Novel Non-Carbonate Based Electrolytes for Silicon Anodes

Project ID: ES219
Dee Strand, Principal Investigator
Wildcat Discovery Technologies
2015 Annual Merit Review
June 9, 2015
Overview

Timeline
- Start Date: 10/01/2013
- End Date: 12/31/2015
- Percent Complete: 68%

Barriers
- Energy density
  - High capacity silicon anodes required to improve cell energy density
- Cycle life
  - Unstable SEI due to large volumetric changes in silicon result in poor cycle life

Budget
- Total Funding: $1,249,723
- DOE Share: $999,778
- Contractor Share $249,945
- Funding Received:
  - FY2013 $3,974
  - FY2014 $406,104
  - FY2015 (thru 4/10) $72,026

Partners
- Lead organization: Electrolyte discovery and optimization
- 3M: Electrode preparation, large cell format assembly and testing
- Argonne National Laboratory
Relevance

Development of non-carbonate electrolyte formulations that

• form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency* > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes;

• have comparable ionic conductivity to carbonate formulations, enabling high power at room temperature and low temperature;
  • > 5 mS/cm ionic conductivity at 25°C;
  • > 1 mS/cm ionic conductivity at -30°C;

• are oxidatively stable to 4.6V, enabling the use of high energy NMC cathodes in the future; and

• do not increase cell costs over today’s carbonate formulations.

Objectives (3/14 – 3/15)

• Identify best SEI additives for noncarbonate solvent evaluation
• Identify best performing noncarbonate solvents
• Begin optimization
<table>
<thead>
<tr>
<th>Date</th>
<th>Milestones and Go/No-Go Decisions</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/2014</td>
<td>SEI additives identified with non-EC based electrolyte which performs comparably to current carbonate/FEC blends</td>
<td>Complete</td>
</tr>
<tr>
<td>12/2014</td>
<td><strong>Go/No-Go Decision:</strong> Non-EC containing formulation with SEI package achieves &gt; 50 cycles to 70% capacity in NMC full cells</td>
<td>Complete/Go</td>
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<tr>
<td>12/2014</td>
<td>Interim 18650 cells assembled and sent to ANL for testing</td>
<td>Complete</td>
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<tr>
<td>03/2015</td>
<td>Non-carbonate formulations identified which perform comparably to current carbonate/FEC blends</td>
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<tr>
<td>06/2015</td>
<td>Non-carbonate formulations identified with &gt; 200 cycles to 80% capacity</td>
<td>Complete</td>
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<tr>
<td>09/2015</td>
<td>Non-carbonate formulations identified with &gt; 500 cycles to 80% capacity</td>
<td>On Track</td>
</tr>
<tr>
<td>12/2015</td>
<td>Achieve project targets for ionic conductivity and voltage stability</td>
<td>On Track</td>
</tr>
<tr>
<td>12/2015</td>
<td>Final 18650 cells assembled and sent to ANL for testing</td>
<td>On Track</td>
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</tbody>
</table>
Approach

- Stage 1
  - Develop additive package to form stable SEIs on silicon anode
  - Use PC based electrolyte which does not form SEI on its own (such as EC)
  - Go/No-Go Decision > 50 cycles to 70% capacity with no EC in formulation
  - Further improvements done in conjunction with solvent optimization

- Stage 2
  - Identification of non-carbonate solvents that are stable on additive-based SEI
  - Solvents also need to
    - Enable conductivity targets
    - Match current electrolyte solvents in terms of thermal stability/safety

- Stage 3
  - Formulation optimization
  - Selection of additives to ensure high voltage stability target
  - Further SEI improvements for high temperature stability
  - Cost analysis
Technical Accomplishments – Additive Approach

Experiments:
- Evaluated over 200 additives in PC/EMC and EC/EMC formulations
  - 12 chemical categories/families at multiple concentrations
  - Additives chosen based on expected effects on SEI composition/properties

Outcome:
- Established working hypotheses for beneficial structures/functional groups
- Additives identified for noncarbonate solvent evaluation
- 3 patent applications filed

Next Steps:
- Synthesis and testing of new structures based on key learnings
- Combinations of additives with differing functionalities
Technical Accomplishments – Solvent Approach

- Oxidatively stable
- Does not participate in SEI formation (the additives are going to do that)
  - Reductively stable (aprotic)
  - Reduction potential lower than the additives
- High dielectric constant
  - Polar group in structure, necessary to dissociate salt
    - Carbonyl C = O
    - Nitrile C ≡ N
    - Sulfonyl S = O
- Low viscosity
  - Asymmetry
  - Low MW
  - Low melting point
- Liquid over useful temperature range
- Others...

~ 25 HD Solvents
~ 25 LV Solvents
Salt/Concentration
Additive/Concentration

1000’s of possible formulations
## Technical Accomplishments – Solvent Approach

### HD/LV Ratios
- LiPF$_6$ Solubility
- LiPF$_6$ Compatibility
- Electrode Stability

### HD Solvent Screen (~25)
- LV Solvent (EMC)
- HD/LV Ratio (1)
- Salt (1M LiPF$_6$)
- Additive (5)
- Additive Conc (2)

### LV Solvent Screen (~25)
- HD Solvent (6)
- HD/LV Ratio (1)
- Salt (1M LiPF$_6$)
- Additive (1)
- Additive Conc (1)

- Best 6 HD solvents
- Best 5 HD/LV combinations

### Optimization
- # Solvents
- Ratios
- Salts
- Additives

### Key Metrics:
- 1$^{st}$ cycle capacity/CE
- Cycle life

### Current Stage of Project
Technical Accomplishments – Solvent Approach

Identified EC-free combinations similar to control

HD/EMC Combinations

NMC//Si alloy
2.8 – 4.2V
C/10

Colors: Solvent
Shapes: Additive

Control:
EC/EMC (1/2)
1M LiPF₆
Technical Accomplishments – Solvent Approach

- 18650 cells built by 3M, tested by Argonne National Lab
- “Drop-In” new electrolyte formulations – no optimization for cell format change
- Argonne test protocol included pulse testing prior to/during cycle life (not done in Wildcat cells)

Optimization for 18650 cells is required
Technical Accomplishments – Solvent Approach

Noncarbonate formulations similar to control at 50 cycles

- NMC//Si alloy
- 2.8 – 4.2V
- C/10

Colors: Solvent

Control:
- EC/EMC (1/2)
- 1M LiPF₆

HD/LV Combinations

Avg. Cy 50 Capacity Retention (%)

Avg. Capacity (mAh/g, Cy1)
## Technical Accomplishments – Solvent Approach

### New formulations require re-optimization of salt(s)

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<tr>
<th>LV</th>
<th>HD</th>
<th>LiPF6</th>
<th>Salt 1</th>
<th>Salt 2</th>
<th>Salt 3</th>
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<td></td>
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<td>Cy1 Capa. mAh/g</td>
<td>Capa. Reten (%)</td>
<td>Cy1 Capa. mAh/g</td>
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Capacity Retention @ 100 cycles
New formulations require re-optimization of salt(s)
Technical Accomplishments – Summary

- To date, over 5000 cells have been assembled and tested
- Beneficial additives have been identified for
  - EC-containing formulations
  - EC-free formulations
- Additives used to screen non-carbonate solvents
  - “Head start” on additive development for traditional solvents
  - Structure-performance relationships derived from additive screening with purchased and custom compounds
- Non-carbonate solvent formulations identified that outperform the EC-based control formulations
- Gas generation in non-carbonate formulations similar to EC-based control
- Additional testing on other Si sources in progress
Responses to Reviewer Comments

- **Project focus on 3M silicon anode is too narrow; recommend benchmarking formulations on other materials**
  - Wildcat is currently doing testing of promising additives and noncarbonate formulations on Si//carbon composite electrodes received from Argonne National Lab

- **Recommend utilizing more analytical capability; perform post-mortem analysis to gain more understanding**
  - Wildcat plans on doing this as we down-select to the final solvent choices

- **More collaboration is recommended**
  - Now including Argonne to test 18650 cells and supply electrodes
  - Will begin analytical work at UCSD
  - In discussion with other silicon anode suppliers regarding evaluations

- **Recommend breaking out results for “best” formulations to more clearly see the progress**
  - Showed more traditional cycle life graphs on Slide 16 for best formulations in this presentation
Responses to Reviewer Comments

- **Reviewer would like more information about reproducibility of data/experiments**
  - All initial testing is done in duplicate, with averages represented on graphs
  - All promising additives/formulations are repeated
  - As we move into optimization, testing is done in triplicate or quadruplicate

- **Reviewer recommended more intimate knowledge of 18650 cell construction and testing to gain insight**
  - We plan on multiple rounds of 18650 cells with best formulations to optimize for that cell format

![EC/EMC Control (quadruplicate)](image-url)

NMC//Si alloy
2.8 – 4.2V
C/5

Avg. Discharge Capacity (mAh/g)

Cycle #
Collaborations

Lead organization
- Design of experiments/ideas
- High throughput evaluation

Fabrication of electrodes (anodes and cathodes)
- 18650 cell assembly and testing

Fabrication of electrodes (anodes and cathodes)
- Supply of novel additives, salts
- 18650 cell testing

Access to analytical characterization (2015)
Remaining Challenges & Barriers

- Further improvements to cycle life (500 cycles)
- Other metrics
  - High voltage stability
  - Power/rate/conductivity
- 18650 cell optimization
Proposed Future Work

- Cycle life improvements
  - Additive optimization
  - Additive combinations

- High voltage stability
  - Formulation/solvents (expect new solvents to be stable)
  - High voltage additives

- 18650 cell optimization
  - Several rounds of cell builds
  - Optimize formulation for larger cell format

- Test vs. other silicon materials
  - In progress
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Acknowledgements

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