“Batteries 101” overview of battery technologies, markets, and recycling

Robert Spotnitz, President, Battery Design LLC
Public Workshop on Lead-acid Batteries and Alternatives
9:30 – 10:00 am Monday, November 6, 2017
CalEPA Headquarters, Pacific Time Klamath Room
1001 I Street, Sacramento, CA 95814
### Electrochemical Series

[http://www.glogster.com/nanospecs/electrochemical-series/g-6lkta0gu7ju9io54qu4q8a0](http://www.glogster.com/nanospecs/electrochemical-series/g-6lkta0gu7ju9io54qu4q8a0)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrode reaction</th>
<th>$E^0/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$Au^{3+} + 3e^- \rightleftharpoons Au$</td>
<td>+1.43</td>
</tr>
<tr>
<td>Ag</td>
<td>$Ag^+ + e^- \rightleftharpoons Ag$</td>
<td>+0.80</td>
</tr>
<tr>
<td>Cu</td>
<td>$Cu^{2+} + 2e^- \rightleftharpoons Cu$</td>
<td>+0.34</td>
</tr>
<tr>
<td>H</td>
<td>$H^+ + e^- \rightleftharpoons H$</td>
<td>0</td>
</tr>
<tr>
<td>Pb</td>
<td>$Pb^{2+} + 2e^- \rightleftharpoons Pb$</td>
<td>−0.13</td>
</tr>
<tr>
<td>Sn</td>
<td>$Sn^{2+} + 2e^- \rightleftharpoons Sn$</td>
<td>−0.14</td>
</tr>
<tr>
<td>Ni</td>
<td>$Ni^{2+} + 2e^- \rightleftharpoons Ni$</td>
<td>−0.25</td>
</tr>
<tr>
<td>Cd</td>
<td>$Cd^{2+} + 2e^- \rightleftharpoons Cd$</td>
<td>−0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>$Fe^{2+} + 2e^- \rightleftharpoons Fe$</td>
<td>−0.44</td>
</tr>
<tr>
<td>Zn</td>
<td>$Zn^{2+} + 2e^- \rightleftharpoons Zn$</td>
<td>−0.76</td>
</tr>
<tr>
<td>Ti</td>
<td>$Ti^{2+} + 2e^- \rightleftharpoons Ti$</td>
<td>−1.63</td>
</tr>
<tr>
<td>Al</td>
<td>$Al^{3+} + 3e^- \rightleftharpoons Al$</td>
<td>−1.66</td>
</tr>
<tr>
<td>Mg</td>
<td>$Mg^{2+} + 2e^- \rightleftharpoons Mg$</td>
<td>−2.37</td>
</tr>
<tr>
<td>Na</td>
<td>$Na^+ + e^- \rightleftharpoons Na$</td>
<td>−2.71</td>
</tr>
<tr>
<td>K</td>
<td>$K^+ + e^- \rightleftharpoons K$</td>
<td>−2.93</td>
</tr>
<tr>
<td>Li</td>
<td>$Li^+ + e^- \rightleftharpoons Li$</td>
<td>−3.05</td>
</tr>
</tbody>
</table>

Electrochemistry

$$E = \phi_1 - \phi_2$$

$i_0$ exchange current density
What is a battery?

- A battery or “galvanic cell” converts chemical energy to electrochemical energy using **at least one of reactant stored in a cell**.
- A fuel cell converts chemical energy to electrochemical energy using reactants stored externally.
- A capacitor stores and releases electrical energy using double-layer charge separation or a pseudo-capacitive effect such as surface adsorption, reaction or bulk intercalation.

March 1800, "... *In this manner I continue coupling a plate of silver with one of zinc, and always in the same order, that is to say, the silver below and the zinc above it, or vice versa, according as I have begun, and interpose between each of those couples a moistened disk.* ".

Volta’s pile
Ag/Zn (1800)
Battery consists of one or more cells
Cell consists of a pair of electrodes and an ion conductor
Electrode consists of active material, current collector, and tab
Positive electrode is called “cathode”
Negative electrode is called “anode”
Package, separator, insulators, etc.
In 1866, Georges Leclanché invented a battery that consisted of a zinc anode and a manganese dioxide cathode wrapped in a porous material, dipped in a jar of ammonium chloride solution. The manganese dioxide cathode had a little carbon mixed into it as well, which improved conductivity and absorption.[7] It provided a voltage of 1.4 volts.[8] This cell achieved very quick success in telegraphy, signaling and electric bell work.

https://en.wikipedia.org/wiki/History_of_the_battery

The use of porous electrode provides power and energy.
Alkaline Chemistry

Dry cell invented in 1866 by G. Leclanché (1839-1882).


\[
\begin{align*}
\text{MnO}_2 + \text{H}_2\text{O} + e^- & \rightarrow \text{MnOOH} + \text{OH}^- \\
3\text{MnOOH} + e^- & \rightarrow \text{Mn}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \\
\text{Zn} + 2\text{OH}^- & \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^- \quad \text{(II)} \\
\text{Zn} + 4\text{OH}^- & \rightarrow \text{Zn(OH)}_4^{2-} + 2e^- \quad \text{(III)}
\end{align*}
\]

Zincate can migrate into separator and precipitate.
Lead-Acid Battery

In 1859, Gaston Planté invented the lead–acid battery, the first-ever battery that could be recharged by passing a reverse current through it. A lead acid cell consists of a lead anode and a lead dioxide cathode immersed in sulphuric acid.

Planté’s first model consisted of two lead sheets separated by rubber strips and rolled into a spiral.[6] His batteries were first used to power the lights in train carriages while stopped at a station.

https://en.wikipedia.org/wiki/History_of_the_battery

In 1880, Faure patented a method of coating lead plates with a paste of lead oxides, sulphuric acid and water, which was then cured by being gently warmed in a humid atmosphere. The curing process caused the paste to change to a mixture of lead sulphates which adhered to the lead plate. During charging the cured paste was converted into electrochemically active material (the "active mass") and gave a substantial increase in capacity compared with Planté’s battery.[5] This was a significant breakthrough that led to the industrial manufacture of lead-acid batteries, as now used for starting motor cars.

https://en.wikipedia.org/wiki/Camille_Alphonse_Faure

The porous electrode is one of the most important innovations in battery technology.
Lead-Acid Batteries

- 1859, invented by Gaston Planté
- Key characteristics
  - low-cost
  - must be stored at full state of charge
  - best for shallow discharge cycles
  - poor high-rate charge acceptance
  - good low-temperature performance
  - high voltage (~2 V)

\[
2\text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 4\text{H}^+ + 4\text{e}^- \\
\text{PbO}_2 + 4\text{e}^- + 2\text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} + 2\text{SO}_4^{2-} \\
\text{PbO}_2 + 2\text{Pb} + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{PbSO}_4 + 2\text{H}_2\text{O}
\]

Major innovation: Gas recombination (1947)
- Flooded
- Valve Regulated Lead Acid (VRLA) or SLA
Major application: car battery for Starting Lighting Ignition (SLI)

http://www.lead-battery-recycling.com/the-history-of-battery.html
The lithium-ion intercalation battery is becoming the dominant battery technology.
Li-Ion Batteries

• Invented in 1985 by Akira Yoshino (Asahi Kasei Corp.)
• Commercially introduced in 1991 (Sony)
• Key advantages
  • Long cycle life
  • Good calendar life
  • Good Wh/kg, Wh/liter
  • High discharge rate
  • High voltage ~3.7 average
  • Low self discharge

\[ LiC_6 \rightleftharpoons C_6 + Li^+ + e^- \]
\[ Li^+ + e^- + 2Li_{0.5}CoO_2 \rightleftharpoons 2LiCoO_2 \]
\[ LiC_6 + 2Li_{0.5}CoO_2 \rightleftharpoons 2LiCoO_2 + C_6 \]

Downsides are safety (flammability of organic electrolyte, overcharge and internal short circuit) and cost.

http://www.mst.or.jp/prize/english/winners/material/material2011_en.html

Robotics
Grid storage
Electric vehicles
Industrial (forklifts, etc.)
Tablets
Cellphones
Laptops
Camcorders
Li-Ion + Pb-acid + primary MnO₂/Zn are 91% (=46+16+19+10) of battery market.
Worldwide Rechargeable Battery Market 1990-2016 5% average growth per year

SLI: Start light and ignition batteries for cars, truck, moto, boat etc...
PORTABLE: consumer electronics (cellular, portable PCs, tablets, Camera, ...), data collection & handy terminals,
POWER Tools: power tools but also gardening tools

Pb-acid is largest market ($) for rechargeable batteries
Lithium-ion is fastest growing chemistry.
Abundance of Elements in Earth’s Crust

Raw materials for lithium-ion batteries are relatively plentiful.
# Typical properties of major battery chemistries

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemistry</th>
<th>Size mm</th>
<th>Capacity Ah</th>
<th>% Capacity retained after 6 months</th>
<th>Specific Energy Wh/kg</th>
<th>Energy Density Wh/l</th>
<th>Discharge time h</th>
<th>Retail Price $</th>
<th>Use</th>
<th>Retail Price, $/Wh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>Alkaline</td>
<td>AA (14.5 dia x 50.5 tall)</td>
<td>2.85</td>
<td>100%</td>
<td>145</td>
<td>410</td>
<td>50</td>
<td>0.8</td>
<td>Toys</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Zinc-Air</td>
<td>Button (7.8 dia x 3.6 tall)</td>
<td>0.13</td>
<td>100%</td>
<td>360</td>
<td>1110</td>
<td>300</td>
<td>0.5</td>
<td>Hearing aid</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>Li/MnO2</td>
<td>2/3 A (17 dia x 27 tall)</td>
<td>1.3</td>
<td>100%</td>
<td>200</td>
<td>315</td>
<td>1</td>
<td>5</td>
<td>Camera</td>
<td>1.28</td>
</tr>
<tr>
<td>Secondary</td>
<td>Pb acid</td>
<td>273 x 173 x 229</td>
<td>44</td>
<td>50%</td>
<td>29</td>
<td>52</td>
<td>6</td>
<td>68</td>
<td>Car</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Ni/Cd</td>
<td>AA</td>
<td>1</td>
<td>70%</td>
<td>40</td>
<td>120</td>
<td>0.1</td>
<td>2.5</td>
<td>Power tool</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Ni/MH</td>
<td>AA</td>
<td>1.7</td>
<td>80% (3 months)</td>
<td>67</td>
<td>220</td>
<td>1</td>
<td>2.8</td>
<td>Camcorder</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>Li-Ion</td>
<td>18650 (18 dia x 65 tall)</td>
<td>1.8</td>
<td>&gt;90%</td>
<td>100-250</td>
<td>330-750</td>
<td>2</td>
<td>2.5</td>
<td>Cellphone</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Li-ion is superior to Alkaline and Pb acid on nearly every metric except **price**.
Audi claims to be buying batteries at ~$114/kWh for its upcoming electric cars, says CTO

Fred Lambert - Jun. 28th 2017 12:14 pm ET  @FredericLambert

https://electrek.co/2017/06/28/audi-electric-car-battery-cost/

BATTERY CELL COST
ABLE TO ACHIEVE LOWER COSTS EARLIER WITH MUCH LESS CAPITAL AND VOLUME DEPENDENCY

LG Chem “Ticked Off” With GM For Disclosing $145/kWh Battery Cell Pricing – Video
Projected Battery Cell Cost Glide Path

Sealed Lead Acid (SLA)

- SLA is simple, dependable, robust, and inexpensive, and can be used in a wide range of temperature environments.
- The batteries must be stored full state-of-charge (SOC), and they don’t lend themselves to fast charging.
- The flip side to the charge constraints is that SLA batteries can use simple float or trickle chargers.
- SLA batteries are very heavy; their gravimetric energy density is very low.
- Cycle life is usually 200 to 300 cycles, but even a “deep cycle” SLA is damaged by repeated full discharges, causing cycle life to be as low as 50 cycles.
- The sloped discharge curve enables SOC measurement with simple voltage monitoring.
- Lighter & Smaller - More portability
  - Half the weight of SLA
  - Half the volume of SLA
  - 2x energy density per unit weight
- Longer Shelf Life
  - Replacement every 5-7 year vs. 18 months - 2 years with SLA
- Temperature Range
  - No degredation at high temperatures
  - No air conditioning required
- Efficiency
  - Faster recharge time
  - 20-25% higher turnaround charge efficiency
- Cycling
  - More discharge cycles (5-10x)
  - Full depth of discharge capability vs. only 50% for SLA
- State of Charge & Remote Monitoring
  - Can be easily & remotely monitored
- Service
  - No servicing or watering required
  - No need for hydrogen gas extraction provisions
Conventional System
Lead Acid Battery
Replacement

Generator
Maintenance
Refueling

New LiB Solution
Li-ion

Outstanding Cyclic life ⇒ Less Replacement

Excellent Charge Acceptance
⇒ Fully charged with a limited power
⇒ Possible to eliminate generators.

Remote Monitoring
⇒ Less frequency of sending engineers to sites.

Cost Reduction
Waste Prevention Information Exchange

Batteries

Also see Fluorescent Lamps and Tubes and Universal Waste.

All batteries are considered hazardous waste in California when they are discarded. This includes all batteries of sizes AAA, AA, C, D, button cell, 9 Volt, and all other batteries, both rechargeable and single use. **All batteries must be** recycled, or taken to a household hazardous waste disposal facility, a universal waste handler (e.g., storage facility or broker), or an authorized recycling facility.
What are the issues with battery recycling?

Posted by Cindy Miller on Tue, Nov 25, 2014 7:30:00 AM

Batteries, like many other types of electronic waste, contain harmful chemicals that can wreak havoc on the environment as well as being hazardous to people. A variety of materials are used to make batteries, some more dangerous than others.

Lithium-ion (Li-ion) is the fastest growing type of battery, and is often found in notebook computers and mobile phones. Nickel-cadmium (Ni-cad) batteries have been used heavily in photography equipment and portable electronics. Lead-acid batteries are typically reserved for car batteries because of their large power-to-weight ratio and low cost.

Alkaline batteries are the single-use AA, AAA, and C batteries often utilized in household electronics. Alkaline batteries account for 80% of manufactured batteries in the US and over 10 billion individual units produced worldwide. An important difference between these single-use alkaline batteries and the majority of other types of e-waste is that these batteries are not rechargeable and are rarely recycled, so they often end up in a landfill.

Unlike single-use batteries, rechargeable batteries typically have a very high rate of recycling. Most rechargeable batteries are recycled along with the device that contained them at the end of their usable life.

Lead-Acid batteries are the most recycled consumer product. (Courtesy of Battery Council International)
New Lead-Acid Battery Fees
Beginning April 1, 2017

Effective April 1, 2017, the Act imposes a $1.00 California battery fee on the purchase of a replacement lead-acid battery and a $1.00 manufacturer battery fee on the sale of a lead-acid battery to a dealer, wholesaler, distributor or other person in California. On April 1, 2022, the California battery fee will increase to $2.00 and the manufacturer battery fee will no longer be due. The California State Board of Equalization (BOE) is responsible for the administration of these new fees in cooperation with the Department of Toxic Substances Control (DTSC).

Exide lead contamination

From Wikipedia, the free encyclopedia

The Exide lead contamination, in southeast Los Angeles County, California, United States, came from a battery recycling plant that emitted lead, arsenic and other dangerous pollutants over decades that contaminated as many as 10,000 homes in half a dozen working-class, Latino communities near the plant. Exide Technologies, owner of the lead-acid battery smelter located in Vernon, agreed in 2015 to close the facility while the massive cleanup of the contaminated soil will take years and cost hundreds of millions of dollars.\[1\] The residents have
Lead-battery recycling has moved to Mexico

Originally published March 25, 2013 at 9:35 pm Updated March 25, 2013 at 11:46 pm

https://www.seattletimes.com/nation-world/lead-battery-recycling-has-moved-to-mexico/

http://www.worstpolluted.org/projects_reports/display/90
What is Lead Poisoning?

- Is a medical condition caused by increased levels of heavy metal lead in the body
- Lead is known to be a cumulative toxicant
- Children and pregnant women are particularly vulnerable
- Major health risk and challenge in most developing countries and CEITs

Sources of Lead Poisoning in Developing Countries

- Lead mining and smelting
- Battery recycling
- Leaded gasoline
- Paint - Continuous use of lead in paint irrespective of safer alternatives known to be globally available.
- Traditional medicines
- Toys
- Discarded electronic devices

Above are also main source of global lead poisoning

Countries with Economies in Transition (CEITs)

“Issues of Lead Poisoning and Developing Countries”, Babajide Alo (UNIVERSITY OF LAGOS, AKOKA, LAGOS, NIGERIA)
### Composition/Value of Spent Lithium-Ion Batteries (LIBs)

Typical metal composition of spent mixed LIBs powder (wt.%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_2$O$_3$</td>
<td>46.72</td>
</tr>
<tr>
<td>MnO</td>
<td>24.94</td>
</tr>
<tr>
<td>CuO</td>
<td>4.11</td>
</tr>
<tr>
<td>Li</td>
<td>2.67</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.39</td>
</tr>
<tr>
<td>F</td>
<td>0.75</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.46</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.27</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.25</td>
</tr>
<tr>
<td>CaO</td>
<td>0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.11</td>
</tr>
<tr>
<td>NiO</td>
<td>0.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>0.07</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.04</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
</tr>
</tbody>
</table>

#### Table 1: LIB cathode compounds and their market values

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value (US$ per kg)</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>37.00</td>
<td>[13]</td>
</tr>
<tr>
<td>LiCO$_3$</td>
<td>6.40</td>
<td>[13]</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>18.30</td>
<td>[14]</td>
</tr>
<tr>
<td>Li$_3$Ni$_2$Co$_3$Mn$<em>4$O$</em>{16}$</td>
<td>10.80</td>
<td>[14]</td>
</tr>
<tr>
<td>LiMnO$_2$</td>
<td>3.70</td>
<td>[14]</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>1.50</td>
<td>[14]</td>
</tr>
</tbody>
</table>


Recycling Process for Lithium-Ion: Smelter

Co, Ni, and Cu recovered. Li, Al, Mn go to slag which has some application as concrete additive.

Fig. 1: Umicore process for 1 ton of lithium ion and Ni-Mh batteries

What’s next in lithium-ion for next 5 years?

➢ Continued growth! Especially automotive and industrial markets.

➢ Improved Safety
  • Electrode coatings
  • More thermally stable separators
  • Composite electrolytes (Blend with solids to reduce solvent content)

➢ Higher energy cells
  • Higher voltage cells (LiCoO2 > 4.4 V, NMC 811, 4.4 V)
  • Higher capacity cells (silicon blends with graphite)
Lithium-ion is well poised to be dominant battery chemistry

- Industrial applications such as UPS, forklifts, are switching to lithium ion
- Some cars eliminating lead acid (Hyundai Ioniq)
- Rechargeable lithium-ion replacing primary cells in some toys
- Li-ion share increasing in electric bike market in China

Over time, lithium-ion battery costs will decline while regulation may drive up costs of lead acid and primary cells.

Impact of Li-ion recycling on costs?
Summary

• Major battery chemistries are alkaline (disposable), lead-acid and lithium-ion (rechargeable).

• Lithium-ion chemistries offer advantages over traditional alkaline and lead-acid chemistries in terms of performance but have cost and safety issues.

• Large scale production of lithium-ion is driving down costs; markets for lithium-ion continue to grow.

• Total cost of ownership analysis indicates advantage for lithium-ion over lead acid for some applications.

• Alkaline cells typically go to landfills, while lead-acid is mostly recycled. Regulations on lead recycling have driven many operations out of highly developed countries.

• Recycling of lithium-ion still immature; will recycling reduce lithium-ion cost even further?
Back-up
Lithium price per metric ton
<table>
<thead>
<tr>
<th>Battery attribute</th>
<th>VRLA</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry</td>
<td>Lead-acid</td>
<td>LMO/NMC</td>
</tr>
<tr>
<td>Rated power capacity</td>
<td>1 MW</td>
<td>1 MW</td>
</tr>
<tr>
<td>Runtime at 25°C (77°F)</td>
<td>6 minutes</td>
<td>6 minutes</td>
</tr>
<tr>
<td>Calendar life at 25°C (77°F)</td>
<td>5 years</td>
<td>17 years</td>
</tr>
<tr>
<td>Battery service life at 25°C (77°F)</td>
<td>4 years</td>
<td>12 years</td>
</tr>
<tr>
<td>Battery footprint</td>
<td>5.4 m² (59 ft²)</td>
<td>2.2 m² (23 ft²)</td>
</tr>
<tr>
<td>Battery weight</td>
<td>11,340 kg (25,000 lbs)</td>
<td>2,767 kg (6,100 lbs)</td>
</tr>
<tr>
<td>Fixed losses from trickle charging (as % of rated UPS capacity)</td>
<td>0.2%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Battery materials cost</td>
<td>$0.06/W</td>
<td>$0.12/W</td>
</tr>
<tr>
<td>Battery management system cost</td>
<td>Incl. in battery cost</td>
<td>Incl. in battery cost</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TCO</th>
<th>VRLA</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital expense</td>
<td>$72,549</td>
<td>$132,366</td>
</tr>
<tr>
<td>Operational expense</td>
<td>$236,706</td>
<td>$55,762</td>
</tr>
<tr>
<td>TOTAL</td>
<td>$309,255</td>
<td>$188,128</td>
</tr>
</tbody>
</table>