Advanced Cathode Material Development for PHEV Lithium Ion Batteries

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3M Electronics Materials Marketing Division

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Project ID #
ES006

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Overview

- **Timeline**
  - start: 4/06/2009
  - finish: 4/1/2011
  - 100% complete

- **Budget**
  - Total project funding
  - USABC share: $1,137,726
  - Contractor share: $1,137,726
  - Funding received in FY09: $185,264
  - Funding received in FY10: $674,349
  - Funding to Feb in FY11: $208,477

- **Barriers**
  - Cost, Capacity, Rate and Thermal Control.

- **Targets**
  - Increase capacity 5-10%
  - Reduce Cost >10%
  - Maintain thermal stability and cycle life

- **Partners**
  - Major automakers
  - DOE Labs
Project Objective

To design an advanced cathode materials with the following performance improvement compared to MNC 111 for PHEV applications:

- 5 ~ 10% higher capacity improvement (mAh/g)
- ~ 15% lower raw material cost
- Comparable or higher thermal stability
- Comparable or higher cycle life

Achieving Objectives will Result in a New Cathode Material with Cost and Performance Advantages for Vehicle Applications.
Milestones

- **Phase I – Identify Material Candidate**
  - Lab scale material R&D - two compositions meetings program objectives
  - Optimized & validated 18650 test vehicle (≥ 1250 cycles)

- **Phase II – Material Scale Up**
  - Optimize, validate & verify process parameters on pilot plant scale
  - Pilot plant production & validation of final cathode material

- **Phase III – Material Validation in 18650 Cells**
  - Build and evaluate 18650 cells with advanced cathode materials
  - 18650 data package generation & performance validation
  - 18650 shipment to DOE labs for performance verification
Approach – Cathode Material Development

Area of interest for new cathode development because of the low Co content – cost, thermal stability and energy density

Mixture Design and Statistical Modeling used to Identify most Promising Compositions

Capacity above 164mAh/g
DSC higher than 310°C
Raw Material cost < 10.5 $/kg
Approach – Process Optimization

Process Optimization

- Reactor Temperature
- Reactor pH
- Rate of material addition
- Reaction Time
- Residence Time
- Sintering condition
- Lithiation

Best Composition and Process Conditions Identified from over 50 Samples
Approach – Performance Validation

- Lab Scale Material / Coin Cell Evaluation
- Pilot Scale Material / 18650 Cell Evaluation
  - Comparative Cell Design
  - Electrolyte Additives
  - Electrode capacity (mAh/cm²)
- Evaluation Methods
  - 18650 Abuse Testing
    - Thermal Ramp, Hot Block, Nail Penetration Tests
  - 18650 evaluation in accordance with “Battery Test Manual for Plug – In Hybrid electric Vehicle”
    - Static Capacity Test, HPPC, Self Discharge Test, Charge Depleting Cycle Life Test & Cold Crank Test

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>Advanced Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>3M BC618 (MNC 111)</td>
<td>Advanced MNC 2</td>
</tr>
<tr>
<td>Anode</td>
<td>Graphite</td>
<td>Graphite</td>
</tr>
<tr>
<td>Separator</td>
<td>Celgard 2325</td>
<td>Celgard 2325</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1M LiPF₆ EC/EMC/DMC</td>
<td>1M LiPF₆ EC/EMC/DMC</td>
</tr>
<tr>
<td>Additive</td>
<td>A and B</td>
<td>A and B</td>
</tr>
<tr>
<td>Cell</td>
<td>18650-Size</td>
<td>18650-Size</td>
</tr>
</tbody>
</table>
### Accomplishment – Lab Scale Material Identification

<table>
<thead>
<tr>
<th>Requirement</th>
<th>BC618 (111)</th>
<th>Target</th>
<th>Adv. MNC 1</th>
<th>Adv. MNC 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity C/10 (mAh/g)</td>
<td>156</td>
<td>&gt;172</td>
<td>173</td>
<td>174</td>
</tr>
<tr>
<td>Capacity C/2 (mAh/g)</td>
<td>145</td>
<td>&gt;161</td>
<td>164</td>
<td>163</td>
</tr>
<tr>
<td>Thermal Stability DSC (°C)</td>
<td>315</td>
<td>≥315</td>
<td>321</td>
<td>315</td>
</tr>
<tr>
<td>Materials Cost (relative)</td>
<td>100%</td>
<td>≤85%</td>
<td>81%</td>
<td>72%</td>
</tr>
</tbody>
</table>

2 Advanced MNC Candidates Meet Primary Objectives. Material Down Selected on Storage Capacity Retention & Cost
Accomplishment - Material Capacity Improvement

Advanced MNC 2 Demonstrates ~8% Increase in Capacity
Accomplishment - Material Cost Reduction

Advanced MNC 2 Offers >20% Lower Raw Material Cost
Accomplishment - Thermal Stability

18650 Cell -
160°C Hot Block Test

18650 Cell -
6°C/min Thermal Ramp

Advanced MNC 2 Demonstrates Equivalent Thermal Stability
Accomplishment - Low Temperature Performance

Advanced MNC 2 Demonstrates Better Performance at Low Temp

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>3rd Discharge Pulse Resistance (mΩ)</th>
<th>Cold Crank Power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC618</td>
<td>412.0</td>
<td>9.67</td>
</tr>
<tr>
<td>Adv. MNC 2</td>
<td>374.4</td>
<td>10.98</td>
</tr>
</tbody>
</table>

18650 Cell - Cold Crank Test

18650 Cell - Rate Test (-30 C)
Accomplishment – Cycle Life Performance

18650 Cell - BC618 (111)

18650 Cell - Advanced MNC 2

BOL, 250 Cycles, 500 Cycles

Advanced Material 2 Demonstrates Equivalent Cycle Life Performance after 500 Cycles
# Accomplishment – Gap Analysis

<table>
<thead>
<tr>
<th>Requirement</th>
<th>BC618 (111)</th>
<th>Target</th>
<th>Adv. MNC 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity C/10 at 30°C (mAh/g)</td>
<td>156</td>
<td>≥ 172</td>
<td>174</td>
</tr>
<tr>
<td>Capacity 2C at 30°C (mAh/g)</td>
<td>135</td>
<td>≥ 149</td>
<td>150</td>
</tr>
<tr>
<td>Irreversible Capacity at 30°C</td>
<td>10%</td>
<td>≤ 15%</td>
<td>9</td>
</tr>
<tr>
<td>Raw material Cost</td>
<td>100%</td>
<td>≤ 85%</td>
<td>72%</td>
</tr>
<tr>
<td>DSC Peak Max (ºC)</td>
<td>317</td>
<td>≥ 317 ± 3</td>
<td>320</td>
</tr>
<tr>
<td>18650 Thermal Ramp Runaway (ºC)</td>
<td>227</td>
<td>≥ 227 ± 2</td>
<td>229</td>
</tr>
<tr>
<td>18650 Cold Cranking Power at -30ºC, 2 sec, 3rd Pulse (kW)</td>
<td>10</td>
<td>≥ 7</td>
<td>11</td>
</tr>
<tr>
<td>18650 Maximum Self Discharge (Wh/day)</td>
<td>15</td>
<td>≤ 50</td>
<td>15</td>
</tr>
<tr>
<td>18650 Charge Depleting Cycle Life (Cycles)</td>
<td>500*</td>
<td>≥ 500</td>
<td>500*</td>
</tr>
<tr>
<td>18650 Available Energy for CD Mode, 500 Cycles, (kWh)</td>
<td>4.1</td>
<td>≥ 3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>18650 Peak Discharge Pulse Power, 10sec, 500 Cycles, (kW)</td>
<td>101</td>
<td>≥45</td>
<td>100</td>
</tr>
</tbody>
</table>

* Testing Meets Goal. Continued Cycling in Progress
Collaboration & Co-ordination with Other Institutions

- 18650 shipment to DOE labs
  - 10 cells with BC618 (111) material
  - 10 cells with advanced MNC 2

- Electrochemical PHEV tests at ANL
  - Static capacity tests, HPPC, self discharge test, cold crank test & cycle life test

- Abuse tests at SNL
  - Thermal & nail penetration test
Proposed Future Work

- Continue charge depleting cycle life study in 18650 cells till End Of Life conditions are reached
  - Cell analysis after EOL is reached

- Collaborate with Argonne National and Sandia National Laboratories to complete performance verification in 18650 cells
Summary

- Developed advanced cathode material meeting all project objectives.
  - 5-10% Increased Capacity
  - 10% Reduced Cost
  - Equivalent Thermal stability
  - Cycle Life > 500 cycles
- Optimized pilot scale material production (≥ 25kg)
- Demonstrated advanced cathode material performance in 18650 cells
- Prepared and shipped 40, 18650 cells to Sandia & Argon National Laboratories for performance verification

All Project Goals Met or Exceeded