A (Very Brief) History of The Battery

However, jars have been discovered outside Baghdad dating to 200 B.C.: iron rod, encased in copper, and soaked in vinegar or wine (0.78 V)

Alessandro Volta’s battery (circa 1800 A.D.): copper and zinc separated by cardboard soaked in brine
How Batteries Affect Your Life
The Main Components of a Typical Li-ion Battery

Components

- Anode (Carbon)
- Cathode (LiCoO$_2$)
- Electrolyte (EC/DMC with LiPF$_6$)
- Separator (Polypropylene)

Topics to be discussed

- Stability of Li (dendritic growth)

- Volume expansion challenges in electrode materials *(anodes)*

- Redox reactions in batteries
  - Energy level diagrams, which determine the electrochemical window of a battery
  - Solid-electrolyte-interfaces

- The importance of diffusion rates
Rich Battery Chemistry

Advantages to Li: light, large electrochemical window

Intercalation Chemistry: Anodes

Dendritic growth of Li onto Li metal anodes

Li-Dendrite Growth: Cause of Safety Failures

- Li dendrites puncture the separator, causing a short
- liquid electrolyte is flammable
- LiCoO$_2$ cathodes decompose to generate O$_2$

One solution: Graphite

Current commercial batteries have graphite anodes. The trade-off is lower energy density.

Graphite based materials are the current standard
Theoretical capacity of 372 mAh g\(^{-1}\) (818 mAh ml\(^{-1}\)) (LiC\(_6\))

\(\text{Cu}_2\text{Sb}\) improves cyclic stability
Experimental value of 290 mAh g\(^{-1}\) (1914 mAh ml\(^{-1}\))

Strong structural relationship between parent and child compound

*No danger of plating Li metal*

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Lithiation of Cu$_2$Sb

- Lithiation of Cu$_2$Sb has two main characteristic plateaus:
  - 1$^{\text{st}}$ at $\sim0.8$ V vs. Li/Li$^+$
    
    \[
    \text{Cu}_2\text{Sb} \rightarrow \text{Li}_2\text{CuSb}
    \]
  - 2$^{\text{nd}}$ at $\sim0.6$ V vs. Li/Li$^+$
    
    \[
    \text{Li}_2\text{CuSb} \rightarrow \text{Li}_3\text{Sb}
    \]

- The charge before 0.8 V is due to SEI formation and formation of Li$_2$O (if oxide is present)

Depositing onto TEM Grids

The 1\textsuperscript{st} step in the lithiation process occurs at 0.8 V vs Li/Li\textsuperscript{+}

\[ \text{Cu}_2\text{Sb} + 2e^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{CuSb} + \text{Cu} \]

\( \sim \)0.4 mole to 1 mole of Cu per mole of Cu\textsubscript{2}Sb is extruded

The extruded Cu particles surround the nucleation sites
Second Charge Plateau

The 2\textsuperscript{nd} step in the lithiation process occurs at 0.6 V vs Li/Li$^+$

$$\text{Li}_2\text{CuSb} + 1\text{e}^- + \text{Li}^+ \rightarrow \text{Li}_3\text{Sb} + \text{Cu}$$

Extruded copper is further from nucleation site

Cu rich
Sb rich

Relative to $\text{Cu}_2\text{Sb}$

500 nm

Extruded copper is further from nucleation site
Extruded Cu Particles

The extruded Cu is in the form of small < 10 nm particles

By 0.6 V the Cu particles have traveled from the core and lattice fringes that match Cu(200) are present

For examples of other systems that extrude metal particles see E. Takeuchi (Ag)
Using a Physical Barrier to Keep the Cu in Contact

Cu₂Sb Film

AlPO₄ Coated Cu₂Sb Film

AlPO₄ can be coated onto the Cu₂Sb surface ‘electrochemically’
AlPO$_4$ coated Cu$_2$Sb films have a higher capacity retention

Enhanced Capacity Retention

- (a) Charge AlPO$_4$
- (b) Discharge AlPO$_4$
- (c) Charge Bare
- (d) Discharge Bare
There is still a significant interest in solving the Li-dendrite problem.

Voltage profiles of common cathodes

Energy level diagrams

Tunability Using Crystal Chemistry

Goodenough and Kim, Chemistry of Materials, 2010, 22, 587
But if you take all of the Li+ out, the structure collapses and it isn’t reversible.

Changing the transition metal

The challenge is that when you make the voltages large, you have to worry about unwanted reactions with the electrolyte.
The kinetic stability of a battery is due to the formation of a stable solid electrolyte interface (SEI)

\( \Phi_A = \) Anode work function
\( \Phi_C = \) cathode work function
\( E_g = \) window of the electrolyte for thermodynamic stability
Voltage window of the electrolyte

Voltage versus capacity relative to the window of 1 M LiPF₆ in EC/DEC (1:1)

The SEI is still poorly characterized, although people have developed ways to control its growth with the addition of various additives.
# Summary of electrolytes

## Table 1. Nonaqueous Electrolytes for Li-Ion Batteries

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Example of classical electrolytes</th>
<th>Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp</th>
<th>Electrochemical window (V) vs Li$^+/\text{Li}^0$</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid organic</td>
<td>1M LiPF$_6$ in EC:DEC (1:1)</td>
<td>7$^3$</td>
<td>1.3$^7$</td>
<td>4.5$^6$</td>
</tr>
<tr>
<td></td>
<td>1M LiPF$_6$ in EC:DMC (1:1)</td>
<td>10$^3$</td>
<td>1.3$^7$</td>
<td>&gt; 5.0$^3$</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>1M LiTFSI in EMI-TFSI</td>
<td>2.0$^{15}$</td>
<td>1.0$^{15}$</td>
<td>5.3$^{15}$</td>
</tr>
<tr>
<td></td>
<td>1M LiBF$_4$ in EMI-BF$_4$</td>
<td>8.0$^{15}$</td>
<td>0.9$^{16}$</td>
<td>5.3$^{16}$</td>
</tr>
<tr>
<td>Polymer</td>
<td>LiTFSI-P(EO/MEEGE)</td>
<td>0.1$^{24}$</td>
<td>&lt; 0.0$^{24}$</td>
<td>4.7$^{24}$</td>
</tr>
<tr>
<td></td>
<td>LiClO$_4$-PEO$_8$ + 10 wt % TiO$_2$</td>
<td>0.02$^{26}$</td>
<td>&lt; 0.0$^{26}$</td>
<td>5.0$^{26}$</td>
</tr>
<tr>
<td>Inorganic solid</td>
<td>Li$_{4-x}$Ge$_x$P$_2$S$_4$ (x = 0.75)</td>
<td>2.2$^{28}$</td>
<td>&lt; 0.0$^{28}$</td>
<td>&gt; 5.0$^{28}$</td>
</tr>
<tr>
<td></td>
<td>0.05Li$_4$SiO$_4$ + 0.57Li$_2$S + 0.38SiS$_2$</td>
<td>1.0$^{30}$</td>
<td>&lt; 0.0$^{30}$</td>
<td>&gt; 8.0$^{30}$</td>
</tr>
<tr>
<td>Inorganic liquid</td>
<td>LiAlCl$_4$ + SO$_2$</td>
<td>70$^{20}$</td>
<td>-</td>
<td>4.4$^{20}$</td>
</tr>
<tr>
<td>Liquid organic + Polymer</td>
<td>0.04LiPF$_6$ + 0.2EC + 0.62DMC + 0.14PAN</td>
<td>4.2$^{38}$</td>
<td>-</td>
<td>4.4$^{38}$</td>
</tr>
<tr>
<td></td>
<td>LiClO$_4$ + EC + PC + PVdF</td>
<td>3.0$^{39}$</td>
<td>-</td>
<td>5.0$^{39}$</td>
</tr>
<tr>
<td>Ionic liquid + Polymer</td>
<td>1M LiTFSI + P$_{13}$TFSI + PVdF-HFP</td>
<td>0.18$^{43}$</td>
<td>&lt; 0.0$^{43}$</td>
<td>5.8$^{43}$</td>
</tr>
<tr>
<td>Ionic liquid + Polymer + Liquid organic</td>
<td>56 wt % LiTFSI–Py$_{24}$TFSI + 30 wt % PVdF-HFP + 14 wt % EC/PC</td>
<td>0.81$^{44}$</td>
<td>1.5$^{44}$</td>
<td>4.2$^{44}$</td>
</tr>
<tr>
<td>Polymer + Inorganic solid</td>
<td>2 vol % LiClO$_4$–TEC-19 + 98 vol% 95 (0.6Li$_3$S + 0.4Li$_2$S) + 5Li$_4$SiO$_4$</td>
<td>0.03$^{46}$</td>
<td>&lt; 0.0$^{46}$</td>
<td>&gt; 4.5$^{46}$</td>
</tr>
<tr>
<td>Ionic liquid + Liquid organic$^{19}$</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
SEI Formation on the First Cycle

Industrial batteries are cycled several times before they are sold: forming process
Cu$_2$Sb electrochemical half-cell galvanostatically charged at 10 $\mu$A cm$^{-2}$ in a 1M LiClO$_4$ EC/DEC/DMC (1:1:1) electrolyte solution.

Back to Cu$_2$Sb
Decomposition of Liquid Electrolyte on Cu$_2$Sb

(a) XPS HRES C 1s and Cu 2p (inset) spectra of a Cu$_2$Sb electrode charged to 1.8 V vs Li/Li$^+$
(b) SEM micrographs of the SEI layer formed on the surface of the Cu$_2$Sb. The cubic morphology of the bare electrode (inset) is still present under the SEI layer.
Potential Range is Important in Morphology

SEM micrographs of an SEI grown in the MPR for (a) 5 cycles and (c) 20 cycles. The SEI formed in the HPR for (b) 5 cycles and (d) 50 cycles.
Potential Range is Important in Performance

High potentials  intermediate potentials  low potentials
Take Home Messages Thus Far

• Stability of Li (dendritic growth)
  – This hasn’t been solved on Li metal anodes, and is a significant safety hazard
  – Alternative anode materials can be safer, but you lose on energy density and voltage

• Volume expansion challenges in electrode materials (anodes)
  – Mechanical pulverization is a problem in all electrode materials, but especially in dense intermetallics
  – Structural similarities between the parent and child compounds can be used to reduce the overall volume changes

• Solid-electrolyte-interfaces
  – Big voltage windows lead to redox reactions with the electrolyte
  – Interfaces are critical in batteries!

• The importance of diffusion rates
Framework Structures: NASICON

MO$_6$ octahedra linked to XO$_4$ tetrahedra

The diffusion rates of Li$^+$ ions into solid state structures is critical for how fast your battery will charge and discharge.
A123’s Cathode Material: LiFePO$_4$

Li$^+$ ions in 1D channels.
Charging Behavior: Must be Mixed With Carbon

C rate = capacity/time, or C/n denotes the rate at which a full charge or discharge takes in hours

Advantages: stable over a wide composition range
A Current Example: Kang and Ceder

Battery materials for ultrafast charging and discharging

*Nature 2009*

The storage of electrical energy at high charge and discharge rate is an important technology in today’s society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with supercapacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material. Here we show that batteries which obtain high energy density by storing charge in the bulk of a material can also achieve ultrahigh discharge rates, comparable to those of supercapacitors. We realize this in LiFePO$_4$ (ref. 6), a material with high lithium bulk mobility, by creating a fast ion-conducting surface phase through controlled off-stoichiometry. A rate capability equivalent to full battery discharge in 10–20 s can be achieved.

Kang, B. & Ceder, G. Nature **2009**, 458, 190
Diffusion of Li$^+$ is Direction Dependent

Kang and Ceder explained that Li$^+$ ions move into the bulk of LiFePO$_4$ primarily through the [010] direction. The oxygen is shown in red, lithium is blue, phosphorous is grey, and iron is mustard yellow.

[010] has fairly open channels….ideal for cation diffusion
A: poorly crystallized lithium phosphate (good Li conductors)

B: Li-excess or C: Li-deficiency leads to Fe-oxides or Fe-phosphates
Control of Composition is Really Important!
Making A ‘Coated’ Battery Material

Our synthesis strategy has been to create an appropriate off-stoichiometry in the starting materials so that the coating constituents phase-separate from LiFePO$_4$ as it forms during the heat treatment, thereby creating the active storage material and coating in a single process. Here we describe results with an iron:phosphorus deficiency ratio of 2:1 (for example LiFe$_{1-2y}$P$_{1-y}$O$_{4-\delta}$, $y = 0.05$), as indicated by arrow A in Supplementary Fig. 1. We note that the more common one-to-one iron:phosphorus deficiency (arrow B in Supplementary Fig. 1, equivalent to lithium excess$^{22}$) creates a mixture of Li$_3$PO$_4$ and iron oxides, which are not likely to conduct well under the synthesis conditions used to prepare LiFePO$_4$. 
LiFe$_{0.9}$P$_{0.95}$O$_{4-\delta}$ was synthesized by ball-milling Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O and NH$_4$H$_2$PO$_4$ in appropriate amounts, heating the mixture at 350 °C for 10 h and then heating at 600 °C for 10 h under argon. X-ray diffraction (Fig. 1a and Supplementary Fig. 2) shows that despite the off-stoichiometric starting mixture, stoichiometric LiFePO$_4$ forms with lattice parameters ($a = 10.3134$ Å, $b = 6.002$ Å and $c = 4.691$ Å) very similar to those reported in the literature$^{23}$. 
Aiming for LiFePO$_4$ and Li$_x$P$_y$O$_{1-\delta}$
Data for Surface Coating
The capacity retention is really impressive at high rates. 

50C is completely discharged in 72s
Cycle Life at High Rates

You still see a capacity loss at high rates, but it’s among the best performing fast rate materials currently known. *competitive with supercapacitors*
Final Take Home Messages

• **Stability of Li (dendritic growth)**
  – *This hasn’t been solved on Li metal anodes, and is a significant safety hazard*
  – *Alternative anode materials can be safer, but you lose on energy density and voltage*

• **Volume expansion challenges in electrode materials (anodes)**
  – *Mechanical pulverization is a problem in all electrode materials, but especially in dense intermetallics*
  – *Structural similarities between the parent and child compounds can be used to reduce the overall volume changes*

• **Solid-electrolyte-interfaces**
  – *Big voltage windows lead to redox reactions with the electrolyte*
  – *Interfaces are critical in batteries!*

• **The importance of diffusion rates**
  – Can improve diffusion by nanostructuring (Prof. Bruce)
  – Structural features are critical

Questions? You can reach me at alprieto@lamar.colostate.edu