The Inside Story of the Lithium Ion Battery

John Dunning, Research Scholar in Residence
Daniel Forbes, Graduate Student Electrical Engineering
Outline

• Background - Why this is important
• Electrochemistry/Battery Reactions
• Design of the Cells/Structure
• Manufacturing
• Performance
• Safety
  – Daniel Forbes’ Experimental Study
Why This is Important

Portable Electronics
Telecommunications/Personal Computers/Personal Networks

Energy/Transportation

Lithium Ion Battery
- ~200 Wh/k
- ~400 Wh/L
- ~ 10 cents/kWh charge
FF-->Heat-->Mech-->Elec-->Mech

Gasoline
- ~13,000 Wh/kg
- ~10,000 Wh/L
- ~ 5 cents/kWh refill
FF-->Heat-->Mech
<table>
<thead>
<tr>
<th>Year</th>
<th>Inventor/Location</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1791</td>
<td>Galvani (Italy)</td>
<td>Animal Electricity</td>
</tr>
<tr>
<td>1800</td>
<td>Alessandro Volta (Italy)</td>
<td>Invention of Voltaic Cell (Cu/brine/Zn)</td>
</tr>
<tr>
<td>1833</td>
<td>Micchael Faraday (UK)</td>
<td>Faraday’s Law of Electrolysis</td>
</tr>
<tr>
<td>1836</td>
<td>John Daniell (UK)</td>
<td>Daniell Cell (Cu/CuSO$_4$/ZnSO$_4$/Zn)</td>
</tr>
<tr>
<td>1859</td>
<td>Gaston Plante (France)</td>
<td>PbO$_2$ (s) + Pb(s) + 2H$_2$SO$_4$ = 2 PbSO$_4$ (s) + 2 H$_2$O</td>
</tr>
<tr>
<td>1868</td>
<td>Georges Leclanche (France)</td>
<td>Zn(s) + 2 MnO$_2$(s) + 2 NH$_4$Cl(aq) → ZnCl$_2$ + Mn$_2$O$_3$(s) + 2 NH$_3$(aq) + H$_2$O</td>
</tr>
<tr>
<td>1899</td>
<td>Waldemar Jugner (Sweden)</td>
<td>Cd+2NiO(OH)+2H$_2$O=Cd(OH)$_2$+2Ni(OH)$_2$</td>
</tr>
<tr>
<td>1901</td>
<td>Thomas Edison (USA)</td>
<td>Fe+2NiO(OH)+2H$_2$O=Fe(OH)$_2$+2Ni(OH)$_2$</td>
</tr>
<tr>
<td>Mid 1960</td>
<td>Union Carbide (USA)</td>
<td>Zn (s) +2MnO$_2$ (s) → ZnO (s) +Mn$_2$O$_3$ (s)</td>
</tr>
<tr>
<td>1970s</td>
<td>Various</td>
<td>Valve Regulated Lead Acid Cells</td>
</tr>
<tr>
<td>1990</td>
<td>Various</td>
<td>MH+NiO(OH)=M+Ni(OH)$_2$</td>
</tr>
<tr>
<td>1991</td>
<td>Yoshio Nishi (Japan)</td>
<td>Lithium Ion Cell</td>
</tr>
</tbody>
</table>
Performance of Various Chemistries
Electrochemical Cell

• Consists of Positive Electrode (Cathode), Negative Electrode (Anode) and Electrolyte

• An open circuit voltage is created by the free energy of reaction of the primary reaction and the influence of side reactions

• In the case of the lithium ion cells, we start with the discharged materials and give the cell a first charge
Starting Materials

- Anode: Graphite, finely divided
- Cathode: Layered Lithium Metal Oxide, e.g., Lithium Cobalt Oxide LiCoO$_2$
- Both Materials are layered materials, through which lithium can move easily due to the layered structures.
- Since water reacts with lithium, we must use nonaqueous electrolytes
Electrolytes

- **Solvent**: Mixtures of Organic Carbonates such as dimethyl carbonate (DMC) and ethylene carbonate (EC)

- **Salt** such as Lithium hexafluoro phosphate
The First Charge of a Lithium Ion Cell

Electrolyte oxidation

Cobalt oxide

Electrolyte:
LiPF$_6$ in Ethylene carbonate/diethyl carbonate

Solvent reduction

Graphite

Lithium deposition

LiCoO$_2$→Li$^+$+e$^-$+CoO$_2$

Li$^+$+e$^-+$C$_6$→LiC$_6$
Inconvenient Truths

• On the first charge the carbonates react to form a Solid-Electrolyte Interphase (SEI) layer on the graphite electrode that prevents further decomposition and allows the lithium to intercalate into the graphite.

• The conductivity of the electrolyte is very low relative to acid or alkaline aqueous electrolytes so the electrode spacing must be very small.
Modern Li-ion Battery

Lithium-ion battery

Anode: \( \text{Li}^{+} + e^{-} + C_6 \rightarrow \text{LiC}_6 \)

Cathode: \( \text{LiCoO}_2 \rightarrow \text{Li}^{+} + e^{-} + \text{CoO}_2 \)

Electrolyte: \( \text{LiPF}_6 \) in Ethylene carbonate/diethyl carbonate

Innovation can occur via new material development, or by better engineering.
Manufacturing

• Slurry Coating
• Calendaring
• Winding
• Cell Assembly
• Electrolyte Fill
• Cap and Seal
• Electrochemical Formation Charge
Starting Materials

Current Collectors
- Aluminum foil (Cathode) 20µm
- Copper foil (Anode) 14 µm

Separator
- Polyethylene
  - 50% porosity, 3-8 µm
Slurry Coating
Manufacturing Equipment

Coating and Drying of Electrodes

Calendaring

Final Assembly, Filling, Sealing
Cans, Caps, Mandrels
Parts of the Cells
Finished Product
Panasonic CGR18650EA

2.55 Ah Capacity
46.5 g Mass
3.7 V Nominal
9.43 Wh
209 Wh/kg
Typical life characteristics

Charge Condition: CVCC 4.2V Max. 0.71A (1715mA), 50mA cut-off at 25deg.C
Discharge Condition: CONSTANT CURRENT 1.0A (2450mA), 3.0V cut-off at 25deg.C
Charge/Discharge Rest Time: 20min.
Safety

• The lithium ion cell is safe if carefully controlled

• If not controlled serious problems can occur including
  – Venting of flammable electrolyte
  – Fire
  – Explosion
Thermal Runaway Events

External Abuse Conditions
- External Heating
- Over-Charging
- Over-Discharging
- High Current Charging
- Nail penetration
- Crush
- External Short

Causing or Energizing Internal Events or Exothermic Reactions
- Lithium Plating
- Decompositions
- Internal Short Circuit
- Electrochemical Reactions

If Heating-Rate exceeds Dissipation-Rate

Thermal Runaway
- Leak
- Smoke
- Gas Venting
- Flames
- Rapid Disassembly
Preventing Thermal Runaway

- Use a cathode where oxygen is not released (LiFePO$_4$ cathode from A123)
  - However, note that temperature of the cell can still increase

- Move away from a material that forms an SEI on the anode.
  - Anodes do exist that have this feature, but they also have a low voltage (Li$_4$Ti$_5$O$_{12}$ from Altair).

- Find a way to provide a overcharge protection similar to lead-acid and Ni-MH cells
  - Attempts are being made to find additives, or redox shuttles, that oxidize on the cathode on overcharge, and reduce on the anode.
  - However, as of today no ideal shuttle mechanism has been found.
Electronic Control

- For Safety
- For Long Life
- For State Of Charge Knowledge
- Daniel Forbes will discuss
Single-Cell Control Circuit Verification

STW 4102 Integrated Circuit for Lithium Ion Cells

Daniel Forbes
Objectives

- Experiment with charging and discharging a lithium ion battery
- Research available devices
- Test device to verify operation and learn about cells
- Provide battery lab with simple means to cycle battery while gathering data
Approach

- Surveyed control strategies / available ICs
- Selected control IC
- Designed a test circuit
- Fabricated test board
- Obtained sample cells
- Designed and executed test plan
- Compiled gathered data into graphs for analysis
Hardware:
STw4102 Charger and Gas Gauge
Hardware:
Complete Demonstration Board

- Power Switch
- Power Input 4.5 V – 16 V
- STw4102 Eval. Board
- RS-232 Serial Port
- Discharge Resistor (4.7 Ω)
- Buttons and LEDs
- Battery Connection
Hardware

Expected Constant-Current Constant-Voltage (CCCV) Charge Curves

Sample Test Cell: 750 mAh, 3.7 V
Results
Charging (mostly CV)
Results
Charging (mostly CV)
Results

Discharging Through a 4.7 Ω Resistor

![Graph showing discharge and voltage over samples.](image-url)
Conclusions

• STw4102 appears to operate as advertised, providing charging and gas gauging

• Problems encountered
  – I²C communication debugging
  – PCB quality
  – Loose connection or bad STw4102 demo. board

• Tested test equipment as well as cell

• Tool for battery lab for future use
Recommendation for further work

• Expand system to work with multiple cells
• Build a pack and instrument each cell
• Some fallbacks of STw4102
  – 32 kHz input needed
  – Limited to 914 mAh cell maximum
  – Alternative: TI BQ27541
    • Offers more features (6000 mAh limit, temperature, time-to-empty)
    • Doesn’t integrate charger, separate IC required
• Fix experimental problems (new boards on the way, testing daughter board)
• Automate testing (build a cycler) to increase cell data acquisition speed
Tesla Roadster

uncompromised design, performance, and technology

- 0-60 mph in 3.9 seconds
- 236-mile range
- 2x more efficient than a hybrid
Interesting Sites

Electropaedia
http://www.mpoweruk.com/index.htm

Wikipedia
http://en.wikipedia.org/wiki/Lithium-ion_battery

The Battery University
http://www.batteryuniversity.com/index.htm

Books


**Mathematical Models of John Newman (UC Berkeley)**

Supplementary Material

- Cost
- Market Growth
- Advanced Chemistries
Cost

For consumer electronics, energy and cost are the biggest drivers.
Advanced Chemistries

Equilibrium Potential of a Few Cathodes

Electrolyte oxidation

Cathodes have different voltage, different capacity

Higher the voltage, or higher the capacity, more energy in the cell
Thermal Runway in Li-ion Cells

Stage 1
- Initial thermal runaway/ramp regime
- Separator Melt

Stage 2
- Cell venting
- Cell runaway and explosive decomposition

Stage 3
- Cell runaway and explosive decomposition
- Duration: 2.2 min
## Biomedical Applications

<table>
<thead>
<tr>
<th>Biomedical Devices</th>
<th>Applications</th>
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</thead>
<tbody>
<tr>
<td>Cardiac Pacemakers</td>
<td>Conduction disorders</td>
</tr>
<tr>
<td>Cardiac Defibrillators</td>
<td>Ventricular and atrial tachyarrhythmia and fibrillation</td>
</tr>
<tr>
<td>Muscle Stimulators</td>
<td>Incontinence</td>
</tr>
<tr>
<td>Neurological Stimulators</td>
<td>Essential tremors (Parkinsons disease)</td>
</tr>
<tr>
<td>Cochlear Implants</td>
<td>Hearing disorders</td>
</tr>
<tr>
<td>Monitoring Devices</td>
<td>Synapse, Seizures</td>
</tr>
<tr>
<td>Drug Pumps</td>
<td>Pain caused by cancer and injury</td>
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<td></td>
<td>Diabetes (insulin pumps)</td>
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<tr>
<td></td>
<td>Spasticity (intrathecal baclofen pumps)</td>
</tr>
<tr>
<td>Left Ventricle Assist Devices</td>
<td>Heart failure — bridge to transplant or recovery</td>
</tr>
</tbody>
</table>
### Candidate Anodes

<table>
<thead>
<tr>
<th>Anode Material</th>
<th>Average Voltage</th>
<th>Gravimetric Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (LiC₆)</td>
<td>0.1-0.2 V</td>
<td>372 mA·h/g</td>
</tr>
<tr>
<td>Hard Carbon (LiC₆)</td>
<td>? V</td>
<td>? mA·h/g</td>
</tr>
<tr>
<td>Titanate (Li₄Ti₅O₁₂)</td>
<td>1-2 V</td>
<td>160 mA·h/g</td>
</tr>
<tr>
<td>Si (Li₄.₄Si)</td>
<td>0.5-1 V</td>
<td>4212 mA·h/g</td>
</tr>
<tr>
<td>Ge (Li₄.₄Ge)</td>
<td>0.7-1.2 V</td>
<td>1624 mA·h/g</td>
</tr>
</tbody>
</table>
# Candidate Cathodes

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>Average Voltage</th>
<th>Gravimetric Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>3.7 V</td>
<td>140 mA·h/g</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>4.0 V</td>
<td>100 mA·h/g</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>3.5 V</td>
<td>180 mA·h/g</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>3.3 V</td>
<td>150 mA·h/g</td>
</tr>
<tr>
<td>Li$_2$FePO$_4$F</td>
<td>3.6 V</td>
<td>115 mA·h/g</td>
</tr>
<tr>
<td>LiCo$<em>{1/3}$Ni$</em>{1/3}$Mn$_{1/3}$O$_2$</td>
<td>3.6 V</td>
<td>160 mA·h/g</td>
</tr>
<tr>
<td>Li(Li$<em>{a}$Ni$</em>{x}$Mn$_{y}$Co$_z$)O$_2$</td>
<td>4.2 V</td>
<td>220 mA·h/g</td>
</tr>
</tbody>
</table>
Fig. 1: Comparison of conductivity of 4 different Li-salts
(1 M Li-salt in EC:DMC 50:50 wt%)