Nanomaterials for Battery Applications

Energy Storage Technology

Arnold Stux
Naval Research Laboratory
Washington, DC 20375-5342
Energy Storage Methods

• Grid Energy Storage
  – Increase reliability
  – Immediate need to meet demand fluctuations
  – Need to reduce cost of energy storing, retrieval, and energy losses \(\rightarrow\) technology cost

• Pumped water
• Compressed air
• Thermal energy
• Flywheel
• Superconducting magnetic energy
• Hydrogen fuel cells
• Battery
Military uses of off-grid power

Fuel cells operating laptop computers, battery chargers in the CMOC area

Hybrid fuel cell, photovoltaic, battery system operating a ham radio at the refugee camp (Global Solar)
Energy/Power Ranges

- MEMS
- “BA5590”
- Home Electricity & Field Generators
- UUV/MCM
- High power, 12 V NiMH, Li ion
- Sodium/Sulfur Flow batteries Lead-Acid Power Station
- 4 – 12 V Li-ion (LiCoO₂, nanomaterials)
- 12V, 120 V, 240 V Lead-acid
- SSN Emergency Power
Inside of a battery

- Battery components

- Cathode
- Anode
- Electrolyte/separator
- Current collectors
- Packaging
- Interconnects

\[
\text{e.g. Li-ion: } \text{Li}_{0.5}\text{Co}^{3+}_{0.5}\text{Co}^{4+}_{0.5}\text{O}_2 + 0.5\text{Li}^+ + 0.5\text{e}^- \rightarrow \text{LiCo}^{3+}\text{O}_2
\]

Energy stored

Primary battery - discharge once
Secondary battery - charge and discharge (charge storage systems)
Current stored is proportional to the amount of material in the cathode and anode.
Specific energy (Wh/kg) dependent on battery chemistry (No Moore’s law)

Specific Power (W/kg) is also chemistry dependent

- NiMH *high power*
- Li/CF$_x$ *low power*

Specific energy highest when batteries discharged at low rates
Primary batteries have more energy than secondary ones
Energy Storage and Uninterruptible Power Supply (UPS)

Battery energy storage concerns
  Need giant batteries
    - cheap materials
    - cheap manufacturing processes
  Maintenance problem
    - difficult and requires service
Cycle life
Capacity
Shelf life

Most advanced batteries are too expensive for very large scale grid applications
Energy Storage Battery Technologies

• Utility Storage Commercial Applications
  – Sodium/Sulfur - NGK, Japan Tokyo Electric Power Co
  – Zinc/Bromine - USA, Austria Powercell, DOE
  – Li-ion - USA, France SAFT

• Demonstrated Applications
  – Santa Barbara, CA (SBETI)
    • 30 ft bus with sodium nickel chloride battery
  – Clark County, NV
    • Zn-air battery combined with high specific power auxiliary battery on bus and ultracapacitors
# Energy Storage Battery Comparison

<table>
<thead>
<tr>
<th>Rechargeable (Secondary) Battery Technology</th>
<th>Cost</th>
<th>Theoretical Specific Capacity (mAh/g)</th>
<th>Theoretical Specific Energy (Wh/kg)</th>
<th>Cycle Life</th>
<th>Practical Specific Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-acid (stationary)</td>
<td>Low</td>
<td>120</td>
<td>252</td>
<td>800</td>
<td>20</td>
</tr>
<tr>
<td>Nickel Metal Hydride</td>
<td>High</td>
<td>178</td>
<td>240</td>
<td>900</td>
<td>75</td>
</tr>
<tr>
<td>Li-ion (LiCoO₂ v Li-C)</td>
<td>Moderately High</td>
<td>160</td>
<td>360</td>
<td>1000+</td>
<td>150</td>
</tr>
<tr>
<td>Li-ion (LiFePO₄ v Li-C)</td>
<td>Medium</td>
<td>170</td>
<td>400</td>
<td>1000+</td>
<td>164</td>
</tr>
<tr>
<td>Li-ion (Li₃V₂(PO₄)₃ v Li-C)</td>
<td>Medium*</td>
<td>190</td>
<td>450</td>
<td>1000+</td>
<td>180</td>
</tr>
</tbody>
</table>
How much capacity needed?

- **House:**
  
  6 kWh/day \(\rightarrow\) with a 12 V system
  
  - \(\frac{6000}{12} = 500\) Ah
  - 50% discharge \(\rightarrow\) need 1000 Ah
  - 4 days needed supply \(\rightarrow\) 4000 Ah

- **Uninterruptible Power Supply:**
  
  6 kWh/day \(\rightarrow\) with same 12 V system
  
  - 12 hours needed supply \(\rightarrow\) 500 Ah
Lead-Acid

- Plante, 1860
- 50 MWh at 1000 V needed for energy-storage systems
- Smaller batteries used for interruptible renewables (wind, PV)

- Anode:
  - \( \text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^- \) discharge (dissolution)
  - \( \text{SO}_4^{2-} + \text{Pb}^{2+} \rightarrow \text{PbSO}_4 \) discharge (precipitation)

- Cathode:
  - \( \text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O} \) (dissolution)
  - \( \text{SO}_4^{2-} + \text{Pb}^{2+} \rightarrow \text{PbSO}_4 \) discharge (precipitation)

- Overall:
  - \( \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \) (want to avoid \( \text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2 \))
Sodium/Sulfur

• 1970s, variation is Sodium /Nickel Chloride
• 270-350 °C
• Anode:
  – Liquid Na$\rightarrow$ $2\text{Na}^+$ + $2e^-$ discharge
• Cathode:
  – $x\text{S} + 2e^-$ $\rightarrow$ $S_x^{2-}$ discharge
• Overall:
  – $x\text{S} + 2\text{Na} \rightarrow \text{Na}_2S_x$

NRL built, 150 Wh/kg, 2 V/cell
Lithium-ion cell

Electrode material characteristics - good hosts for Li intercalation

- Layers, tunnels, interstitial sites
- Rigid lattice, unchanging with Li insertion and extraction
  - Accept or eject electrons
Cycling

e.g. charging LiCoO$_2$ to 4.2 V
-0.55Li$^+$
LiCoO$_2$ $\rightarrow$ Li$_{0.45}$Co$^{3+}_{0.45}$Co$^{4+}_{0.55}$O$_2$
Electrode materials

Cathode materials
classical: LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$
low voltage cathode materials:
V$_2$O$_5$, V$_6$O$_{13}$
phosphates: LiFePO$_4$, Li$_3$V$_2$(PO$_4$)$_3$

Anode materials
intercalation: cokes, graphite:
e.g. MCMB
alyloying: SnO$_2$ to Sn → Li$_{0.44}$Sn
Si → Li$_{4.4}$Si
Li metal oxide: Li$_4$Ti$_5$O$_{12}$
Nanomaterials

- Nanomaterials for Li-ion
  - Nano-painting carbon on LiFePO$_4$ (Phostech, NEI)
  - Carbothermal Reduction Method leaves remaining fine carbon behind (Valence Technology)
  - Li$_4$Ti$_5$O$_{12}$ (NEI, Altair Nano)

- allow higher rates of charge
- way to combine bulk and surface properties $\rightarrow$ unusual macroscopic properties
Recent interest in Li$_4$Ti$_5$O$_{12}$ for anodes

1.5 V vs Li - about 1 V higher than C

Performance related to particle size - 15 to 20 nm particles charge to 80% capacity

Nanoscale carbon not viable because high surface area can lead to high resistance ("SEI")

Preferred for use with ionic liquid based electrolytes
Advantages of nanostructured electrodes

- Advantages:
  - Accommodation of strain of Li\(^+\) insertion/extraction
  - Higher electrode/electrolyte area allows higher charge/discharge rate
  - Short path lengths for electronic transport
  - Short path length for Li\(^+\) transport
  - Less reactive as bulk

\[
\text{Li}_{0.5}\text{CoO}_2 + 0.5\text{Li}^+ + 0.5\text{e}^- \rightarrow \text{LiCoO}_2
\]
Nanoparticles can improve rate capability

![Graph showing voltage and specific capacity at different rates for Li4Ti5O12/LiCoO2](image)

- High rate
- Low rate

25°C
Disadvantages

- Increase undesirable side reactions electrode/electrolyte
- High surface area can lead to self discharge and poor cycle life
- More involved synthesis procedure
  - Wet chemistry
  - Templating
- Require compacting methods
Nanoparticles, electrolyte, and conductivity

- Create block copolymers self-assembling into nanophases for high Li conductivity (MIT)

- TiO$_2$, SiO$_2$, Al$_2$O$_3$ nanoparticles increase conductivity

- Carbothermal Reduction Method*

Li source + metal oxide + carbon $\rightarrow$ LiMO$_x$

C + O$_2$ $\rightarrow$ CO$_2$

2C + O$_2$ $\rightarrow$ 2CO

Example of adverse effect of nanomaterial: LiMn$_2$O$_4$

- Li ion LiMn$_2$O$_4$ – based rechargeable batteries have poor storage and cycling performance at high temperatures

$\Rightarrow$ LiMn$_2$O$_4$ is a “high voltage” material for Li-ion cathodes. Manganese dissolution and electrolyte oxidation is proportional to the surface area. The lowest irreversible self-discharge is observed for samples with the lowest surface area.

Summary

- Most advanced batteries with nanomaterials - too expensive for very large scale grid applications

- Nanoparticles in Li-ion batteries can allow high rates of charge (currents), but there are possible side reactions at voltages over 3.5 V and nanomaterials often discharge

- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is one of the few nanomaterials with good reversibility, capacity, and rate capability but lowers cell voltage to 2.3 V as an anode

- Low voltage, carbon-coated materials is a promising direction especially using the Carbothermal Reduction Method for medium scale Li ion battery materials as onsite backup system.

- Low cost manufacturing process may offset high cost materials in large quantities
Thank You!!

- James A. Baker III Institute for Public Policy
- Conference organizing committee

astux@ccs.nrl.navy.mil