Lithium-Ion Batteries: Challenges and Opportunities in an Evolving Lithium Economy

presented by

Michael M. Thackeray

Almaden Institute 2009

Scalable Energy Storage: Beyond Lithium Ion

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    Center for Electrical Energy Storage: Tailored Interfaces
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The First Oil Crisis (mid 1970’s)

- Non aqueous batteries - *sodium* or *lithium*?

- High temperature systems (300-450°C) already established
  
  - \( \text{Na} / \beta\text{-Al}_2\text{O}_3 / \text{S} \)  
  Chloride Silent Power, British Rail (UK)  
  Brown Boveri (Germany)

  - \( \text{LiAl} / \text{LiCl}, \text{KCl} / \text{FeS}_x \)  
  Argonne National Laboratory (USA)

- Oil crisis sparked the development of the sodium-metal chloride ‘Zebra’ battery (1978)
  
  - \( \text{Na} / \beta\text{-Al}_2\text{O}_3, \text{NaAlCl}_4/\text{MCl}_2 (M=\text{Ni, Fe}) \)  
  CSIR  
  (South Africa)

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# Theoretical and Practical Properties of Batteries

( theoretical values based on the masses of active electrode and electrolyte components)

<table>
<thead>
<tr>
<th>System</th>
<th>Negative electrode</th>
<th>Positive electrode</th>
<th>OCV (V)</th>
<th>Th. Cap (Ah/kg)</th>
<th>Th En. (Wh/kg)</th>
<th>Pr. En. (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead – acid</td>
<td>Pb</td>
<td>PbO₂</td>
<td>2.1</td>
<td>83</td>
<td>171</td>
<td>20-40</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>Cd</td>
<td>NiOOH</td>
<td>1.35</td>
<td>162</td>
<td>219</td>
<td>40-60</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>MH alloy</td>
<td>NiOOH</td>
<td>1.35</td>
<td>~178</td>
<td>~240</td>
<td>60-80</td>
</tr>
<tr>
<td>Na-S (350°C)</td>
<td>Na</td>
<td>S</td>
<td>2.1-1.78 (2.0)</td>
<td>377</td>
<td>754</td>
<td>120-150</td>
</tr>
<tr>
<td>Na-MCl₂ (300°C)</td>
<td>Na</td>
<td>NiCl₂</td>
<td>2.58</td>
<td>305</td>
<td>787</td>
<td>80-100</td>
</tr>
<tr>
<td>Li-Ion</td>
<td>LiₓC₆ (M=Co, Ni, Mn)</td>
<td>Li₁₋ₓMO₂</td>
<td>4.2-3.0 (4.0)</td>
<td>95 (for x=0.6)</td>
<td>380</td>
<td>150-200</td>
</tr>
<tr>
<td>Li-polymer</td>
<td>Li</td>
<td>VOₓ</td>
<td>3.3-2.0 (2.6)</td>
<td>~340</td>
<td>~884</td>
<td>~150</td>
</tr>
</tbody>
</table>

⇒ Lithium-ion systems offer the best near-term opportunities  
⇒ What lies ‘beyond lithium-ion’?
Ragone Plot of Various Electrochemical Energy-Storage Devices

Source: Amended from Product data sheets
The Sodium-Nickel Chloride Battery

Cell Configuration: Na / $\beta$-Al$_2$O$_3$, NaAlCl$_4$ / NiCl$_2$
Operating Temperature: 300 °C
Cell Reaction: $2 \text{Na} + \text{NiCl}_2 \rightleftharpoons \text{Ni} + 2 \text{NaCl}$

- Cells are assembled in the discharged state
- The close-packed Cl$^-$ lattice provides a stable framework for Na$^+$ and M$^{2+}$ ions
- The ‘insertion – displacement’ reaction is 100% efficient
- The volume expansion of the Cl$^-$ array during discharge = 45.6%
- Cells fail in short circuit mode – excellent for enhancing safety
- Excellent reversibility achieved through an *electronically conducting* $M$ matrix, and through *control of M grain growth* at 300 °C

$\Rightarrow$ Implications for room temperature reactions? Intermetallic compounds?

Photos: Courtesy of J. Coetzer and J. Sudworth, ‘Out of Africa’
The Advent of Li-Ion Batteries  
(Sony Corporation - 1991)

- Lithium insertion/extraction reactions
- Highly energetic (4 V) systems
- Inherently unsafe; individual cells are protected from overcharge by costly electronic circuitry
- Flammable electrolytes
  ⇒ scientific and technological motivation to discover and study alternative electrodes and electrolytes
- Cell voltage can be tailored by selection of anode and cathode materials
Impact of Li-Ion Batteries

- ~$8-10 billion market created over the past 18 years

- Applications:
  - Consumer electronics and communications
  - Transportation (‘Li economy’ driver)
    - Hybrid-electric vehicles ‘and plug-in’ HEVs
    - Pure electric vehicles – longer term viability
  - Implantable medical devices
    - Neuro-stimulators, pacemakers, defibrillators
  - Aerospace, defense, power tools, toys

- Lithium batteries have become a strategic commodity in U.S. energy security
Li-Ion Batteries: 3.5 – 4 V Cathode Materials

**Ordered Rocksalt**
Layered LiMO$_2$ (M=Co, Ni, Mn)
- **Capacity limited** to $\sim 0.5$ Li per M atom (i.e., $\sim 140$ mAh/g)
- Co$^{4+}$ and Ni$^{4+}$ unstable/highly oxidizing
- Structure destabilized at low Li content
- Layered LiMnO$_2$ transforms to spinel

**Spinel**
LiM$_2$O$_4$ (M=Mn)
- **Capacity limited** to $<0.5$ Li/Mn at 4 V
- Robust M$_2$O$_4$ spinel framework; 3-D channels
- **High rate capability**
- Jahn-Teller (Mn$^{3+}$) distortion at 3 V
- Solubility problems at high potentials

**Olivine**
LiMPO$_4$ (M=Fe, Mn)
- **Capacity limited** to 1 Li/Fe; P inactive
- Excellent structural and thermal stability
- 1-D channels
- Poor electronic and Li-ion conductivity
- Poor packing density
Li-Ion Batteries: Anode Materials

- **Carbon**
  - *Graphite*: <100 mV vs. Li$^0$
  - Moderate capacity (372 mAh/g)
  - Highly reactive, unsafe, SEI necessary

- **Metals, Semi-metals and intermetallic compounds**
  - Al, Si, CoSn, Cu$_6$Sn$_5$: <0.5 V vs. Li$^0$
  - High gravimetric/volumetric capacities
  - Large volume expansion on reaction with lithium
  - Reactive, SEI necessary
  - *Greatest opportunity and challenge*

- **Metal Oxides**
  - $Li_4Ti_5O_{12}$ (Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$) Spinel: 1.5 V vs. Li$^0$
  - Low capacity (175 mAh/g)
  - Very high rate capability
  - Stable in nanoparticulate form
Hazards of Highly Energetic Batteries

- Despite the good statistical safety record of batteries in consumer electronics products, the occasional serious mishap does occur.
- A significant number of recalls of lithium ion batteries
- Millions of passengers fly every month
- Millions of batteries fly every day
- In air travel, it only takes one
- So far, we’ve been lucky

During boarding, a laptop started burning in an overhead bin. The fire was extinguished on ramp.

Dan Halberstein
Lithium Battery Public Awareness Initiative
U.S. Department of Transportation,
25th Annual Battery Seminar, Fort Lauderdale, March 17-19, 2008
## USABC HEV Battery Goals

### Power Assist HEV

<table>
<thead>
<tr>
<th></th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Discharge Power, kW</strong></td>
<td>25 (10s)</td>
<td>40 (10s)</td>
</tr>
<tr>
<td><strong>Regen Power, kW</strong></td>
<td>20 (10s)</td>
<td>35 (10s)</td>
</tr>
<tr>
<td><strong>Available Energy, kWh</strong></td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Available Energy, Wh/kg</strong></td>
<td>7.5</td>
<td>12.5</td>
</tr>
<tr>
<td><strong>Battery Mass, kg</strong></td>
<td></td>
<td>60</td>
</tr>
</tbody>
</table>

### Barriers

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calendar Life, years</strong></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td><strong>Operating Temperature, °C</strong></td>
<td>-30 to 52</td>
<td></td>
</tr>
<tr>
<td><em><em>Cold Cranking Power</em>, kW</em>*</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td><strong>Selling Price</strong>, $</td>
<td>500</td>
<td>800</td>
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</table>

*Three 2s pulses at -30°C with 10s rest between pulses

**Price based on 100,000 batteries/year production level
## PHEV Battery Goals

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Short-Term</th>
<th>Long-Term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge Power, kW</td>
<td>45</td>
<td>38</td>
</tr>
<tr>
<td>Regen Power, kW</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Available Energy, kWh (Charge-Depleting)</td>
<td>3.4</td>
<td>11.6</td>
</tr>
<tr>
<td>Available Energy, Wh/kg</td>
<td>~80</td>
<td>~140</td>
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<tr>
<td>Available Energy, kWh (Charge-Sustaining)</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Range, miles</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Battery Mass, kg</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>Calendar Life, years</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Operating Temperature, °C</td>
<td>-30 to 52</td>
<td></td>
</tr>
<tr>
<td>Cold Cranking Power*, kW</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Selling Price**, $</td>
<td>1,700</td>
<td>3,400</td>
</tr>
</tbody>
</table>

* Three 2s pulses at -30°C with 10s rest between pulses  **Price based on 100,000 batteries/year production level
# USABC EV Battery Goals

<table>
<thead>
<tr>
<th>Parameter of Fully Burdened System</th>
<th>Minimum Goals for Long Term Commercialization</th>
<th>Long-Term Goals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density, W/L</td>
<td>460</td>
<td>600</td>
</tr>
<tr>
<td>Specific Power (80% DOD), W/kg</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>Energy Density, (C/3) Wh/L</td>
<td>230</td>
<td>300</td>
</tr>
<tr>
<td>Specific Energy, (C/3) Wh/kg</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Specific Power:Energy Ratio</td>
<td>2:1</td>
<td>2:1</td>
</tr>
<tr>
<td>Battery Mass, kg</td>
<td>267</td>
<td>200</td>
</tr>
<tr>
<td>Normal Recharge Time, hr</td>
<td>6</td>
<td>3-6</td>
</tr>
<tr>
<td>Operating Temperature, °C</td>
<td>-40 to +50</td>
<td>-40 to +85</td>
</tr>
<tr>
<td>Cycle Life – 80% DOD (Cycles)</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Life, years</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Selling Price – 25000 units, $/kWh</td>
<td>&lt;150</td>
<td>100</td>
</tr>
<tr>
<td>Selling Price – 25000 units, $/kWh</td>
<td>&lt;6000</td>
<td>&lt;4000</td>
</tr>
</tbody>
</table>

**Barriers**

- **Barriers**
- **Parameter**
- **Minimum Goals for Long Term Commercialization**
- **Long-Term Goals**

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[Argonne National Laboratory]
Major Challenges

- Improve the **energy** and **safety** of Li-ion cells, without compromising power
  - suppress oxygen release from high capacity *metal oxide cathodes* on charge at high potentials
  - find alternative *anodes* to graphite that provide a high electrochemical capacity at 0.5 – 1.0 V vs. Li
    ⇒ lithium alloys/intermetallic compounds, metal oxides?
  - Exploit nano-particulate electrodes
    ⇒ access intrinsic capacity (energy) of electrodes at high rates
    ⇒ LiFePO$_4$, Li$_4$Ti$_5$O$_{12}$; high potential metal oxides?
  - stabilize electrode surfaces (ANL-NU-UIUC EFRC)
  - find alternative *electrolytes and additives*
  - find effective redox shuttles to prevent overcharge
Designing High Capacity and Safe Electrode Structures for High Voltage Lithium-Ion Cells

**Argonne’s Approach:**

- Use two-component ‘composite’ structures in which an electrochemically *inactive* $\text{Li}_2\text{MnO}_3$ component stabilizes an electrochemically *active layered or spinel component*

  - layered-layered systems: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$

  - layered-spinel systems: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiM}_2\text{O}_4$

- M = Mn, Ni, Co

- focus on manganese-rich systems (cost advantage)
Li$_2$MnO$_3$ (Li$_2$O•MnO$_2$) is electrochemically **inactive** with respect to lithium insertion/extraction, whereas LiMO$_2$ is **active**

**Strategy:** Embed inactive Li$_2$MnO$_3$ component within layered LiMO$_2$ structure to stabilize the electrode and to reduce the oxygen activity at the surface of charged (delithiated) electrode particles
Use Structural Units (instead of ion dopants) to Stabilize Electrochemically–Active Materials

Electrodes

\( \beta\)-MnO\(_2\)

\( r\)-MnO\(_2\)

\( \gamma\)-MnO\(_2\): Intergrowth of \( \beta\)-MnO\(_2\) and ramsdellite-MnO\(_2\)

Li\(_2\)O-stabilized \( \alpha\)-MnO\(_2\): 0.15Li\(_2\)O•MnO\(_2\)

Solid Electrolytes

\( \beta\)-alumina, Na\(_2\)O•11Al\(_2\)O\(_3\)

44AgI•3(C\(_{11}\)H\(_{22}\)N\(_3\))I\(_3\)

\( \beta\)-alumina, Na\(_2\)O•11Al\(_2\)O\(_3\)
Compositional Phase Diagram: 
\( x\text{Li}_2\text{MnO}_3 \bullet \{1-x\}\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2 \) Electrodes

Mn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) \((\text{Mn}^{4+}; \text{Ni}^{4+})\)

\(-0.33\text{Li}_2\text{O}\)

\((0.33\text{Li}_2\text{MnO}_3 \bullet 0.67\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2)\)

close-packed planes

Li\(_2\)MnO\(_3\) \((\text{Mn}^{4+})\)

Li\(_{x}\)Mn\(_{1-y}\)Ni\(_{y}\)O\(_2\) tie-line

\((0 \leq x \leq 2)\)

\(x = 0.67\)
\(x = 0.33\)

LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) \((\text{Mn}^{4+}; \text{Ni}^{2+})\)

\((\text{LiMn}_{0.67}\text{Ni}_{0.33}\text{O}_2; \text{Mn}^{3.5+}; \text{Ni}^{2+})\)

\(x = 0.50\)

\(x = 0.50\)

Li\(_2\)Mn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) \((\text{Mn}^{2+}; \text{Ni}^{2+})\)

\((\text{Li}_2\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2; \text{Mn}^{2+}; \text{Ni}^{2+})\)

U.S. Pat. 6,677,082 (2004); U.S. Pat. 6,680,143 (2004)

Li\(_2\)O is removed from the Li\(_2\)MnO\(_3\) component at high potentials (>4.5 V)

Mn\(^{3+}\) concentration at the end of discharge is tailored by the Li\(_2\)MnO\(_3\) content in the parent electrode \((x)\) to suppress the Jahn-Teller distortion

Electrochemistry of a Li/0.3Li$_2$MnO$_3$•0.7LiMn$_{0.5}$Ni$_{0.5}$O$_2$ Cell (C/3)

Irreversible capacity can be used to offset SEI formation at anode

Average Mn valence in discharged state = 3.54

4.8-2.75 V
0.25 mA/cm$^2$
50 °C

262 mAh/g
90% of theoretical value

Safety Characteristics

$xLi_2MnO_3 \cdot (1-x)LiMO_2$ Cathode (M=Mn, Ni, Co)

Thermal Stability (DSC)

Argonne cathode charged to 4.6 V
$\Delta H=650\text{j/g}$

Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ charged to 4.2 V
$\Delta H=1550\text{j/g}$

Courtesy of K. Amine, Argonne National Laboratory
Charging high-capacity xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrodes to a high potential (>4.4 V) damages the electrode surface and reduces the rate capability of the electrode:

1. LiMO$_2$ $\rightarrow$ MO$_{2-\delta}$ + Li$^+$ + $\delta/2$ O$_2$ + (1+2$\delta$)e
2. Li$_2$MnO$_3$ $\rightarrow$ MnO$_2$ + 2 Li$^+$ + O$_2$ + 2e

Oxygen loss, particularly through process (1), increases M cation concentration at the electrode surface that restricts Li diffusion and rate capability?

$\Rightarrow$ Li$_x$Ni$_{1-x}$O rock salt structure at surface of Li$_{1-x}$Ni$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$

How does one prevent corrosion and cation disorder at the surface to allow high rate discharge and charge? (Thrust of EFRC)
Fluorination

- Fluorination of layered $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ electrodes (e.g., LiF, AlF$_3$ - Sun et al., Amine et al.) is known to improve capacity and cycling stability.
- F$^-$ ions within the bulk or at the surface? – gradient?

**Alternative Approach**

- Use mildly acidic solutions containing fluorine to form robust oxy-fluoride (partially reduced) surface on electrode particles lowering oxygen activity.
- Use soluble salts with stabilizing cations and anions, e.g., (NH$_4$)$_3$AlF$_6$; NH$_4$PF$_6$; NH$_4$BF$_4$ in water, methanol, etc
- Molarity of solutions $\sim 2.5 \times 10^{-3}$ M; pH $\approx 6.0 - 6.5$
- pH can be varied to tailor stability and first-cycle irreversibility loss
Relative Rate Capability: Li-ion cells

$C_6/0.1Li_2MnO_3\cdot0.9LiMn_{0.256}Ni_{0.372}Co_{0.372}O_2$

- Fluorinated electrodes provide higher capacity, lower impedance and improved rate: ~175 mAh/g at C/1 rate
- Insufficient energy/power for 40-mile PHEVs.
- Yardstick for PHEV: 200 mAh/g at a C/1 rate, average 3.5 V (or higher)

Integrated Olivine-Metal Oxide Structures/Surfaces?

- Olivine (LiFePO$_4$) and Spinel (LiMn$_2$O$_4$) both have AB$_2$O$_4$ formulae with the A cations in tetrahedral sites and the B cations in octahedral sites.
- In LiFePO$_4$, the P cations are in tetrahedral sites.
- In LiMn$_2$O$_4$, the Li cations are in tetrahedral sites.
- Olivine has a hexagonally close packed structure.
- Spinel has a cubic close packed structure.
- Relatively small difference in the d-spacings of the close-packed layers in LiFePO$_4$ and LiMn$_2$O$_4$.
  
  ➢ Can we synthesize ‘olivine-spinel’ composite structures, ‘olivine-layered’ structures or other close-packed phosphate structures to stabilize ccp spinel and layered metal oxide bulk structures and/or surfaces?
In principle, a spinel-olivine intergrowth structure seems possible

Experiment shows otherwise: CBED patterns and EDS signals (Ni/V or Ni/P) suggest that discrete olivine and spinel phases exist.

Can Li-M-PO$_4$ films provide effective surface protection on metal oxides?

Vaughey et al., Argonne National Laboratory
**Li-M-PO₄ surface treatment (e.g., M=Ni)**

(0.5Li₂MnO₃•0.5LiNi₀.₄₄Co₀.₂₅Mn₀.₃₁O₂ electrodes in Li half cells)

- **Concept:** Use Li-Ni-PO₄ as a solid electrolyte below 5.0 V to protect surface of xLi₂MnO₃•(1-x)LiMO₂ electrode at high potentials
- **Sol-gel treatment technique used**
- **Olivine LiNiPO₄, Li₃PO₄ or defect Li₃PO₄, e.g., Li₃-2ₓNiₓPO₄?**
- **First-principles calculations indicate a small solid solution range in Li₃-2ₓMₓPO₄ materials (Shin, Wolverton (NU – EFRC))**

Treated electrodes meet the 200 mAh/g, C/1 rate, 3.5 V average, capacity/power yardstick for a 40-mile range PHEV *at room temperature*

Playing it Safe

Li$_4$Ti$_5$O$_{12}$ (Spinel) / Li$_{1+x}$Mn$_{2-x}$O$_4$ (Spinel) Cells

- Relatively low energy cells (2.5 V)
- Outstanding power and cycling stability
- Safety is achieved by operating well above the potential of metallic lithium
- Being developed for HEV applications

Courtesy of K. Amine and Enerdel
TiO$_2$ Anodes?

- Li$_4$Ti$_5$O$_{12}$ (2Li$_2$O$\cdot$5TiO$_2$) *spinel* accommodates 3 Li$^+$ ions per formula unit during its transformation to rock-salt Li$_7$Ti$_5$O$_{12}$ (Ti$^{4+}$ to Ti$^{3.4+}$): relatively low capacity – **175 mAh/g**

- TiO$_2$ structures, e.g., *anatase, rutile, hollandite and TiO$_2$-B* would be more attractive anodes if, in nanoparticulate form, they could accommodate lithium reversibly and rapidly to the rock-salt stoichiometry LiTiO$_2$ (Ti$^{3+}$), for which the theoretical capacity is **335 mAh/g**.
A single-step, autogenic (solvent-less), and scalable process has been used to prepare single-phase TiO$_2$ (anatase) nanoparticles encapsulated by an interconnected, electronically-conducting network of carbon nanoparticles that also protect the surface.

V. Pol et al., Argonne National Laboratory
FESEM and HRTEM images of C-coated TiO$_2$

The images demonstrate the likelihood that every TiO$_2$ nanoparticle is completely encapsulated by a 2-4 nm layer of x-ray amorphous carbon, the thickness of which can be tailored by the temperature and length of the carbon combustion process.

V. Pol, Thackeray et al., Argonne National Laboratory (EFRC)
200 mAh/g is delivered by both the TiO$_2$ anode and metal oxide cathode.

Cells provide higher energy than Li-ion cells with Li$_4$Ti$_5$O$_{12}$ anodes.

The autogenic process can be used to prepare a wide variety of C-protected nanoparticulate materials; the approach has implications for advancing the electrochemical properties of both anode and cathode nano-materials.

V. Pol, Thackeray et al., Argonne National Laboratory (EFRC)
Alternative Anodes for Li Cells
*Lithium Alloys and Intermetallic Compounds*

- Metals have dense structures and therefore expand significantly on reaction with Li, e.g. Al, Si, Sn, Sb

```
+ Li
300 mV
```

**LiAl**

- Major structural rearrangement on lithium insertion
- Lithium alloys offer significantly higher gravimetric and volumetric capacities than graphite (372 mAh/g; 820 mAh/ml)


**Cu₆Sn₅ Anodes**

### Cu₆Sn₅ to Li₂CuSn transition

21.25 Li + Cu₆Sn₅ → 5 Li₂⁺ₓCu₁⁻ₓSn + (1+5x) Cu → 6 Cu + 5 Li₄.₂₅Sn

- Strong structural relationship between Cu₆Sn₅, Li₂CuSn and “Li₃Sn” (x=1) exists.
- Li insertion/Cu displacement reaction: Max capacity ≈ 600 mAh/g.
- Mimics Na/NiCl₂ reaction (100% efficient): 2 Na + NiCl₂ → 2 NaCl + Ni.
  - Cells assembled in discharged state; NaCl powder in porous Ni substrate.
- Volume expansion 50-60%.

### Electrochemistry: Cu₆Sn₅ vs. Sn

New approach to electrode design and current collection is required

Electrodeposited Cu$_6$Sn$_5$/Sn on Cu Foam Electrodes

1. As-deposited Cu foam
2. Annealed Cu foam (500 °C)
3. Cu$_6$Sn$_5$/Sn on Cu foam

- 1. As-deposited Cu-foam is brittle and powdery.
- 2. Annealing at 500 °C strengthens Cu-foam to Cu foil contact, providing a sufficiently robust substrate for electrodeposition of Cu and Sn. Overall porosity maintained.
- 3. Morphology maintained after Cu$_6$Sn$_5$/Sn pulsed electrodeposition at -600mV vs. SCE. Sn concentration varies from ~20% within the porous electrode to ~90% at outermost surfaces.

Significant improvement in reversible capacity achieved (650 mAh/g vs. 200 mAh/g for ball-milled Cu₆Sn₅ samples).

Results suggest excellent cycling of Sn within a copper-tin matrix electrode.

Large irreversible capacity drop during early cycles attributed to electrolyte reactions with high surface area electrode to form passivation layer.

Abrupt onset of capacity fade after 30 cycles - Li electrode or mechanical failure of Cu₆Sn₅/Sn electrode?

Beyond Lithium-Ion: Li-Air – The Holy Grail?

<table>
<thead>
<tr>
<th>System</th>
<th>Reaction</th>
<th>OCV (V)</th>
<th>Th. Spec. Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/O₂</td>
<td>2 Li + O₂ → 2 Li₂O₂</td>
<td>3.1</td>
<td>3623 (incl. O)</td>
</tr>
<tr>
<td></td>
<td>4 Li + O₂ → 2 Li₂O</td>
<td>2.9</td>
<td>5204 (incl. O)</td>
</tr>
<tr>
<td></td>
<td>4 Li + O₂ → 2 Li₂O</td>
<td>2.9</td>
<td>11,202 (excl. O)</td>
</tr>
<tr>
<td>Lithium-ion (M=Mn, Ni, Co)</td>
<td>LiₓC₆ + Li₁₋ₓMO₂ → C₆ + LiMO₂</td>
<td>3.6</td>
<td>~900</td>
</tr>
<tr>
<td>Octane</td>
<td>C₈H₁₈ + 12.5O₂ → 8CO₂ + H₂O</td>
<td>-</td>
<td>~13,000 (ex. O)</td>
</tr>
</tbody>
</table>
Exploitation of Li$_2$O-Containing Electrodes: Electrochemical Activation of Li$_2$MnO$_3$

\[ \text{Li}_2\text{MnO}_3 \, (\text{Li}_2\text{O}\bullet\text{MnO}_2) \xrightarrow{4.5-4.8 \, \text{V}} \text{MnO}_2 + 2 \text{Li} + \frac{1}{2} \text{O}_2 \, (459 \, \text{mAh/g}) \]

- Net loss is Li$_2$O at 4.5 to 4.8 V – irreversible reaction
- Two Li$^+$ ions removed during electrochemical activation (charge)
- One Li$^+$ ion reinserted into residual MnO$_2$ component:
  \[ \text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2 \, (229 \, \text{mAh/g, mass of parent electrode}) \]
- Use surplus Li to load anode: C$_6$, metals or even bare substrate (Li metal)
- Use Li$_2$MnO$_3$ (or xLi$_2$MnO$_3\bullet$(1-x)LiMO$_2$, M=Mn, Ni, Co) precursor in combination with high capacity charged cathodes, particularly where two electron transfer reactions are possible, e.g., Li$_{1.2}$V$_3$O$_8$ (372 mAh/g)
Li-O bonds in Li$_2$MnO$_3$ cathode precursor are broken at $\sim$4.5 V vs. Li$^0$
Li is inserted into C$_6$ anode during charge
During discharge, Li is inserted charged Li$_{1.2}$V$_3$O$_8$
and residual MnO$_2$ cathode components
Implications for Li - O$_2$ cells using MnO$_2$ component as catalyst?

Kang et al., Argonne National Laboratory
**Alternative High-Li$_2$O Content Precursors**

Antifluorite structures

- **Li$_2$O (Fm-3m)**
  
  $a=4.614$ Å

- **Li$_5$FeO$_4$ (Pbca)**
  
  $(a=9.218$ Å; $b=9.213$ Å; $a=9.159$ Å )

  - **Defect structures**
    - **Li$_5$FeO$_4$:** 5Li$_2$O•Fe$_2$O$_3$ or Li$_{1.25}$Fe$_{0.25}$□$_{0.5}$O
      
      5 Li per Fe atom
    - **Li$_6$MO$_4$ (M=Mn, Co, Ni):**
      
      3Li$_2$O•MO or Li$_{1.5}$M$_{0.25}$□$_{0.25}$O
      
      6 Li per M atom

  - cf: Layered Li$_2$MnO$_3$ (Li$_2$O:MnO$_2$)
    
    2 Li per Mn atom

Abundant Li in defect structure provides good Li$^+$ mobility
Electrochemical Extraction of Li from Li$_5$FeO$_4$

- 4 Li removed from Li$_5$FeO$_4$ (5Li$_2$O•Fe$_2$O$_3$) in 2 steps at ~3.5 and ~4.0 V
- Slight evidence from XANES data of some Fe$^{3+} \rightarrow$ Fe$^{4+}$ oxidation
  \[ \Rightarrow \text{predominantly Li}_2\text{O extraction?} \]
- Composition of delithiated product = “LiFeO$_2$” (Li$_2$O•Fe$_2$O$_3$)
- Exploit reversibility of the reaction when discharged against O$_2$ electrode
  (Li$_2$O content increases in the residual Fe$_2$O$_3$ electrode matrix)

Johnson et al., Argonne National Laboratory


**XANES Data: Chemical Delithiation of Li$_5$FeO$_4$**

- Li$_5$FeO$_4$ samples chemically delithiated with NO$_2$BF$_4$/acetonitrile solution
- No apparent change in Fe$^{3+}$ oxidation state $\Rightarrow$ Li$_2$O extraction
- EXAFS shows evidence of formation of edge-shared Fe-octahedra as $x \uparrow$.
- Gradual reduction in pre-edge peak height is consistent with conversion from tetrahedral Fe to octahedral coordination and ultimate ‘LiFeO$_2$’ stoichiometry

S. Pol, M. Balasubramanian et al., APS - Argonne National Laboratory
Summary Remarks

- Lithium-ion technology stands to broaden its impact on battery markets.
- Extremely versatile, strategic technology - battery chemistry can be tailored to suit needs.
- State-of-the-art lithium-ion batteries still compromised by **safety, energy, power, life, operating temperature** and **cost** constraints

- New, structurally-stable materials required:
  - Exploitation of high potential metal oxide electrodes (>4.2 V) to increase energy and power
  - Composite cathode structures with high-capacity (layered) / high-power (spinel) components?
  - Nano-particulate metal, semi-metal or intermetallic anodes to replace graphite - increase both specific- and volumetric capacity?
  - Electrode surface protection – use of additives
  - Non-flammable electrolytes

- Li-air: the ultimate scientific and engineering challenge?