Advanced High Energy Li-ion Cell for PHEV and EV Applications

Jagat Singh, 3M

3M-EMSD. June 7th 2016

Project ID - ES210

“This presentation does not contain any proprietary, confidential, or otherwise restricted information”
Overview

Timeline
- Start Date: 10/01/2013
- End Date: 03/31/2016
- Percent Complete: 100%

Budget
- Total Project Funding:
  - $3,145,571
- DOE* Share
  - $2,250,043
- Contractor Share
  - $895,528

Barriers
- Cycle Life,
- Specific Energy,
- Cost

Partners
- Collaboration:
  - GM: Dr. Meng Jiang
  - Umicore: Wendy Zhou
  - Iontensity: Marc Juzkow
  - ARL: Dr. Richard Jow
  - LBNL: Dr. Gao Liu
- Interaction
  - Dalhousie University
  - ANL: Deliverable Testing
- Project Lead: 3M

*3M and the team appreciates the support and funding provided by DOE
A collaborative team approach to leverage crucial Li-ion battery technologies and expertise to help enable

- Advanced High Energy Li-Ion Cell
- Superior Performance Envelope
  - Long Cycle Life,
  - High Power Capability,
  - Wide Operating Temperature
- Lower Cost ($/Wh)
## Milestones

<table>
<thead>
<tr>
<th>Month / Year</th>
<th>Milestone</th>
<th>Status</th>
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<tbody>
<tr>
<td><strong>Phase I (Oct 1st, 2013 to Sept 30th, 2014)</strong></td>
<td><strong>Scale up baseline anode and cathode material</strong></td>
<td>✔️</td>
</tr>
<tr>
<td>Dec / 2013</td>
<td>Scale up baseline anode and cathode material</td>
<td>✔️</td>
</tr>
<tr>
<td>April / 2014</td>
<td>Baseline cells shipment</td>
<td>✔️</td>
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<td><strong>Phase II (Oct 1st, 2014 to March 31st, 2016)</strong></td>
<td><strong>Advanced anode and cathode materials selection</strong></td>
<td>✔️</td>
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<tr>
<td>Aug / 2015</td>
<td>Advanced anode and cathode materials selection</td>
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<tr>
<td>Dec / 2015</td>
<td>Advanced anode and cathode materials scale up</td>
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<td>March / 2016</td>
<td>Data package – Advanced cells</td>
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<td>April / 2016</td>
<td>Advanced cells shipment</td>
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Approach

Synergistic Team Approach to Address Vital Components.

- **Si-Anode**
  - 3M

- **High Energy NMC Cathode**
  - 3M/Umicore

- **Cell Validation**
  - GM/Iontensity/3M

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**Energy (Wh/l or Wh/kg)**

**Specific Power (W/kg)**

**Cycle Life**

**Advanced Electrolyte**
- 3M/ARL/Iontensity

**Advanced Binder Development**
- LBNL

**High Energy Cell**

**Current Cell**

**HE-NMC//Si-anode**
**Approach**

1 - **Develop Advanced Material to meet Energy Targets**

- **Si Alloy Anode**
  Scalable process to develop high capacity Si alloy with stable microstructure

- **Binder - Si Anode**
  Innovative conductive binder for superior Si anode composite

- **High Energy NMC Cathode**
  Develop composition with high Wh/kg to increase cell energy

- **Advanced Electrolyte / Additives**
  SEI and high voltage stability to enhance performance

2 - **Characterize Performance in 18650 / Pouch Cells**

- **Electrode Formulation Study**

- **Tune Formation Protocol**

- **Evaluate Dispersion, Roll to Roll Coating and Drying**

- **Gap Analysis and Diagnostics**

- **Energy and Life Validation**
Silicon Alloy Anode Development - 3M

Developed advanced Si alloy anode with better properties

Baseline Material

3M Si Alloy Anode shows excellent cycling and coulombic efficiency compared to Si nano-particles

Advanced Material

Develop Si alloy to target
- 20% ↑ mAh/g
- 10% ↑ mAh/cc
- Higher efficiency

<table>
<thead>
<tr>
<th>Si Alloy</th>
<th>BET (m²/g)</th>
<th>1st Lithiation (mAh/g)</th>
<th>1st Delithiation (mAh/g)</th>
<th>1st Delithiation (mAh/cc)</th>
<th>First Cycle Efficiency (%)</th>
<th>Manufacturability</th>
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<tr>
<td>Advanced Material</td>
<td>--</td>
<td>1170</td>
<td>1060</td>
<td>3370</td>
<td>90.4</td>
<td>✓</td>
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<td>Baseline Material</td>
<td>3.5</td>
<td>1050</td>
<td>900</td>
<td>3280</td>
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Silicon Alloy Anode Development - 3M

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Technical Accomplishments and Progress

Baseline Material

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Silicon Alloy Anode Scale Up - 3M
Demonstrated material scale up & commercial manufacturing feasibility

High volume manufacturing feasibility underway.

Scale-up plan to meet the demand forecast.

Helping to build a better battery

Article by SUSAN FEYDER, Star Tribune

A 3M pilot project is making longer-lasting lithium ion batteries for consumer electronics. Next up: electric vehicle batteries.
Binder Development - LBNL

Demonstrated higher areal capacity electrodes with Si Alloy Anode

PPyDMA

Coin cell vs. Li

Full coin cell

PPyDMA with Advanced Si anode electrode
C/10, 0.005V-1V; constant voltage until 0.02C at the end of lithiation
1st cycle efficiency: 82.35%, 1st cycle delithiation capacity: 1175.9 mAh/g
50th cycle efficiency: 99.83%, 50th cycle delithiation capacity: 955.3 mAh/g

PPyDMA/ Advanced Si anode electrode w/o graphite; C/10 for 2 cycles, then C/3; 1st cycle efficiency: 82.34% (prelithiation with SLMP); Electrolyte: EC/DEC=3/7, 30% FEC, 1.2M LiPF6; Capacity reported based on cathode active materials
**H.E. NMC Cathode Development - 3M**

Developed advanced cathode material with better properties

Two Concepts: Core-Shell and Coated NMC

- **Core-Shell NMC**
  - Small advantage in energy compared to alternatives
  - Challenges for cycle life, rate capability and gassing

- **3M coatings on NMC**
  - Better cycle life and energy
  - Better rate capability

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<th>Cathode</th>
<th>BET (m²/g)</th>
<th>1st Lithiation (mAh/g)</th>
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<th>First Cycle Efficiency (%)</th>
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<tr>
<td>Advanced Material</td>
<td>0.31</td>
<td>230</td>
<td>211</td>
<td>91.9</td>
<td>✓</td>
</tr>
<tr>
<td>Baseline Material</td>
<td>273</td>
<td>227</td>
<td>83.3</td>
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Technical Accomplishments and Progress
H.E. NMC Cathode Development - 3M

Developed different candidates and demonstrated energy improvement
H.E. NMC Cathode Development - 3M

Developed different candidates and demonstrated energy improvement
H.E. NMC Cathode Scale Up - Umicore

Demonstrated material scale up & commercial manufacturing feasibility

Process chart

- **Precipitation**
- Change to white suspension

**La(NO₃)₃ solution** + **H₃PO₄ solution**

**LaPO₄ Solution** + **HX12-G3**

**Mixing**

**Dry in vacuum 120°C/overnight**

**Firing**

![Discharge capacity (mAh/g) vs. Cycle number](chart.png)

- **Umicore Scaled Lot 1 & Lot 2**
- **3M pilot scale**

Scale-up sample morphology
Electrolyte Development - ARL

Identified cycle life enabling electrolyte for advanced chemistry
Advanced Chemistry 18650 Evaluation - 3M

≥ 93% energy retention at 1C rate

~24% increase in energy by further cell design optimization (12um separator, 58 mm wide cathode, N/P=1.05, Tighter winding)

Si alloy anode from 3M production scale facility; High energy NMC cathode from 3M pilot scale facility
Advanced Chemistry 18650 Evaluation - GM

Improved rate capability at low temperatures

Baseline Material

Advanced Material

Discharge Capacity at C/3

Rate capability at 0°C

Low capacity at high C-rate at low temperature may be due to resistance built up during previous test.

Si alloy anode from 3M production scale facility
High energy NMC cathode from 3M pilot scale facility
Advanced Chemistry 18650 Evaluation - GM

Effect of UCV on Cycle Life

- Si alloy anode from 3M production scale facility
- High energy NMC cathode from 3M pilot scale facility

C/3 cycling 5%-95% SOC; After every 50 cycles at C/3, HPPC and C/10 capacity check were carried out
Effect of UCV on Cycle Life

C/3 cycling 5%-95% SOC; After every 50 cycles at C/3, HPPC and C/10 capacity check were carried out

Si alloy anode from 3M production scale facility
High energy NMC cathode from 3M pilot scale facility
### Technical Accomplishments and Progress

**Gap Analysis, Advanced vs. Baseline - GM**

Improved key cell level properties. Cycle life improvement WIP.

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>Target&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Benchmarks&lt;sup&gt;2&lt;/sup&gt;</th>
<th>4.4-2.5 V</th>
<th>4.5-2.5 V</th>
<th>4.6-2.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cell Level</td>
<td>Wet Laminate Level&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Cell Level</td>
<td>Wet Laminate Level&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gravimetric Energy Density</td>
<td>Wh/kg</td>
<td>400</td>
<td>192&lt;sup&gt;4&lt;/sup&gt;</td>
<td>247&lt;sup&gt;4&lt;/sup&gt;</td>
<td>206</td>
<td>260</td>
</tr>
<tr>
<td>Volumetric Energy Density</td>
<td>Wh/L</td>
<td>600</td>
<td>490&lt;sup&gt;4&lt;/sup&gt;</td>
<td>490&lt;sup&gt;4&lt;/sup&gt;</td>
<td>556</td>
<td>556</td>
</tr>
<tr>
<td>Gravimetric Discharge Power Density</td>
<td>W/Kg</td>
<td>800</td>
<td>366&lt;sup&gt;5&lt;/sup&gt;</td>
<td>471&lt;sup&gt;5&lt;/sup&gt;</td>
<td>676</td>
<td>853</td>
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<tr>
<td>Volumetric Discharge Power Density</td>
<td>W/L</td>
<td>1200</td>
<td>933&lt;sup&gt;5&lt;/sup&gt;</td>
<td>933&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1818</td>
<td>1818</td>
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<tr>
<td>Gravimetric Regen Power Density</td>
<td>W/Kg</td>
<td>400</td>
<td>690&lt;sup&gt;5&lt;/sup&gt;</td>
<td>888&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1396</td>
<td>1761</td>
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<tr>
<td>Volumetric Regen Power Density</td>
<td>W/L</td>
<td>600</td>
<td>1757&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1757&lt;sup&gt;5&lt;/sup&gt;</td>
<td>3756</td>
<td>3756</td>
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<tr>
<td>Cycle life</td>
<td>cycles&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1000</td>
<td>45</td>
<td>45</td>
<td>194</td>
<td>194</td>
</tr>
<tr>
<td>Opt. Temp. Range</td>
<td>°C</td>
<td>-30~65</td>
<td>0~TBD</td>
<td>0~TBD</td>
<td>-20~35</td>
<td>-20~35</td>
</tr>
</tbody>
</table>

<sup>1</sup> - End of life requirement from F; <sup>2</sup> - Beginning of life data; <sup>3</sup> - Including electrode, separator, and electrolyte; <sup>4</sup> - Data from C/3; <sup>5</sup> - 40% SOC; Vm, 25°C; <sup>6</sup> - 35% capacity loss at C/3 with 90% DOD range
Advanced Chemistry 18650 Evaluation - GM

Cycle life testing with deliverable cells in progress

Si alloy anode from 3M production scale facility

High energy NMC cathode from Umicore production scale facility

C/3 cycling 5%-95% SOC; 80% capacity retention: 135 cycles; RPT’s (C/3, HPPC and C/10 capacity) after every 50 cycles
Pouch Cell Evaluation - Iontensity

Identified pouch cell energy levels with varying wt% content of Si alloy anode

Si alloy anode from 3M production scale facility
High energy NMC cathode from 3M pilot scale facility
Cycle life testing initiated
Cell Sampling to Argonne National Lab - 3M

Sampled 18650 cells with advanced chemistry

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>C/15</th>
<th>C/15</th>
<th>Irreversible % (After 1st cycle)</th>
<th>C/10</th>
<th>C/10</th>
<th>Irreversible % (after 3 cycles)</th>
<th>C/5</th>
<th>C/5</th>
<th>C/2</th>
<th>C/2</th>
<th>1C</th>
<th>1C</th>
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<tr>
<td>Avg</td>
<td>3390</td>
<td>2782</td>
<td>17.9%</td>
<td>2865</td>
<td>2881</td>
<td>15.0%</td>
<td>2864</td>
<td>2864</td>
<td>2823</td>
<td>2818</td>
<td>2759</td>
<td>2751</td>
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<tr>
<td>St Dev</td>
<td>52</td>
<td>57</td>
<td>0.5%</td>
<td>56</td>
<td>54</td>
<td>0.5%</td>
<td>53</td>
<td>53</td>
<td>53</td>
<td>52</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>Relative St Dev</td>
<td>1.5%</td>
<td>2.0%</td>
<td>3.0%</td>
<td>2.0%</td>
<td>1.9%</td>
<td>3.0%</td>
<td>1.9%</td>
<td>1.8%</td>
<td>1.9%</td>
<td>1.9%</td>
<td>2.0%</td>
<td>2.0%</td>
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</table>
Response to Previous Year Reviewers’ Comments

• Si Alloy anode and advanced cathode: Cycle life improvements for commercialization
  • Made improvements but achieving long cycle life (>1000 cycles) is still a challenge.
  • Working on key enablers: High voltage electrolyte, anode composite, stable electrochemical couple match

• Si Alloy anode and advanced cathode: Powder production
  • Generated >1000 kg Si alloy anode materials (advanced material).
  • Generated >50 kg of particle coated NMC cathode material.

• Harmonizing test conditions and cycling test
  • Each partner used the same material lot or coated electrode
  • Balanced approach:
    • Cycle life testing in large cells were harmonized for C/3 rate
    • Optional testing via partner’s preferred conditions
Collaboration and Coordination

- **3M**
  - Sample Electrodes (ARL, Iontensity, GM), Si Alloy Anode Powder (Iontensity, GM, LBNL), High Energy NMC Cathode Powder (Iontensity, GM) and Cells (GM).

- **ARL**
  - Develop and Sample Electrolyte and Additives (3M, Iontensity).

- **GM**
  - Evaluate, Analyze and Diagnose Cells (3M, Iontensity).

- **LBNL**
  - Optimize and Evaluate Binder Chemistry for Si Alloy Anode (3M).

- **Iontensity**

- **Umicore**
Remaining Challenges / Barriers

• Long cycle life
  • Electrolyte formulation for high voltage (4.5V) chemistries

• Superior Si anode composite
  • Binder evaluation in large format cells such as 18650 or pouch cells
  • More stable SEI formation
  • Further reduced controlled volumetric expansion over life

• Stable match of high voltage cathode and high voltage electrolyte
Proposed Future Work

• Complete life testing with advanced chemistry

• Analyze life degradation root causes

• Discuss advanced chemistry performance from cells sampled to ANL

• Prepare final project report
Summary

• Successfully leveraged collaborative R&D
  • Anode and Cathode material development at 3M
  • Binder development on 3M Si Alloy Anode at LBNL
  • Cathode material scale up and process optimization at Umicore.
  • Gap analysis, cell evaluation and validation at GM
  • Electrolyte and additive screening for baseline and advanced chemistry at ARL
  • Advanced chemistry’s pouch format cell feasibility at Iontensity.

• Successful Scaled up Baseline and Advanced Materials

• Demonstrated performance improvement