Using Li-ion Battery for Intermittent Renewable Energy Storage: Requirements and Landscape

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• Requirements and Landscape of LiB for Stationary Storage
• Role and Comparison of Current Materials and Chemistries
• Near term future: Very High Energy LiB Materials and Cells
Energy/Power Ratings for Intermittent Stationary Storage

**Power Quality:**
Seconds or less as needed, Continuity of quality power

**Bridging Power:**
Seconds-Minutes Continuity of Service when Switching

**Energy Management.**
Decouple the Timing of Generation and Consumption of electrical energy.
~ Load leveling
~ Cost Optimization
~ Revenue Arbitrage
~ Grid-independency for many hours.
Size/Weight and Efficiency Considerations

Size and Weight Consideration

Output Energy Density
(Input Energy Density x Efficiency)

Metal Air Batteries
(Not rechargeable electrically)

Lithium

Volume Energy Density - kWh / m³

Weight Energy Density - kWh / ton

Cycle Life Efficiency

Efficiency (Wh power electronics)

Lifetime at 80% DoD - Cycles

E.C. Capacitors
Fly Wheels
Pumped Hydro
CAES
Lead-Acid
NaS
Flow Bat.
Ni-Cd
Metal-Air
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Ni-Cd
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Cost Considerations

Capital Cost/Unit Energy-Power

Per Cycle Cost of Stored Energy

Cost basis: 2002 and Changing Fast
Market Considerations: Projections


(Source: File Research)
Appearance of nickel-hydrogen batteries and lithium-ion batteries in the 1990s dramatically improved energy density.

Fig. Improvement in specific energy of secondary batteries

Nissan Presentation (2008)
Specific Energy vs Specific Power: Ragone Plot

- **Lead-acid**
- **Fuel Cells**
- **Ni-MH**
- **Advanced Li-ion**
- **Early Li-ion**
- **Capacitors**

**Source:** Product data sheets
Li-ion Battery Cells

Module of compact Li-ion battery

Tarascon et. al, Nature (2001)
Li-ion Battery: Role of Materials and Chemistries

Tarascon et. al, Nature (2001)
Energy Density of NMC Material and Other Materials

Li-ion Cell and Materials

<table>
<thead>
<tr>
<th>Cathode Materials</th>
<th>Energy Density (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO2</td>
<td>137</td>
</tr>
<tr>
<td>Doped LiCoO2</td>
<td>124-137</td>
</tr>
<tr>
<td>LiMnO2</td>
<td>110</td>
</tr>
<tr>
<td>LiMnCoO2</td>
<td>120</td>
</tr>
<tr>
<td>LiMnCoNiO2</td>
<td>160</td>
</tr>
<tr>
<td>LiMnNiO2</td>
<td>150</td>
</tr>
<tr>
<td>LiFePO4</td>
<td>&lt; 110</td>
</tr>
</tbody>
</table>

Source: Motorola Portable Energy
Example: Li-ion Battery for Stationary Storage

- **High energy density** (300 - 400 kWh/m3, 130 kWh/ton)
- **High efficiency** (near 100%)
- **Long cycle life** (3,000 cycles @ 80% depth of discharge)

Based on LCO or LMO type cathodes and Graphitic/Carbon type Anode and LiPF6 salts dissolved in carbonate electrolyte
Changing the LiB Oxide Cathode Materials Chemistry

- Change the end group
- Change the transition metal
- Ease of Li storage and dynamics within the lattice ~ capacity and power
- Difficulty of removing O from the lattice ~ safety
- Difficulty of Li–transition metal exchange with in the lattice ~ cycling
- Ionic size ~ structural stability
- Intercalation voltage ~ voltage
- Cost

Ceder, MIT 2006
LiB Materials Chemistries: Oxide Cathode

Table II: Effect of metal substitution on the average intercalation voltage in the $\alpha$-NaFeO$_2$ structure

<table>
<thead>
<tr>
<th>M in LiMO$_2$</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>av. voltage (V)</td>
<td>2.33</td>
<td>2.93</td>
<td>3.22</td>
<td>2.95</td>
<td>3.52</td>
<td>3.73</td>
<td>3.32</td>
<td>3.7</td>
</tr>
<tr>
<td>for MO$_2$/LiMO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

Table III: Effect of anion substitution on the average intercalation voltage of LiCoX$_2$ in the $\alpha$-NaFeO$_2$ structure

<table>
<thead>
<tr>
<th>X in LiCoX$_2$</th>
<th>O</th>
<th>S</th>
<th>Se</th>
</tr>
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<tbody>
<tr>
<td>av. voltage (V)</td>
<td>3.75</td>
<td>2.04</td>
<td>1.46</td>
</tr>
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</table>

LiB Materials Chemistries: The Spinel LiMn$_2$O$_4$ Cathode

The LiMn$_2$O$_4$ Spinel System

Manganese Spinel / Carbon-based

- Well-studied system that has a high power capability and excellent safety, but has low energy
  - Capacity is 110 mAh/g, vs. 180 mAh/g for the nickel-based systems
- Known cycle life problems because of manganese dissolution, exacerbated at higher temperatures
  - Use a mixture of spinel and nickelate to enhance life and increase energy, while maintaining safety
- Could satisfy PHEV-10 energy requirements, but meeting PHEV-40 requirements may be more problematic

Low energy and poor life are key challenges for use in PHEV-40

Ideas Being Pursued

- Use electrolytes that prevent dissolution of manganese
- Move to higher energy anodes (without sacrificing life)

T. Duong DOE, 2008
LiB Materials Chemistries: Li-Iron-Phosphate Cathode

LiFePO$_4$ / Carbon-based

- Best chemistry in terms of safety characteristics
- Excellent power capability due to nanosize
- However, energy is low because of low cathode voltage (3.4 V vs. 3.8 V for nickel-based system)
- Cycle life unknown, with conflicting reports and limited data
  - Life appears to be related to impurities formed during material synthesis, and could be prevented
- Flat voltage leads to cell balancing and SOC determination problems

Low energy could impede use in PHEV-40

Ideas Being Pursued

- Move to prismatic designs to increase specific energy and energy density
- Tailor size of nanoparticle to increase tap-density (g/cc of active material)
- Move to alternative phosphates (LiMnPO$_4$) that have higher energy while maintaining safety

T. Duong DOE, 2008
The Lithium-Ion Technology is at the Crossroads

Typically 3-5% performance improvement unless new chemistry or material is introduced

Source: IIT
Gen-3 layer-layer NMC Cathode Materials

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Better Safety than LCO and NCA via Less Heat Generation!

Higher Capacity or Energy Density!

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Li-ion Battery for Stationary Energy Storage: Comments

• LiB is an advanced competitive technology in the Bridging Power and Energy Management areas

• Current Applications ratings are especially suitable for:
  ➔ Re-newable Energy Management/Efficiency
  ➔ Customer Energy Management
  ➔ Up to 1MW power rating and Minutes-Hours Interruption

• The above specifications are based on LMO/ Graphite based Chemistries

• Higher power rating (1-10MW) are possible and starting to happen with Olivine (LFPO) and Spinel (LMnO) type cathode and LTO type anode Chemistries

• Nex-gen LIB Cells based on very high energy density composite cathode and Si-alloy based anodes will be game changer and booster in stationary energy storage area by 3-4x improvement in gravimetric energy density and 2x improvement in volumetric energy density at similar or lower cost

• Coating technology needs significant improvement to increase the discharge time ratings to below few minutes interruption