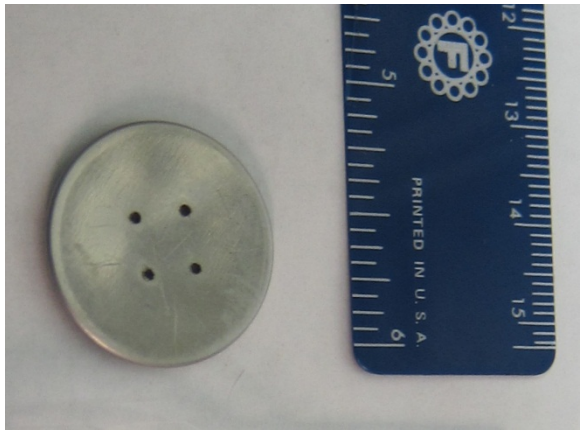
I. Isolated Ionic Liquids
II. Experimental Cell Characterization
III. Ionic Liquid-Electrode Interfaces
IV. Interfacial Chemistry
V. Extra Funding: Li-Air Cells
VI. Summary

Li-Air Coin Cell

Preliminary work with semi-commercial air electrode*

- Samples used to build initial experience
- ~9 mg C/cm² (heavy loading)
- Test in perforated 2325 coin cell
- 2 cm² active area (limited by Li disc area)
- **First testing performed with 0.5 m LiFSI in [P13][FSI] IL**





IL readily wetted this air cathode

Visible flooding of can perforations

Li-Air Coin Cell

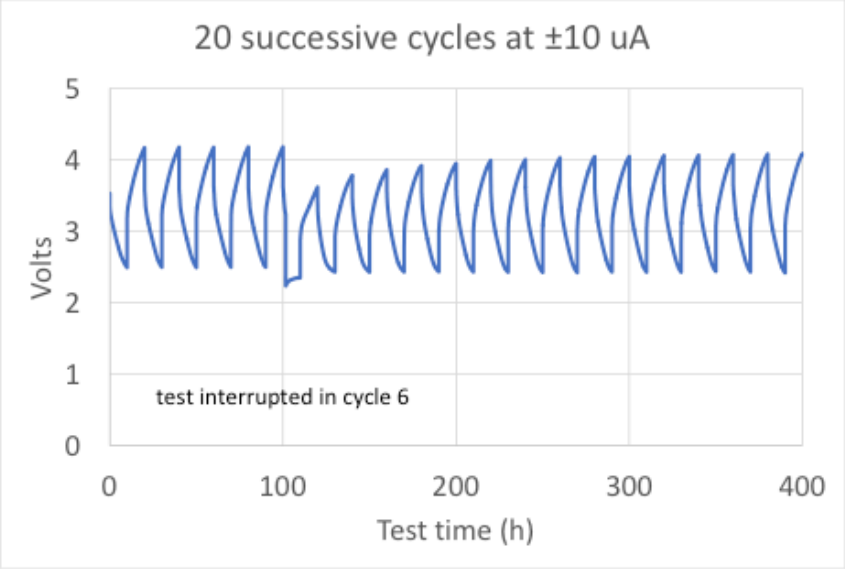
Semi-commercial air electrode

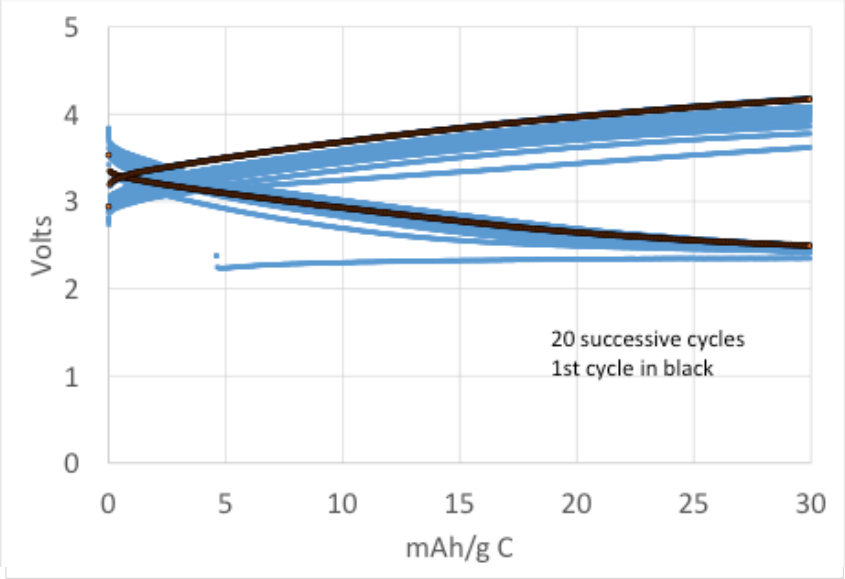
- ±10 uA for 10 hr (0.6 mA/g C)
- No rest
- 6 mAh / g C
- 2 V to 4.8 V cycling limits
- Testing in dry-room air

Results

- 20 cycles completed at shallow discharge
- Low current density (5 uA/cm²)
- Voltage profiles as-expected for Li-air

Cell allowed to continue cycling…

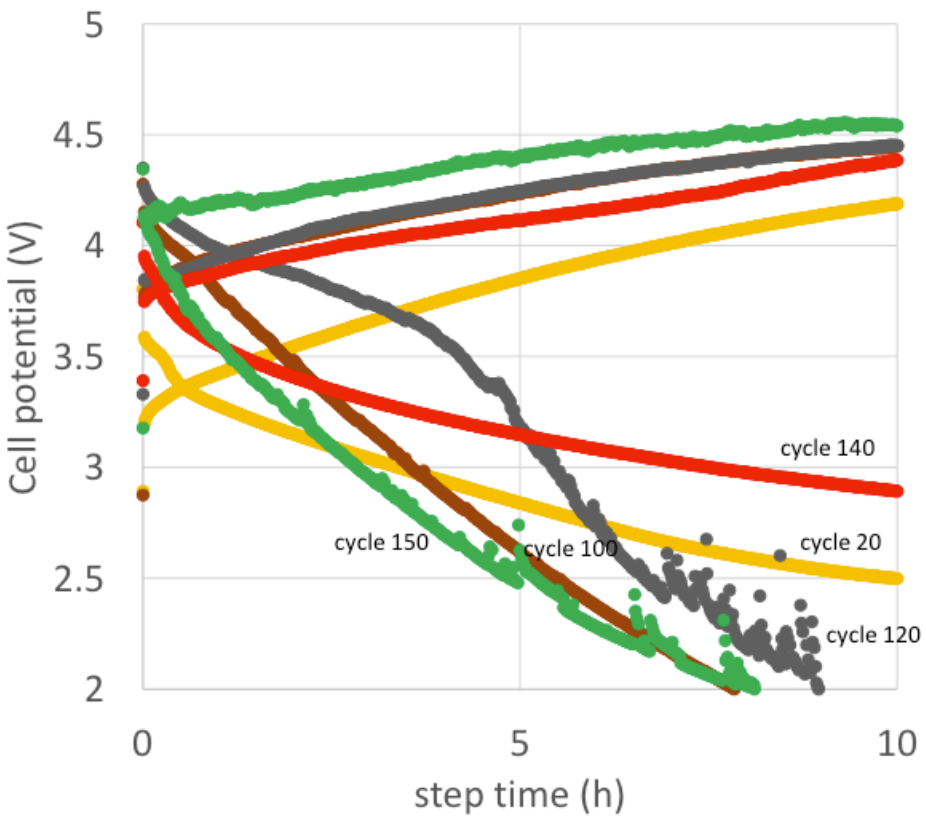




Li-Air Coin Cell

Voltage profiles in extended cycling

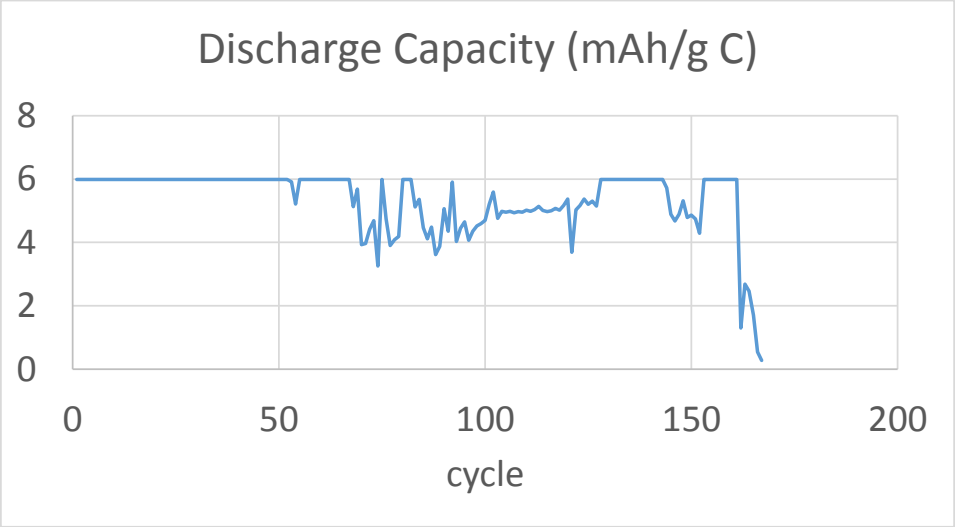
- 160 shallow cycles achieved
- 126 days of exposure to dry-room air
- Erratic discharge performance observed over the life of testing
- 2 V cutoff reached before 10-h limit in many cycles

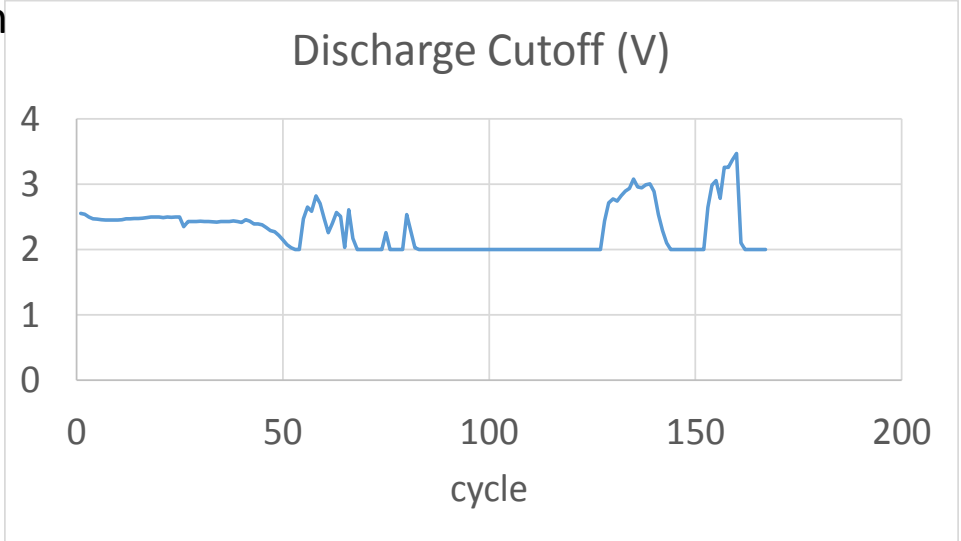


Li-Air Coin Cell

Extended cycling history

- 160 shallow cycles achieved
- 126 days of exposure to dry-room air
- Erratic discharge performance observed over the life of testing
- 2 V cutoff reached in some cycles
- Erratic performance traceable to dry room shutdown events (temperature rise?)





Summary

- **Electrolyte Ionic Conductivity**
  - Implemented high accuracy polarizable force fields for electrolyte simulations
  - Determined detailed structure and *properties* of three bulk ILs electrolytes
  - Excellent agreement between computation and experiment for range of properties
  - New [pyr13][FSI] electrolyte showed significantly better conductivity
  - Analysis of conductivity mechanisms suggest further improvements
- **Experimental Cell characterization**
  - Built and characterized Li cells (cycling, impedance, voltammetry, SEM/EDAX)
  - Identified different surface layers for different electrolytes
  - Correlated morphology of surface layer with cycling performance
  - Identified class of electrolyte with stable cycling
- **Interfacial Structure and Properties**
  - Implemented advanced simulation methods for interface simulations
  - Determined interface double layer properties for all ILs
  - Computed and measured differential capacitance for all ILs studied
  - Correlated molecular structure with capacitance quantitatively.
  - Application to supercapacitors
  - Identified molecular species for decomposition

Summary

- **Interfacial Surface Chemistry**
  - Identified surface decomposition reactions from simulations
  - Analyzed decomposition reactions based on energy level alignment
  - Devised method to charge electrode to study decomposition under voltage
  - Implemented constrained DFT method for computations under voltage
  - Analyzed electron transfer of molecule as a function of voltage
  - Predicted conditions for electrolyte decomposition
- **Full Li-Air Cells**
  - Built and characterized full Li-Air cell
  - Cycled Li-Air cells for more than 140 cycles

Conclusions

- **We made significant progress in developing a *unique*, multifaceted set of experimentally validated computational tools to address major obstacles to high energy, rechargeable, safe batteries**
- Tools are not unique to ILs and can be used for other electrolytes (organics, solid-state, etc)
- **Seedling project provided "proof-of-concept" for these particular tools**
- Significantly more work needed to perform the full analysis, expand the set of reference systems, determine trends, develop further tools, enter design cycle, etc
- **Future work will address**:
  - Further improvements in ion conductivities and other electrolyte parameters
  - Fuller understanding of electrolyte decomposition, stability conditions and surface layer formation
  - Cathode materials and corresponding electrolytes
  - Navigation of huge electrolyte design space, e.g. high-through put screening
  - Chemical synthesis of new, novel electrolytes
  - Establish the relation between chemistry (small scale) and cell performance (large scale)
  - Integration of promising electrolytes into full battery systems
  - Expansion of approach and method to other systems, such as solid state energy storage devices, supercapacitors, etc
- **CAS proposal**: address these questions and go to the next level by bringing in outside partners (IBM, CMU, Berkeley) with expertise in screening, synthesis and design. *Dream Team* of experts *uniquely* positioned to attack these challenges that are at the core of battery cell technology
- **Dissemination:** 2 articles in print, 3 in preparation; 2 conferences(more to come)