Development of High Energy Density Li-ion Chemistry for Next Generation Space Application

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Outline

- Review New Li-ion Chemistries
- Screen and Evaluation of New chemistries
- Cell Performance
- Summary
Demand for Higher Energy density Li-ion Cell

- **Current Li-ion Chemistry**
  - Graphite type anode and conventional LiCoO$_2$
  - Provide Energy density of ~200 Wh/kg

- **New Chemistry is required to deliver higher Capacity**
  - Non graphite type anode (Li metal alloy)
    - Sn, Sn Composite, Si, Si carbon campsite, and SiOx-C

- **Higher capacity Cathode material**
  - Ni based layered oxide (High Ni content)
  - Li rich layered oxide (> 1.2 mol of Li in unit structure)
  - High voltage Manganese based phosphate
EPT Tasks for High Energy Density Li-ion Cell

- **Screen New Electrode Material (Anode/Cathode)**
  - Evaluate intrinsic properties of candidate materials
  - Identify suitable electrode Material
  - Design electrodes and Cell
  - Develop suitable electrolyte system
  - Demonstrate new electrode performance in Full cell configuration

- **Optimize electrode and Cell Design**
  - Optimize cell design
  - Scale up process
  - Evaluate overall cell performance under various condition
    - Cycling
    - Safety
    - Temperature effects
Silicon anode material

- **Electrochemical Characteristic of Si Anode material**
  - High Theoretical capacity: ~ 4200 mAh·g⁻¹
  - High Irreversible capacity loss (IRCL)
  - Poor Rate capability and Cycling
    - Due to volume expansion/contraction

- **Technical Challenges**
  - Improve rate and cycling performance
  - Reduce IRCL

<table>
<thead>
<tr>
<th>Material</th>
<th>Average potential</th>
<th>Specific capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.1-0.2 V</td>
<td>372 mA·h/g</td>
</tr>
<tr>
<td>Titanate</td>
<td>1-2 V</td>
<td>160 mA·h/g</td>
</tr>
<tr>
<td>Sn (Li₄.₄Sn)</td>
<td>0.1 ~ 1.0 V</td>
<td>994 mA·h/g</td>
</tr>
<tr>
<td>Si (Li₄₂Si)</td>
<td>0.5-1 V</td>
<td>4212 mA·h/g</td>
</tr>
</tbody>
</table>
Capacity and Expansion ratio of Anode materials

| Material | PbLi₂₄₋₅₁ | SnLi₂₄₋₅₁ | GeLi₂₄₋₅₁ | SiLi₂₄₋₅₁ | C₆Li | C
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion ratio</td>
<td>3.34</td>
<td>3.59</td>
<td>3.70</td>
<td>4.12</td>
<td>1.10</td>
<td></td>
</tr>
</tbody>
</table>

Theoretical specific gravimetric capacity (mAh/g)

Initial → 1st discharge

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Concerns and Approaches for Si-C anode materials

- **Primary concern**
  - Suppression of rapid Volume change during cycling

- **Partial Incorporation of Carbon with Si material**
  - **Buffering by secondary elements**
    - Carbon/Graphite Structure (macro-meso-nano) effect integrity of electrode
    - Si-deposited Carbon Nano Fiber
    - Si-coated with Carbon
    - Si on nanowire type carbon
    - SiOx carbon composite
    - Composite with graphite
    - Etc
Charge Discharge Curves of various Si-C anodes

Different Voltage Profile and Capacity depending on Si-Carbon Structure

- Si-Graphite composite 10% IRCL
- SiOx-Graphite composite 17% IRCL
- Si-Carbon nano paper 14% IRCL
- Si-Carbon Graphene Type 24% IRCL

Specific Capacity, mAh/g

Voltage, V vs. Li/Li+

550 mAh·g⁻¹ → 1600 mAh·g⁻¹
Si deposited Nano Carbon Fiber paper (S1)

- Max reversible capacity: > 800 mAh/g
- Capacity at C/3: > 600 mAh/g
- IRCL is higher than graphite system

<table>
<thead>
<tr>
<th>Electrochemical Performance</th>
<th>Capacity, mAh/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Capacity, mAh/g C/30</td>
<td>835 mAh/g</td>
</tr>
<tr>
<td>IRCL, mAh/g</td>
<td>165 mAh/g</td>
</tr>
<tr>
<td>IRCL, %</td>
<td>~ 14%</td>
</tr>
<tr>
<td>Capacity, mAh/g at C/10</td>
<td>750 mAh/g</td>
</tr>
<tr>
<td>Capacity, mAh/g at C/5</td>
<td>700 mAh/g</td>
</tr>
<tr>
<td>Capacity, mAh/g at C/3</td>
<td>605 mAh/g</td>
</tr>
</tbody>
</table>
Effect of Si contents

- Reversible capacity increase as Si content increase
- Higher content Si anode showed relatively poor rate capability and Cycling performance
Differential capacity Plot for Si deposited Nano Carbon Fiber paper with different Si Contents

- Peak 1 for Li intercalation shifted to higher potential and became broad peak.
- Peak 2&3 did not show significant potential change or shape from the 1st cycle to 2nd cycles.
Cycling Performance (vs. Li and vs. Cathode)

**Half Cell test vs. Li metal**

- Max Capacity, mAh/g: 986 mAh/g
- IRCL, mAh/g: 155 mAh/g
- Capacity, mAh/g at C/3: 823 mAh/g
- Capacity Retention at 50th: 95.5%

**Compatibility with Ni-based cathode**

- C/10: 100% DoD
- C/3: 100% DoD
- C/3: 80% DoD

<table>
<thead>
<tr>
<th>Full Cell</th>
<th>C/10</th>
<th>C/3</th>
<th>C/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>DoD</td>
<td>100%</td>
<td>94.8%</td>
<td>79.1%</td>
</tr>
<tr>
<td>Capacity, %</td>
<td>100%</td>
<td>94.8%</td>
<td>79.1%</td>
</tr>
<tr>
<td>mAh/cm²</td>
<td>3.12</td>
<td>2.96</td>
<td>2.47</td>
</tr>
<tr>
<td>Utilization, %</td>
<td>99.2% of Theo.</td>
<td>94.8% of C/10</td>
<td>83.5% of C/3</td>
</tr>
</tbody>
</table>

- Capacity retention of Si-C anode at 50th cycles remains as 95.5% (C/3 cycling)
Silicon Graphite Composite Anode (S2)

Voltage profiles for C/10 & C/5 rate charge are very similar

No significant impedance rise
Cycling performance of Silicon Graphite Composite Anode (S2) vs. Li anode

- Tested Si-C composite showed promising cycling performance at C/5 rate

Capacity retention at C/5 : ~ 91.5%
Design Consideration for Electrode Material

- **Cathode**
  - **High** Capacity and Good Rate Capability

- **Anode**
  - **Low Irreversible Capacity Loss** (*Low IRCL*):
    - High IRCL: Decrease Cathode capacity (SEI film formation)
  - **Matching Rate Capability**:
    - Low rate capability: Require more active material to match Cathode capacity
  - **Low Voltage profile at high rate**:
    - Decrease Cell Voltage: Reduce operational voltage window
Silicon Graphite Composite Anode

Rate Capability during Lithiation process

<table>
<thead>
<tr>
<th>Discharge rate</th>
<th>Discharge capacity, mAh/g</th>
<th>Percentage over C/10 Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/10</td>
<td>100.0%</td>
<td></td>
</tr>
<tr>
<td>1C</td>
<td>35.1%</td>
<td></td>
</tr>
<tr>
<td>C/2</td>
<td>77.2%</td>
<td></td>
</tr>
<tr>
<td>C/5</td>
<td>92.3%</td>
<td></td>
</tr>
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Specific Capacity, mAh/g

- 1C Discharge: 186.6 mAh/g (35.1% of Capacity by C/10)
- C/2 Discharge: 410.2 mAh/g (77.2% of Capacity by C/10)
- C/5 Discharge: 490.5 mAh/g (92.3% of Capacity by C/10)
- C/10 Discharge: 531.5 mAh/g

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Silicon Graphite Composite Anode

Rate Capability during Delithiation process

<table>
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<tr>
<th>Charge rate</th>
<th>Charge Cap, mAh/g</th>
<th>Capacity % over C/10 Charge</th>
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<tbody>
<tr>
<td>C/10</td>
<td>524.7</td>
<td>100%</td>
</tr>
<tr>
<td>1C</td>
<td>501.2</td>
<td>95.5%</td>
</tr>
<tr>
<td>C/2</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>C/5</td>
<td>520.8</td>
<td>99.3%</td>
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- 520.8 mAh/g @ C/5 99.3% of Capacity by C/10
- 501.2 mAh/g @ 1C 95.5% of Capacity by C/10
- 524.7 mAh/g @ C/10
## Summary of Rate Capability of Si-C Composite Anode

<table>
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<tr>
<th>Li lithiation process</th>
<th>(pre cycled at C/10)</th>
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<td><strong>Discharge rate</strong></td>
<td><strong>Discharge capacity, mAh/g</strong></td>
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<td>-</td>
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<tr>
<td>C/5</td>
<td>520.8</td>
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- C-rate is based on reversible Capacity: 550 mAh/g
Performance of Cathodes with different loading

- High Load Cathode 1 and 2 show similar rate capability except 2C rate
- Capacity for HL1 and HL 2 cells proportionally increases
Effect of loading of Cathode on Cell Performance

<table>
<thead>
<tr>
<th>Cells</th>
<th>Overall Electrode weigh gain (Cathode + Anode)</th>
<th>Capacity increase per unit area at C/2 rate</th>
<th>Estimated Energy density Increase %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Controlled</td>
<td>100 %</td>
<td>Ref</td>
<td>Ref</td>
</tr>
<tr>
<td>High Load 1</td>
<td>98 % of Controlled</td>
<td>14%</td>
<td>&gt; 14%</td>
</tr>
<tr>
<td>High Load 2</td>
<td>117 % of Controlled</td>
<td>34.9 %</td>
<td>&gt; 15% ~ (34.9 / A)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>A= (Weight increase % in Cell)</td>
</tr>
</tbody>
</table>
Summary

- Several Silicon carbon materials were evaluated for high energy Li-ion Cell.

- The tested Si-C composite materials show higher specific capacity than conventional graphite anode materials.

- The selected Si-C composite anode showed the compatibility with the cathode.

- Introduction of the new anode material and the EPT formulated-high Load cathodes can increase energy density from 15% to more than 22%.

- *Large format Cells with new anode and cathode will be tested to confirm long term cycling performance as well as other properties.*
Thank You & Questions?