

# Low Cost, High Capacity Non-Intercalation Chemistry Automotive Cells

Sila Nanotechnologies, Inc.  
&  
Georgia Institute of Technology  
(Project ID# ES244)

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Presenter: Gleb Yushin (Georgia Tech)

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# Overview

## Timeline

- Project start date: 10/2014
- Project end date: 12/2016
- Percent complete: 70 %

## Budget

- Total project funding
  - DOE share: \$1,000,000
  - Contractor share: \$250,000
- Funding received in FY 2015: 446,807
- Funding for FY 2016: 553,193

## Barriers

- Barriers of batteries addressed
  - High cost
  - Low energy density
  - Short battery life
- Targets: low-cost, scalable, drop-in-replacement materials for high-energy batteries

## Partners

- Sila Nanotechnologies, Inc. – **Lead**
- Georgia Institute of Technology – **subcontractor**
- Army Research Laboratory – **collaborator**

# Relevance & Project Objectives

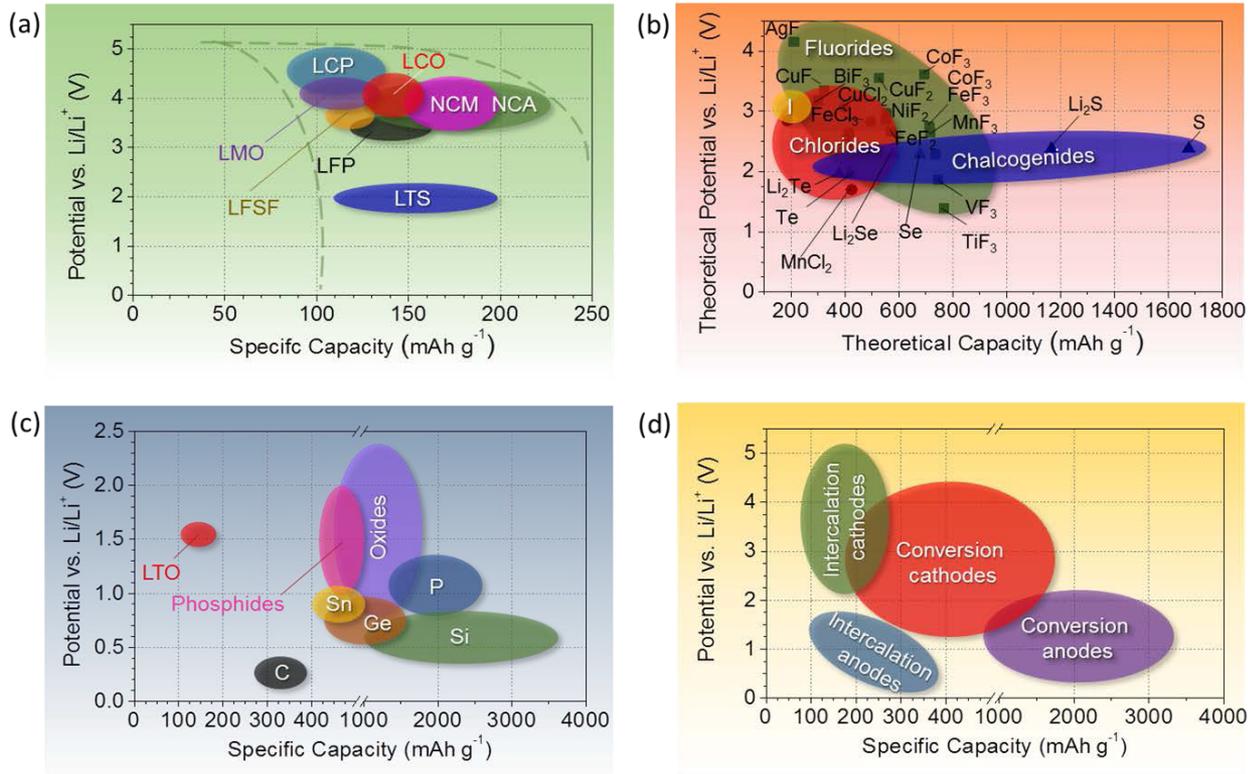
- The overall goal for the project is to conduct focused R&D aimed to demonstrate automotive cells with energy density, specific energy, discharge power density and specific power nearly two times higher than the U.S. DRIVE End of Life Targets for EV Cells: up to ~580 Wh/kg and ~ 1200 Wh/L
- In order to achieve this objective: develop electrochemically stable ultra-high specific capacity metal fluoride ( $\text{MF}_x$ )-based cathodes to be matched with ultra-high specific capacity Si-based anodes.
- Design & fabricate novel core-shell  $\text{MF}_x$  nanocomposite powders that overcomes key material challenges (dissolution, low electrical conductivity of fluorides, volume changes, etc.) that otherwise lead to large voltage hysteresis and rapid capacity fading
- Develop scalable methods of drop-in-replacement material synthesis
- Project targets all listed barriers: high cost, low energy density, short cycle life

# Milestones

Budget Period	Milestones & Go/No-Go Decisions	Status
1	Synthesize porous carbon spheres with tunable size	Complete
1	Develop methodology of uniform infiltration of produced porous carbons with metal fluorides ( $MF_x$ )	Complete
1	Material Characterization (SEM, TEM, EDS, XPS, $N_2$ sorption, etc.)	Complete
1	<p>Electrochemical Characterization: cathode half cells</p> <p><b>Go/No-Go:</b> Half cell stability of 50 cycles with at least 60% of theoretical capacity utilization</p> <p><b>Go/No-Go:</b> Achieve 80% of theoretical capacity utilization</p>	<p>Complete</p> <p>&gt; 800 cycles demonstrated at above 80% of theoretical capacity</p>
2	Material Characterization & Post-Mortem Analyses (SEM, TEM, EDS, XPS, $N_2$ sorption, etc.)	On track
2	<p>Electrochemical Characterization:</p> <ul style="list-style-type: none"> <li>- <math>MF_x</math> cathode half cells</li> <li>- Si-based anode / <math>MF_x</math> based cathode full cells</li> </ul>	On track
2	<p>Optimize electrode fabrication &amp; full cell construction</p> <ul style="list-style-type: none"> <li>- Demonstrate cycle stability of 200 cycles in full cells</li> <li>- Demonstrate unit stack energy density of 1200 Wh/L</li> <li>- Demonstrate unit stack power density of 2400 W/L</li> <li>- Produce 200 mAh+ full cells</li> </ul>	On track

# Approach / Strategy

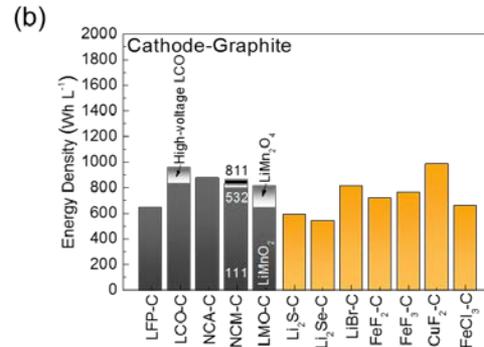
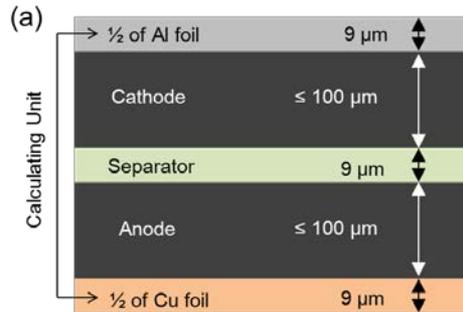
## ➤ Opportunities offered by Conversion Electrodes



- Intercalation materials approach their theoretical limits: increase in specific capacity becomes very challenging and increasing cell voltage raises safety concerns
- Conversion electrodes offer up to 10x higher specific capacity (at the expense of lower cell voltage)
- Replacement of intercalation cell chemistry with conversion-type anodes & cathodes may allow substantial increase in cell specific energy and energy density

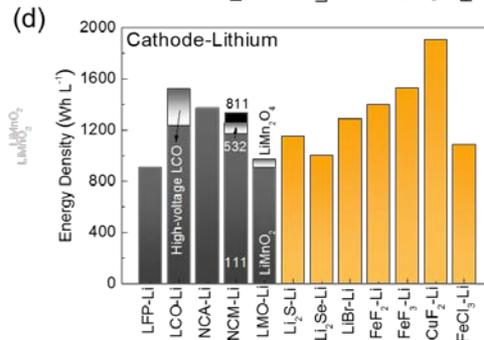
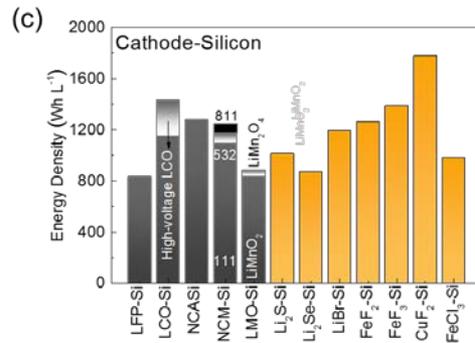
# Approach / Strategy

## ➤ Opportunities offered by Conversion Electrodes



### Assumptions:

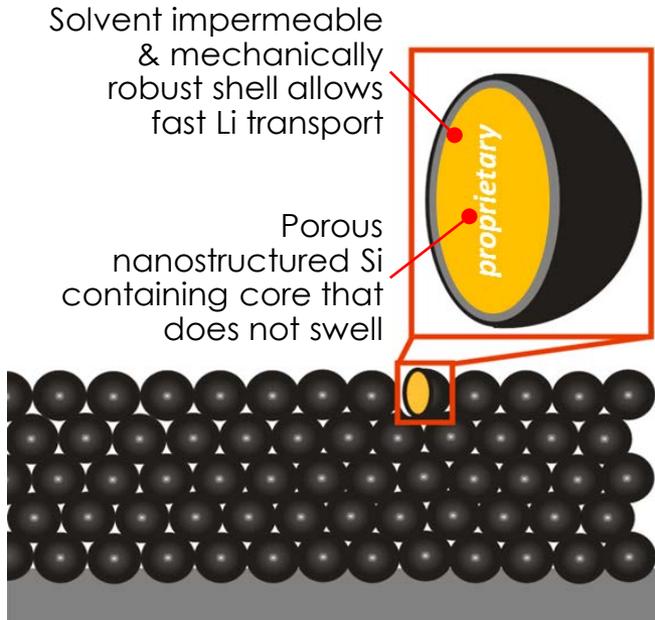
- Calculations of energy density of “building blocks”
- Electrode density: 60 vol.% active in case of conversion materials and 70 vol.% in case of intercalation materials
- Material properties in the fully expanded (lithiated) state are considered
- Average discharge potential = experimental @ slow rate (intercalation) and 0.25V below theoretical (for conversion materials)



- Improvements possible: up to ~ 2.5x vs. further optimized intercalation chemistries (up to ~ 4x vs. state of the art)
- Since the cost of active materials is only ~ 25% of the full cell cost, increase in the cell energy density (assuming comparable electrode cost) directly leads to reduced cell cost (on Wh basis)
- Cells with Si anodes offer nearly the same energy density as with Li, but are safer, cheaper to use (drop-in replacement) and offer much higher power at high capacity loadings
- Conversion electrodes suffer from multiple challenges that must be overcome

# Approach / Strategy

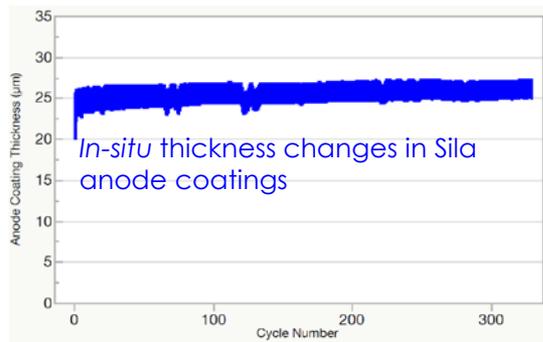
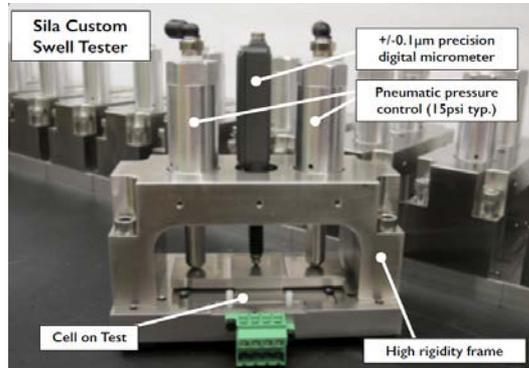
## ➤ Sila Si Anode Materials



- **Drop-in replacement** Si-based anode powder: mechanically stable, **micron-scale, low surface area** powder (compatible with existing equipment & slurry formulations)
- Chemical composition & detailed microstructure is proprietary
- Specific capacity: 800-1800 mAh/g
- Volumetric capacity (at the electrode level after formation): 700-1200 mAh/cc (compared to ~ 400-430 mAh/cc for state of the art graphite anodes)
- Exhibit very small volume changes at a particle level during cycling

# Approach / Strategy

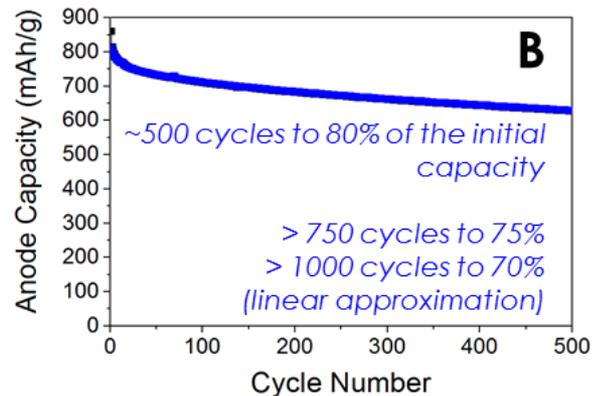
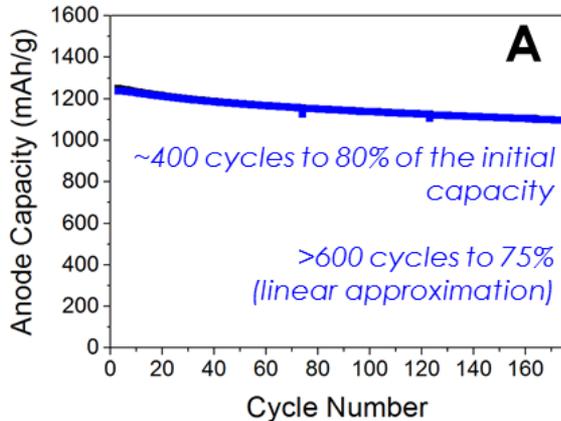
## ➤ Sila Si Anode Materials



- High-precision ( $\leq 100$  nm) custom-designed tools developed for the *in-situ* thickness measurements were calibrated using multiple standards, including commercial graphite electrodes.
- Thickness changes within individual coatings (excluding Cu foils) are derived from the measurements of the full cell swelling data
- Small ( $< 12\%$ ) cycle-to-cycle volume changes within dense (no extra space between the packed individual particles) anode demonstrated (100% Sila anode powder, no graphite)
- Very low lifetime expansion demonstrated
- Smaller volume changes correlate with longer cyclers life in full cells

# Approach / Strategy

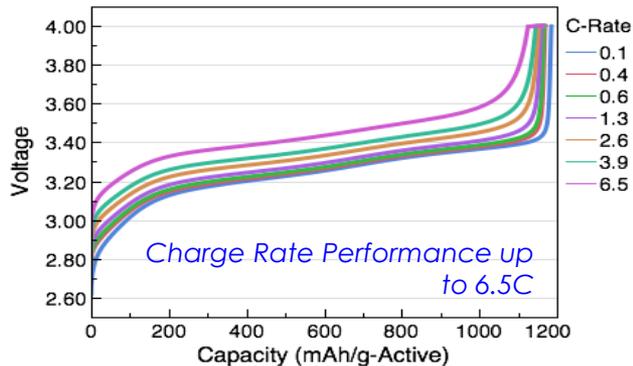
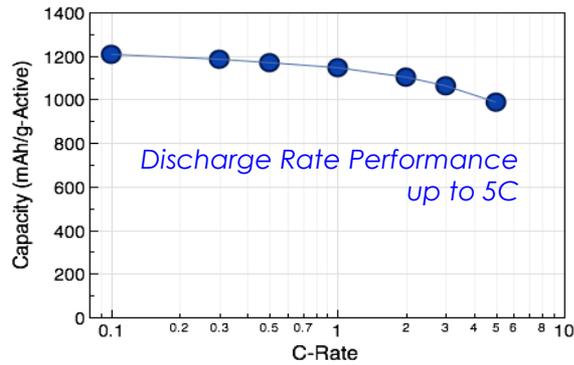
## ➤ Sila Si Anode Materials



- Data from early 2015
- Matched full cells with Si anodes: NCM & LFP Cathodes (no pre-lithiation, no excess capacity, 100% DoD)
- Current capacity loadings: 2-5 mAh/cm<sup>2</sup>; aiming to improve to 8+ mAh/cm<sup>2</sup>
- Anodes are 100% Sila materials (no graphite mixed)
- Current binder & C additive content: 15-22.5 wt. %; aiming to reduce to 5-8 wt. % (capacity is normalized by the mass of active material)
- Degradation rate slows down during cycling
- **A cell:** 400 cycles to 80% of the initial capacity, 600+ cycles to 75%
- **B cell:** 500 cycles to 80% of the initial capacity, 750+ cycles to 75% and 1000+ cycles to 70%

# Approach / Strategy

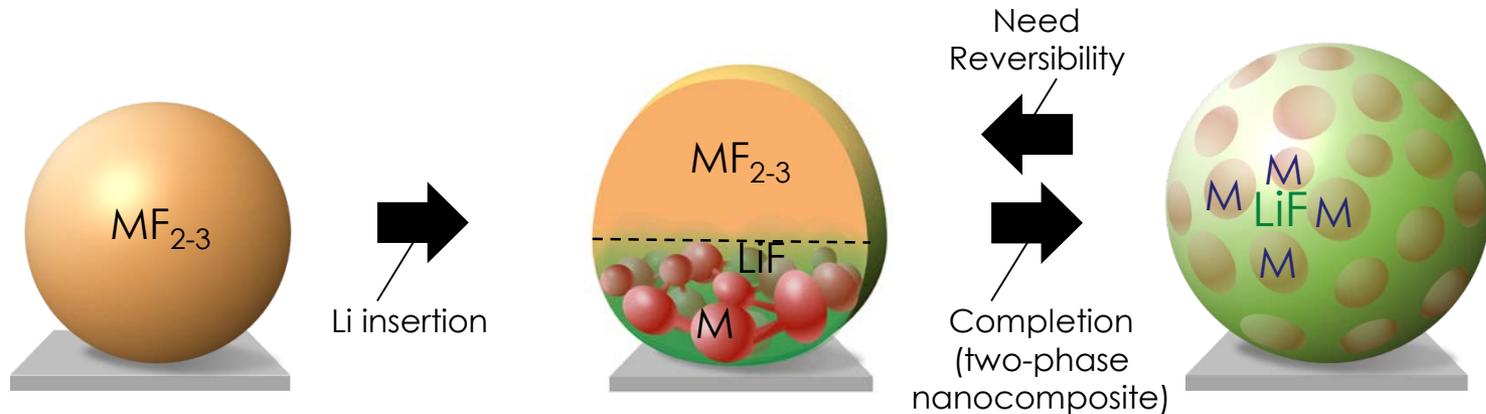
## ➤ Sila Si Anode Materials



- Anode rate tests conducted against LFP cathodes (in matched full cells)
- Anodes are 100% Sila materials (no graphite mixed)
- Discharge rate performance:
  - Capacity @ 1C is 95% of 0.1C
  - Capacity at 5C is 83% of 0.1C
- Charge rate performance:
  - Capacity @ 6.5C is 95% of 0.1C (without taper)
  - Higher anode potential & thinner electrodes help to prevent plating at high charge rates

# Approach / Strategy

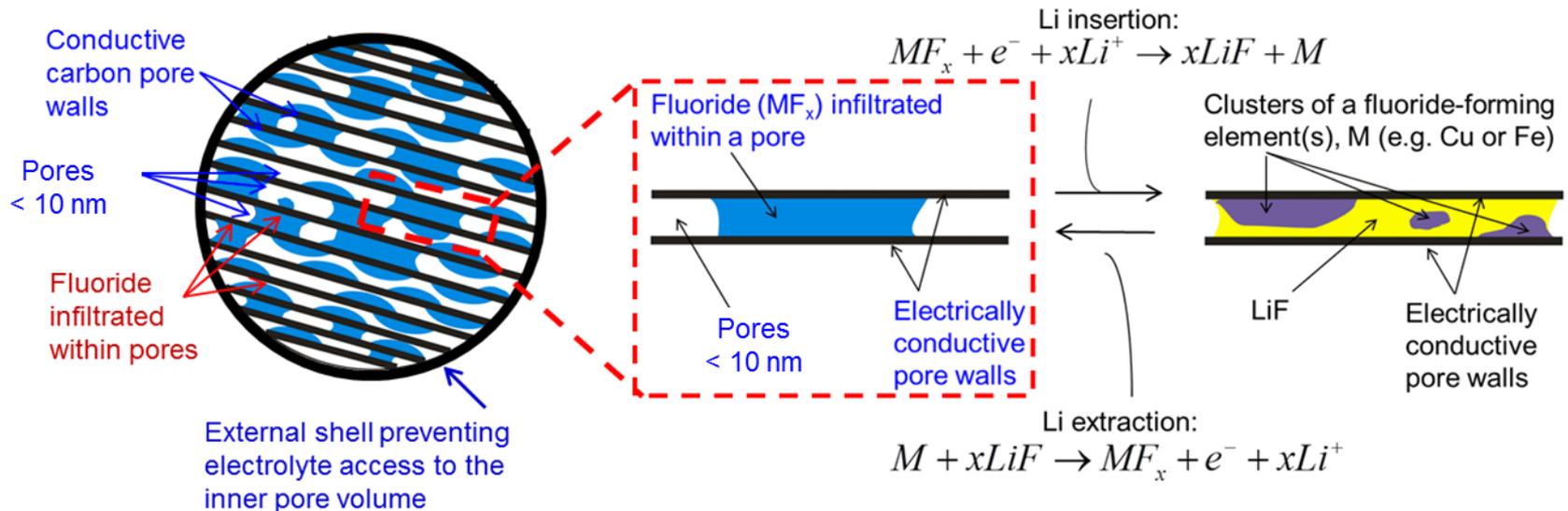
## ➤ Challenges with $MF_x$ Cathode Materials



- High M/LF interfacial energy leads to (i) growth of M & LF clusters during cycling and (ii) separation of LF from conductive M, leading to fast impedance growth and rapid cell degradation
- Electrochemical dissolution of M into electrolyte during cycling leads to (i) cathode capacity fading and (ii) damages induced to the SEI on the anode (Li losses and anode degradation)
- Significant volume changes may induce mechanical damages to the electrode and similarly contribute to cell degradation

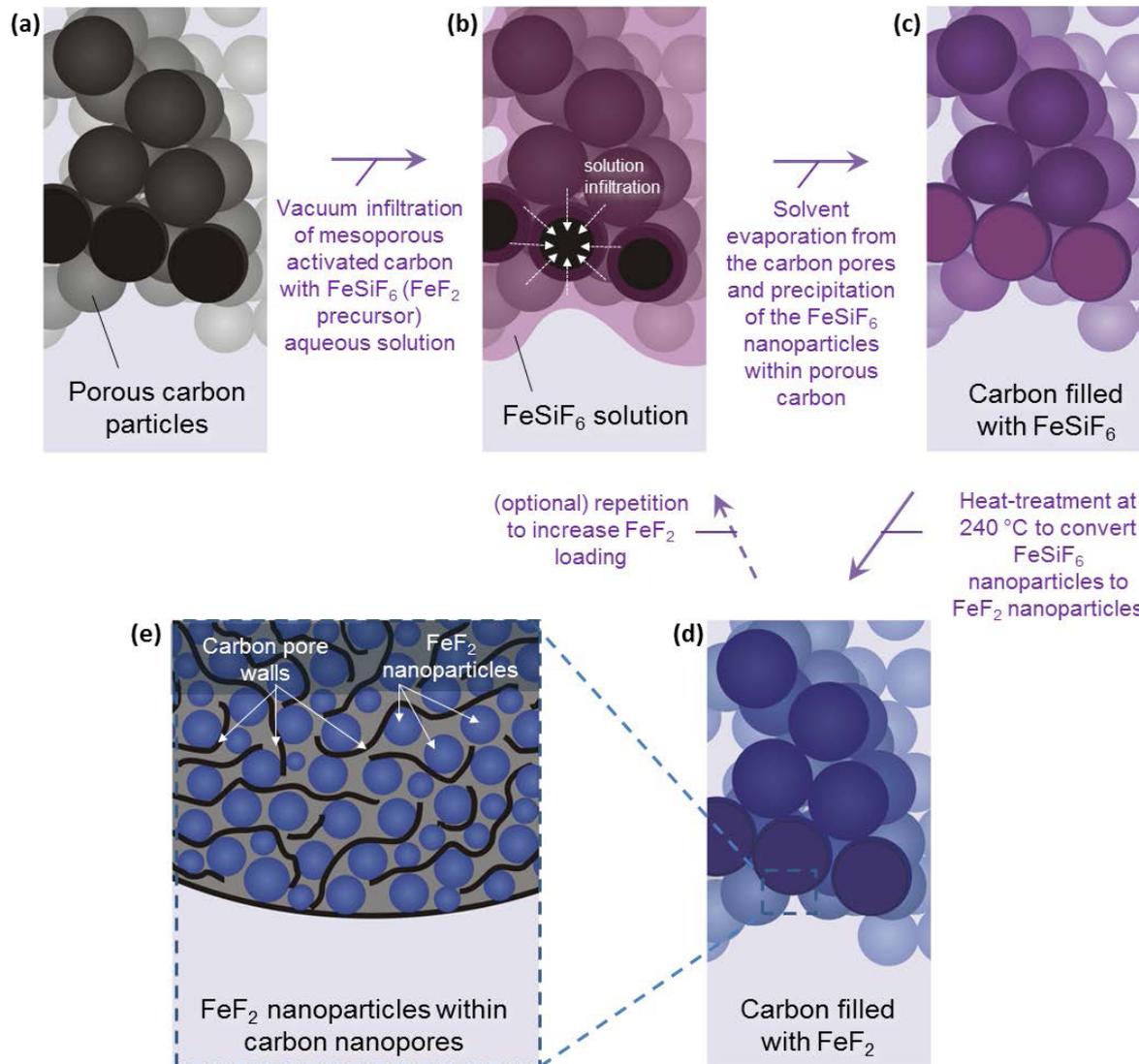
# Approach / Strategy

- **Proposed MF<sub>x</sub> Cathode Materials:** Confinement of MF<sub>x</sub> in Carbon Nanopores combined with the formation of protective outer shell



- Nano-confinement of MF<sub>x</sub> minimizes migration of M and LiF clusters
- conductive carbon pore walls supply electrons to/from electrochemical reaction sites (no need to rely on interconnectivity of M clusters)
- Carbon buffers the volume changes in the MF<sub>x</sub> cathodes
- Shells prevent undesirable interaction between M and liquid electrolyte

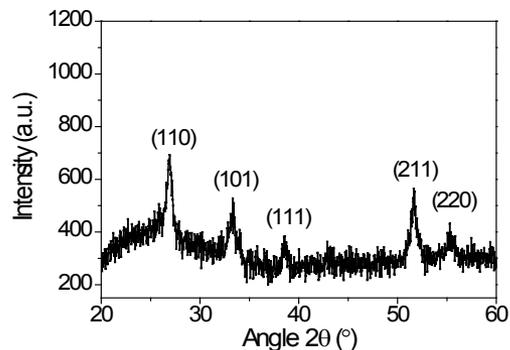
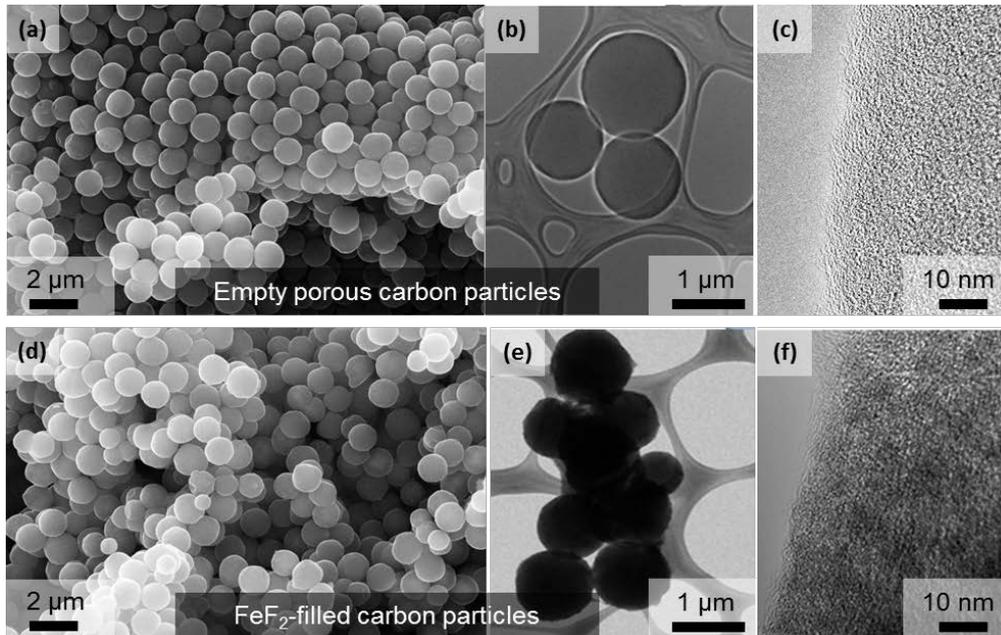
# Accomplishments & Progress



- Methodology: nano-confinement of MFX in carbon pores may be achieved by a low-cost infiltration of MFX precursors (e.g.,  $\text{FeSiF}_6$  in case of  $\text{FeF}_2$ ) into the pores of porous carbons, followed by a heat-treatment in a controlled environment.
- Critical parameters: high solubility of the precursor in a solution; good wetting properties; low-cost solvent; low-cost precursor

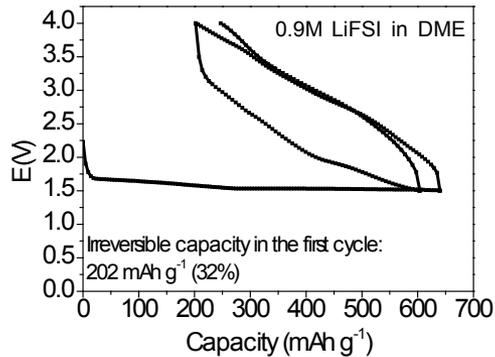
# Accomplishments & Progress

## ➤ FeF<sub>2</sub> – C cathodes

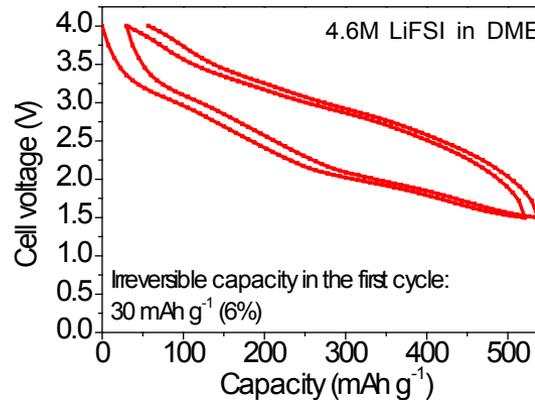
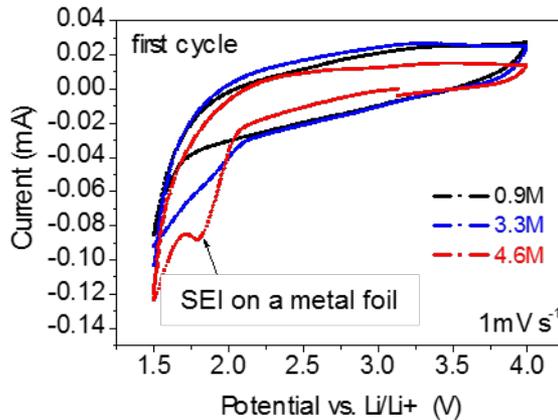


- The average size of the spherical FeF<sub>2</sub>-C nanocomposite particles is ~ 1 μm
- The smooth surface of the FeF<sub>2</sub> infiltrated AC particles indicated a good efficiency of our synthesis procedure, where no nanoparticles present outside the carbon pores.
- XRD confirmed the presence of FeF<sub>2</sub> nanoparticles and the lack of any crystalline impurities
- TEM studies confirmed the infiltration of FeF<sub>2</sub> within the AC spheres

# Accomplishments & Progress

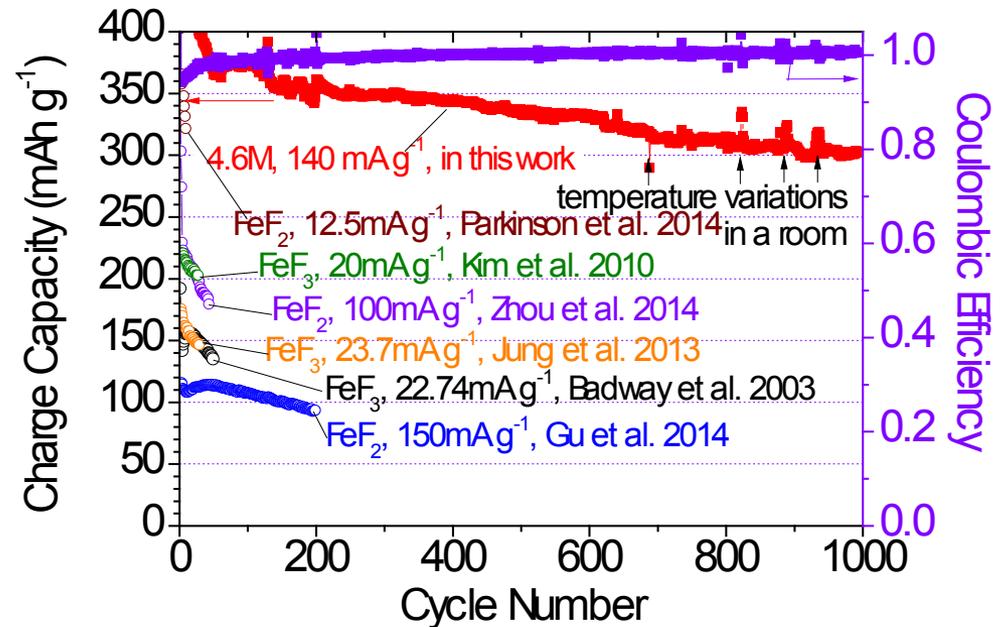
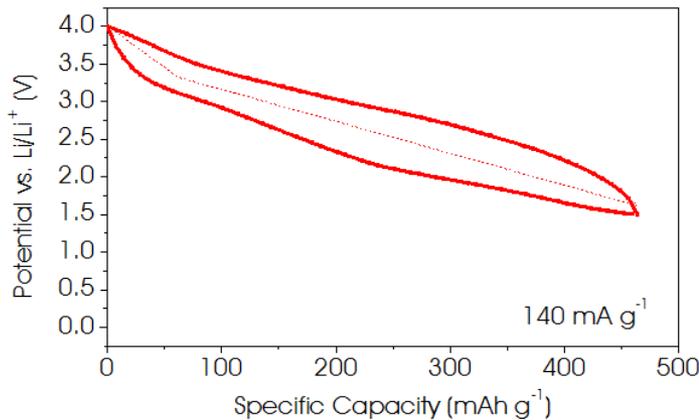


- Initial experiments on  $\text{FeF}_2$
- Large over-potential in first discharge
- (as will be shown later) Fe dissolution during electrochemical cycling



- Concentrated LiFSI/DME undergoes reduction at high potentials and forms a passivating layer
- IDEA:** utilize concentrated LiFSI/DME electrolyte to form a protective layer (SEI), which might be efficient for prevention undesirable reactions between liquid electrolyte and M (Fe, in this case)
- Observed dramatic reduction of over-potential & high (>80%) capacity utilization

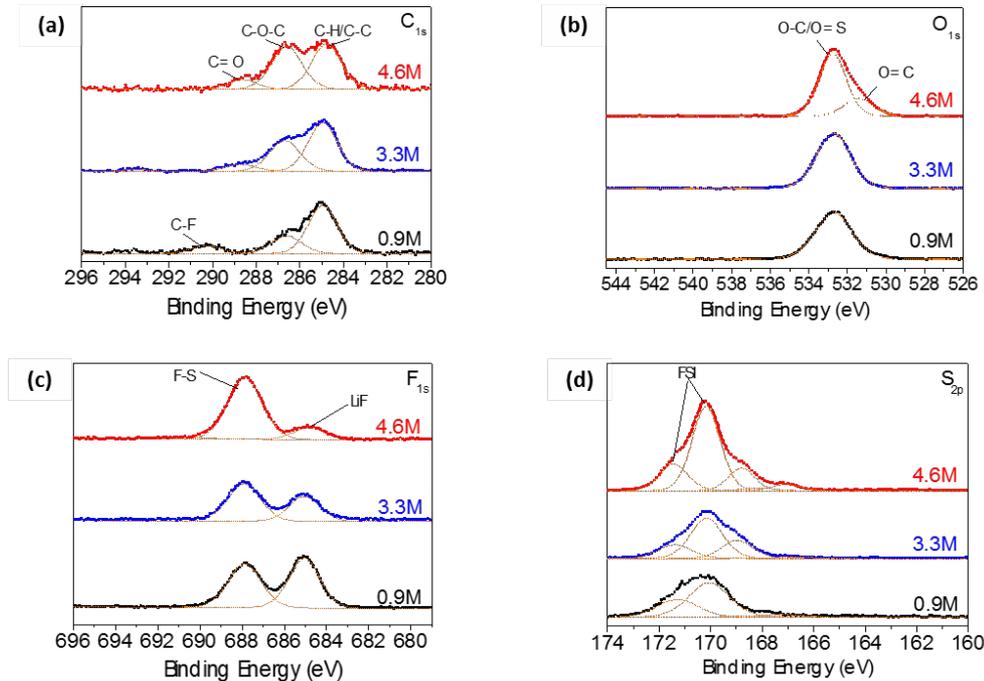
# Accomplishments & Progress



- The longest stability of MFx cathodes demonstrated thus far
- Exceeded the 50 cycle millstone (>1,000 cycles in half cells demonstrated)
- The smallest (for this chemistry @ RT) hysteresis @ 140  $\text{mA/g}$  (C/3) current density
- Unique MFx-electrolyte combination: concentrated LiFSI electrolyte provides *in-situ* surface layer protection

# Accomplishments & Progress

## ➤ Post-mortem analysis on cathode surface

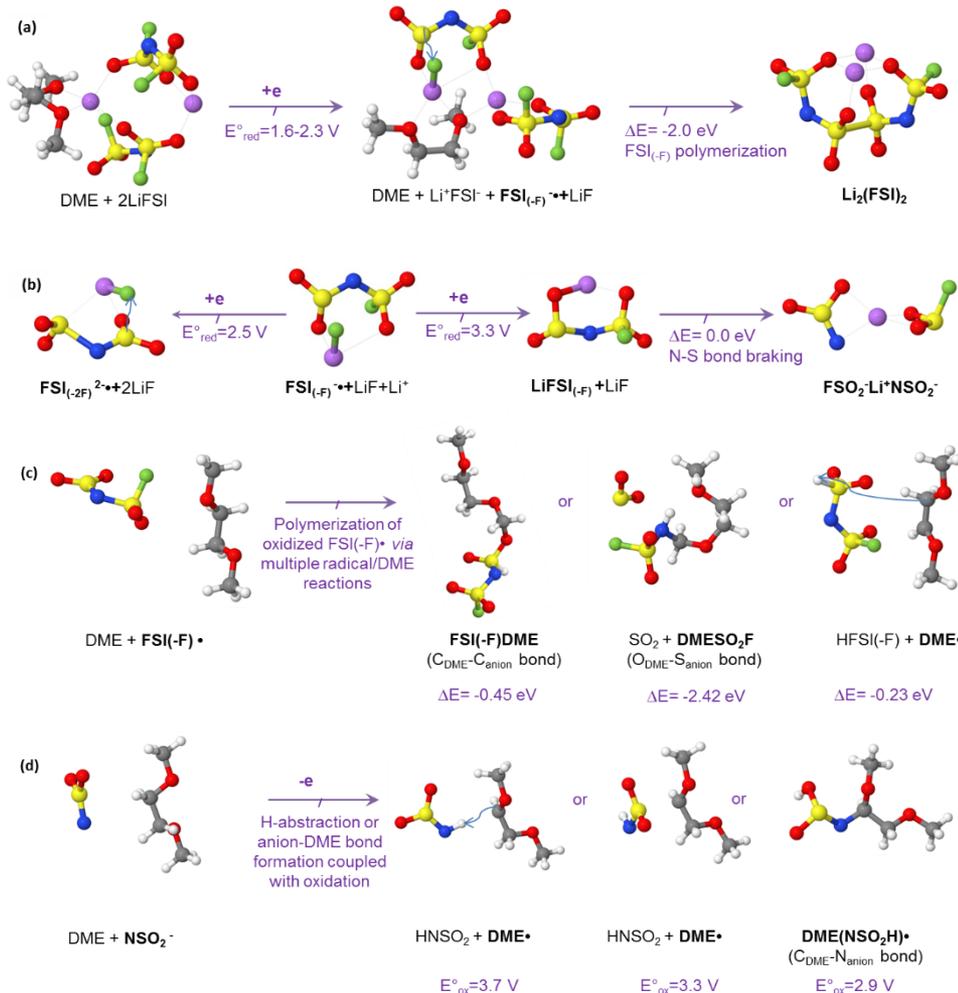


High resolution XPS spectra of  $\text{FeF}_2/\text{C}$  nanocomposite cathode cycled in 0.9M, 3.3M and 4.6M LiFSI/DME electrolytes: (a)  $\text{C}_{1s}$ ; (b)  $\text{O}_{1s}$ ; (c)  $\text{F}_{1s}$ ; (d)  $\text{S}_{2p}$ .

- $\text{C}_{1s}$  peak at 285eV is due to C-C bonds from AC spheres, and - $\text{CH}_2\text{-CH}_2\text{-}$  bonds from polymerized DME; the C-F peak due to PVdF (at 290.5eV) is diminished at higher salt concentration due to thicker layer of the reduced electrolyte; peak at 286.4eV corresponding to C-O-C bonds from polymerized DME; C=O peak - from the breakdown of the backbone of DME.
- $\text{O}_{1s}$ : C=O peak is confirmed; peak at 532.4eV is due to O-C bonds in DME and O=S in LiFSI and its reduction products such as  $\text{LiNSO}_2$  and  $\text{LiFSO}_2$
- $\text{F}_{1s}$ : dampening of the LiF peak at 685eV and rise of the F-S peak at 687.8eV

# Accomplishments & Progress

➤ Collaboration on QC modeling with Dr. Oleg Borodin, ARL

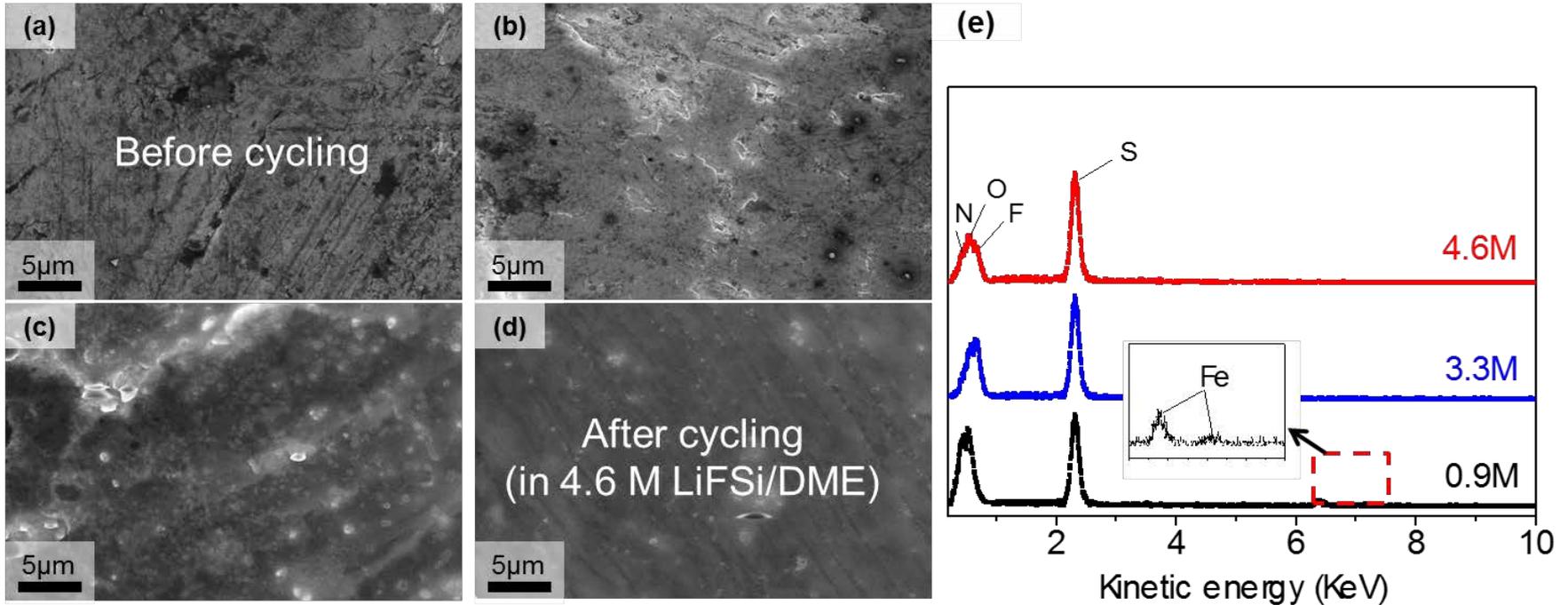


Selected results of G4MP2 quantum chemistry calculations showing the LiFSI(DME) redox, decomposition and polymerization reactions and the expected SEI components:

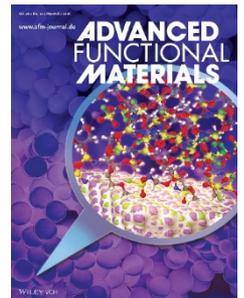
- formation of  $\text{FSI}_{(-F)}^{\bullet}$  radicals and their potential polymerization;
- reduction of  $\text{FSI}_{(-F)}^{\bullet}$  and decomposition of some of the reduction products;
- co-polymerization and other reactions of oxidized  $\text{FSI}_{(-F)}^{\bullet}$  with DME, such as H abstraction;
- $\text{NSO}_2^-$  oxidation coupled with its reaction with DME, leading to H abstraction and the resulting formation of  $\text{DME}^{\bullet}$  radicals or co-polymerization.

# Accomplishments & Progress

➤ Post-mortem analysis on Li anode surface:



- 4.6 M LiFSI in DME Electrolyte: Fe dissolution is eliminated
- **Bonus**: NO DENDRITE GROWTH / very smooth Li surface after 1,000 cycles in our electrolytes (regular Li surface, no coatings, no alloying with other elements)



# Responses to Previous Year Reviewers' Comments

➤ Not applicable

# Collaborations

- Dr. Oleg Borodin, Army Research Laboratory: QM Modeling

# Remaining Challenges & Barriers

- Electrochemical stabilization of  $\text{CuF}_2$  remains a grand challenge
- In-situ formation of protective shells may be insufficient for  $\text{CuF}_2$  (particularly at elevated temperatures)
- Further reduction in voltage hysteresis (and energy efficiency of cells) is also challenging
- Enhancement of rate capabilities (particular at high loadings of  $\text{MF}_x$  into C and small fraction of the remaining pores) is another challenge

# Proposed Future Work

- Form Li-ion permeable (solvent impermeable) shells on  $\text{CuF}_2\text{-C}$  composite powders prior to forming them into electrodes & cycling in order to enhance their cycle stability
- Develop hierarchical composites (with channels for faster Li ion access from the surface into the bulk of the particles) to enhance rate performance
- Explore doping  $\text{MF}_x$  in order to enhance rate performance & stability
- Develop high capacity loading cathodes for matching with Si anodes & optimize electrode construction and electrolyte composition to achieve high rate performance in full cells
- Advantages & limitations of different approaches of introduction Li into the system (e.g., cathode lithiation) needs to be explored