Advanced Battery Technologies

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- **Principal of EnergyPlex Corporation**
  - consulting services for power systems such as batteries and fuel cells
  - more than 30 years of experience:
    - executing research, developing products, and managing manufacturing
    - battery charging, monitoring, control electronics
    - applications engineering
  - member of the Electrochemical Society
    - chairman of the Nanotechnology Committee
    - past member of the Board of Directors
  - published “***Advances in Lithium-Ion Batteries***”
  - affiliate Professor of Chemical Engineering at the University of Washington

Where have we been?

- **Lead-Acid Batteries**
  - Invented in 1859
  - Energy density: 30-40 Wh/kg and 60-75 Wh/L
  - Power density: 180 – 2000 W/kg
  - Different construction and chemistry variants depending on the application
  - Applications:
    - Power back-up, power conditioning, and grid energy storage
    - Motive power and starting-lighting-ignition (SLI)

Where have we been?

- **Nickel-Cadmium Batteries**
  - Invented in 1899, patented in the US by Edison in 1906
  - Energy density: 40-60 Wh/kg and 150 Wh/L
  - Power density: 150 to 1500 W/kg
  - Different construction variants depending on the application. Low impedance.
  - Being legislated out of existence due to toxicity of Cd
  - Applications:
    - Radio-controlled vehicles, power tools, aircraft starting

Where have we been?

- **Nickel-Metalhydride Batteries**
  - The first consumer grade NiMH batteries for smaller applications appeared on the market in 1989 as a variation of the 1970's nickel hydrogen battery
  - Energy density: 30 to 80 Wh/kg and 140 to 240 Wh/L
  - Power density: 250 to 1000 W/kg
  - Applications:
    - Radio-controlled vehicles, toys, power tools, Hybrid Electric Vehicles (HEV) and Plug-in Hybrid Electric Vehicles (PHEV)

Where have we been?

- **Lithium-Cobaltite (C/$LiCoO_2$) Batteries**
  - Concept first proposed at Exxon in the 1970s
  - First commercialized by Sony in 1991
  - Energy density: 160 Wh/kg and 270 to 350 Wh/L
  - Power density: 160 to 2000 W/kg (high power for pulses only)
  - Applications:
    - Most low to moderate consumer, medical, and light industrial electronics

Where are we going?

- **A Lead-Acid Revival**
  - New materials may revolutionize this chemistry
- **Flow Batteries**
  - Making use of redox couples
- **A Lithium-Ion Schism**
  - High energy and high power taking separate paths

Get the Lead out!

- **Lead-acid batteries haven't changed much since 1859**
  - The chemistry is well understood
  - Production costs are low
  - Well established recycling infrastructure
- **Heavy-equipment maker Caterpillar, tired of in-field failures**
  - set out on a two-year mission to find a supplier with a better technology
  - having failed—turned to its R&D staff to come up with a better solution

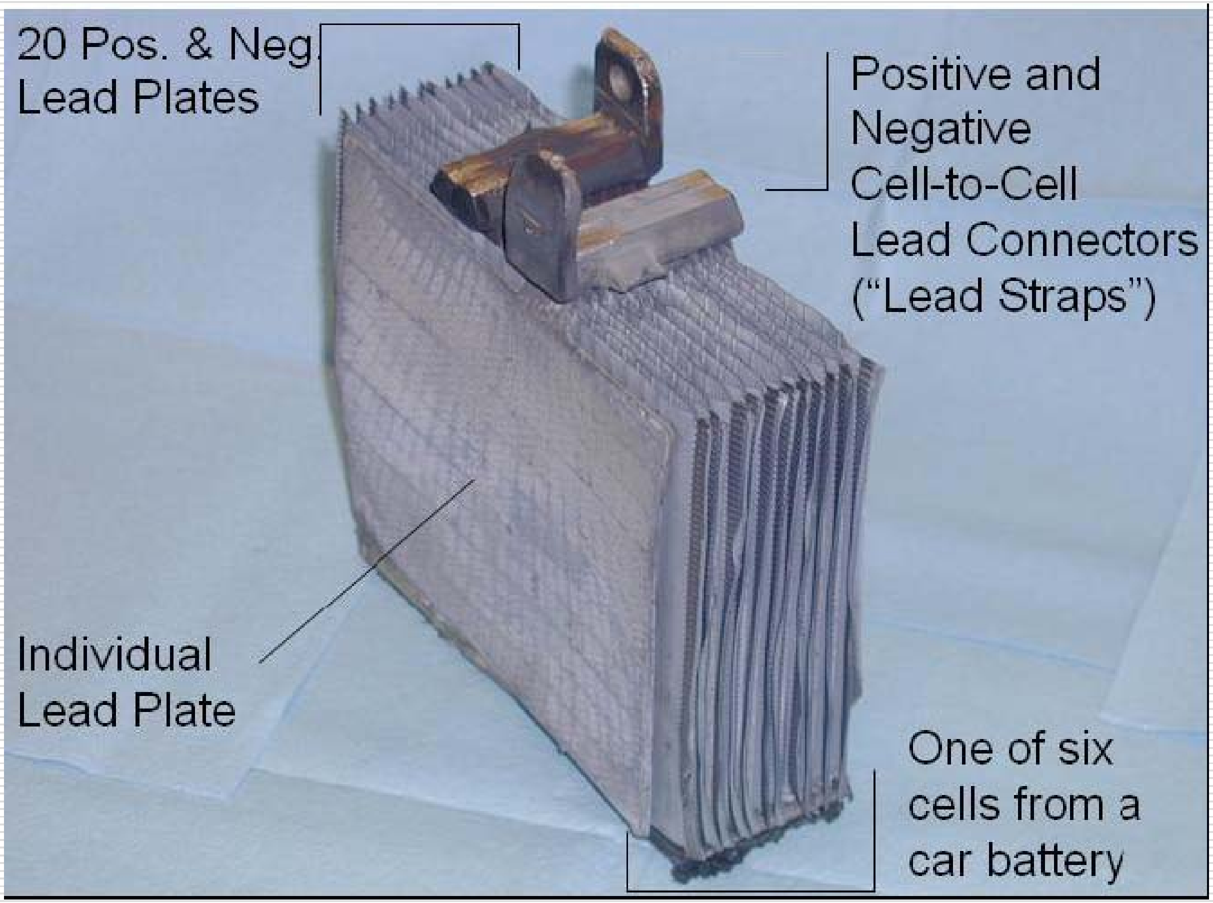
Get the Lead out!

- **Research goals:**
  - Maximize specific energy
  - Maximize the specific power
  - Maximize battery life
  - Do it all at extremely low costs
- **The final point has limited the first three criteria.**
  - improvements in battery current collector (i.e., grid) design and advances in lead-alloys appear to be reaching their limit
- **Conclusion: New materials are needed**

The problem with today's Pb-Acid

- **Both corrosion (on the positive plate) and sulfation (on the negative plate) define two key failure modes of today's lead acid batteries**
  - Accelerates at elevated temperatures or if the battery is left uncharged
- **Cycle life (No of charge/discharge cycles)**
  - Limited by Lead Acid's inability to tolerate discharge below 80% Depth-of-Discharge (DoD)
- **Charge time (8 to 16 hours)**
- **Size and weight**
  - Inefficient power to weight ratio

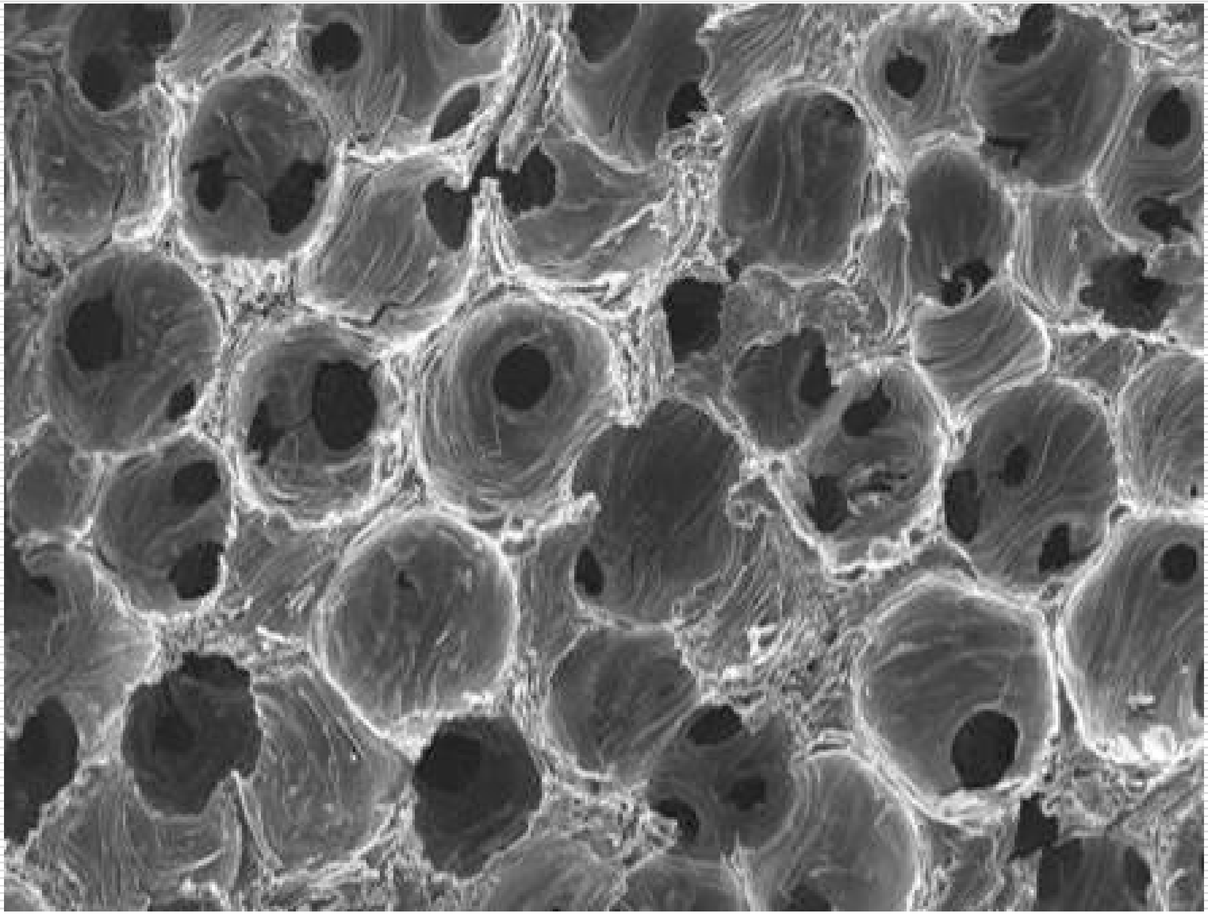
Conventional Lead-Acid SLI cell



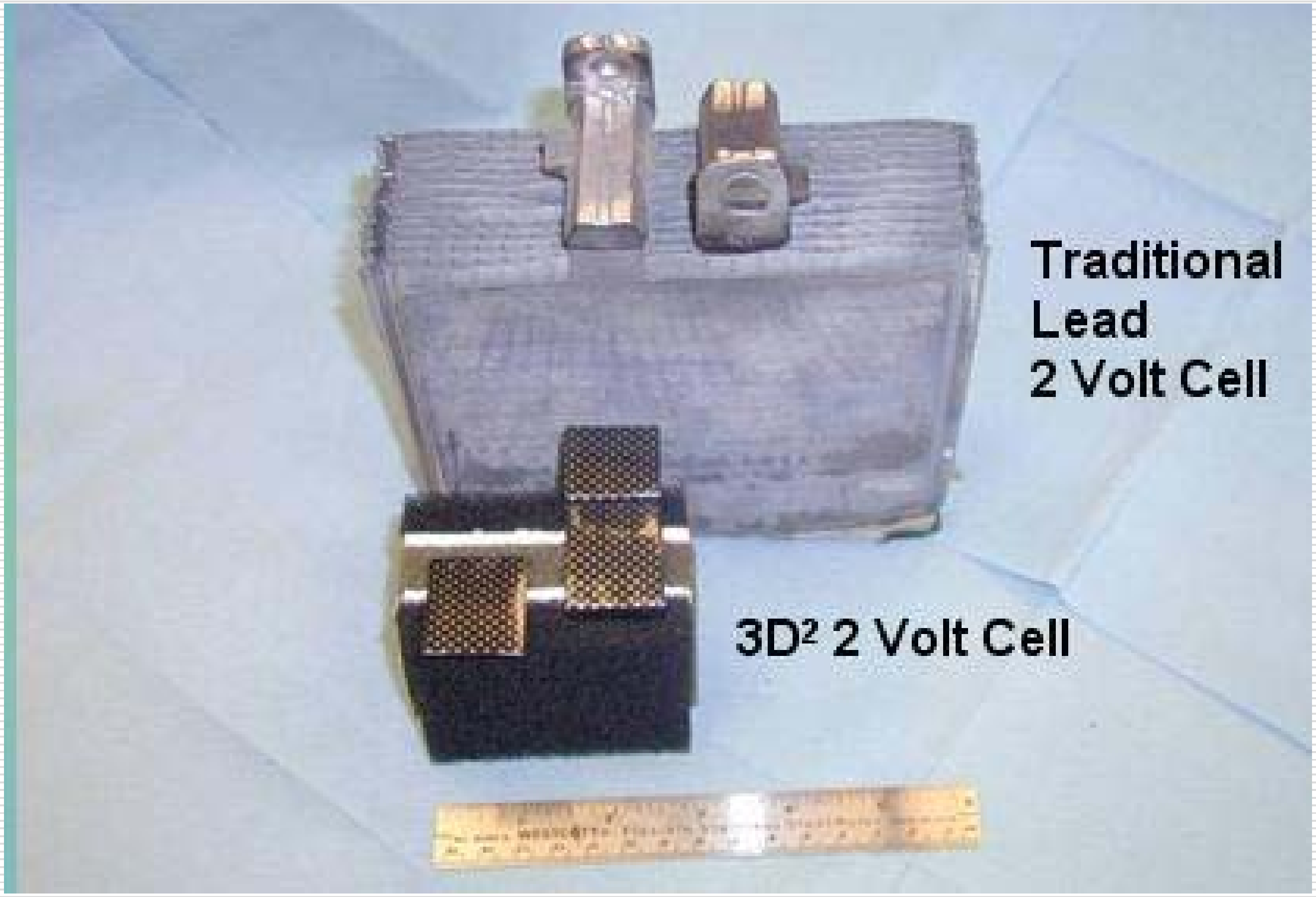
Firefly Energy

- **Caterpillar's spinoff**
- **Much of the lead in the grid structure of conventional batteries can be replaced by a high-strength carbon foam**
  - composite foam "grids" are impregnated with a slurry of lead oxides which are then formed up to the sponge lead and lead dioxide in the normal fashion
- **Higher surface area grid results in:**
  - much-improved active material utilization levels (i.e., from 20-50% up into the range of 70 – 90%)
  - fast-recharge capability

Carbon composite foam



Cell size comparison



Redox Flow Batteries

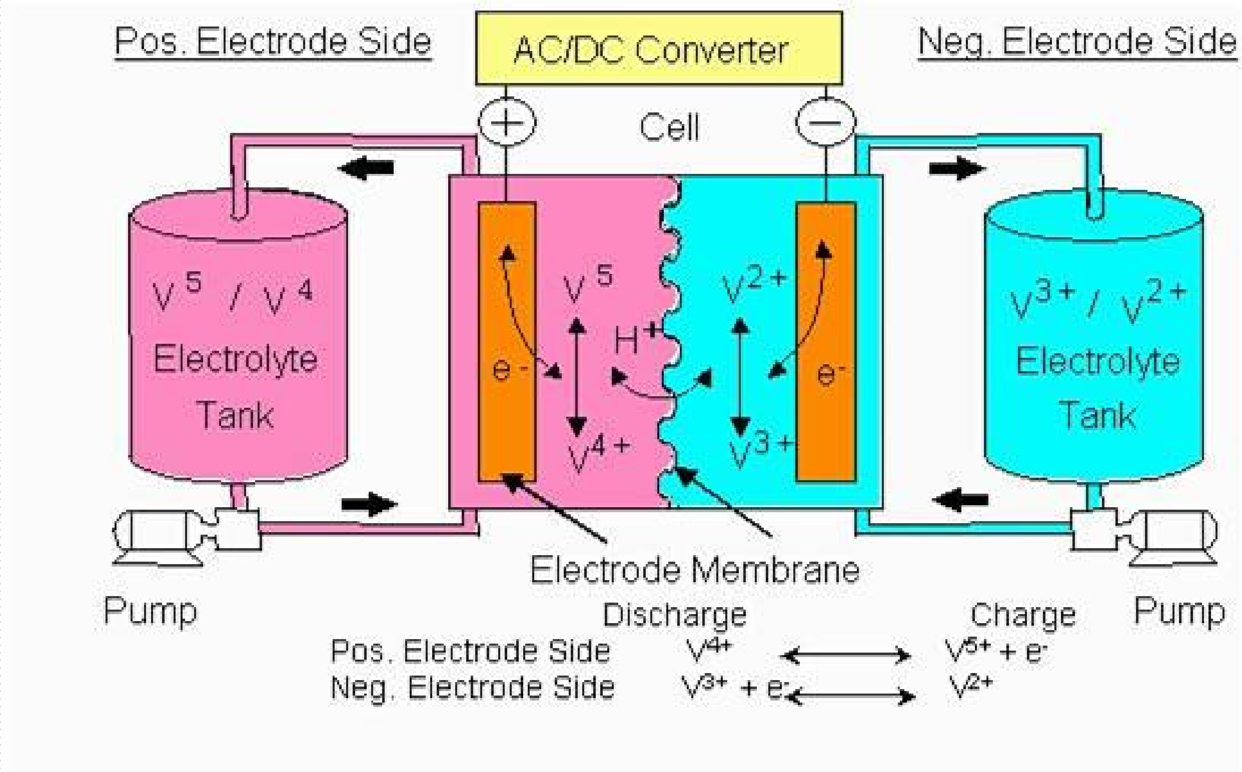
- **The only one of significant interest is the Vanadium Redox Flow battery.**
- **Perceived technical advantages:**
  - High-energy efficiencies: 70% round trip
  - Storage capacity can be easily increased by adding electrolyte
  - Designed for unattended operation with very low maintenance costs
  - Can be discharged and charged >13,000 times (about 18 years) without performance degradation

Redox Flow Batteries

- **Vanadium Redox Batteries (VRB) stores energy by employing Vanadium redox couples V^{2+}/V^{3+} in the negative and V^{4+}/V^{5+} in the positive half-cells of the battery**
  - These are stored in mild sulfuric acid solutions (electrolytes)

- **During the charge/ discharge cycles, H+ ions are exchanged between the two electrolyte tanks through the hydrogen-ion permeable polymer membrane**
  - cell voltage is 1.4-1.6 volts

Schematic Representation of VRB



Adapted from a schematic on Wikipedia.com. Schematic supplied by Sumitomo Electric Industries, Ltd.

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Part of a VRB Installation

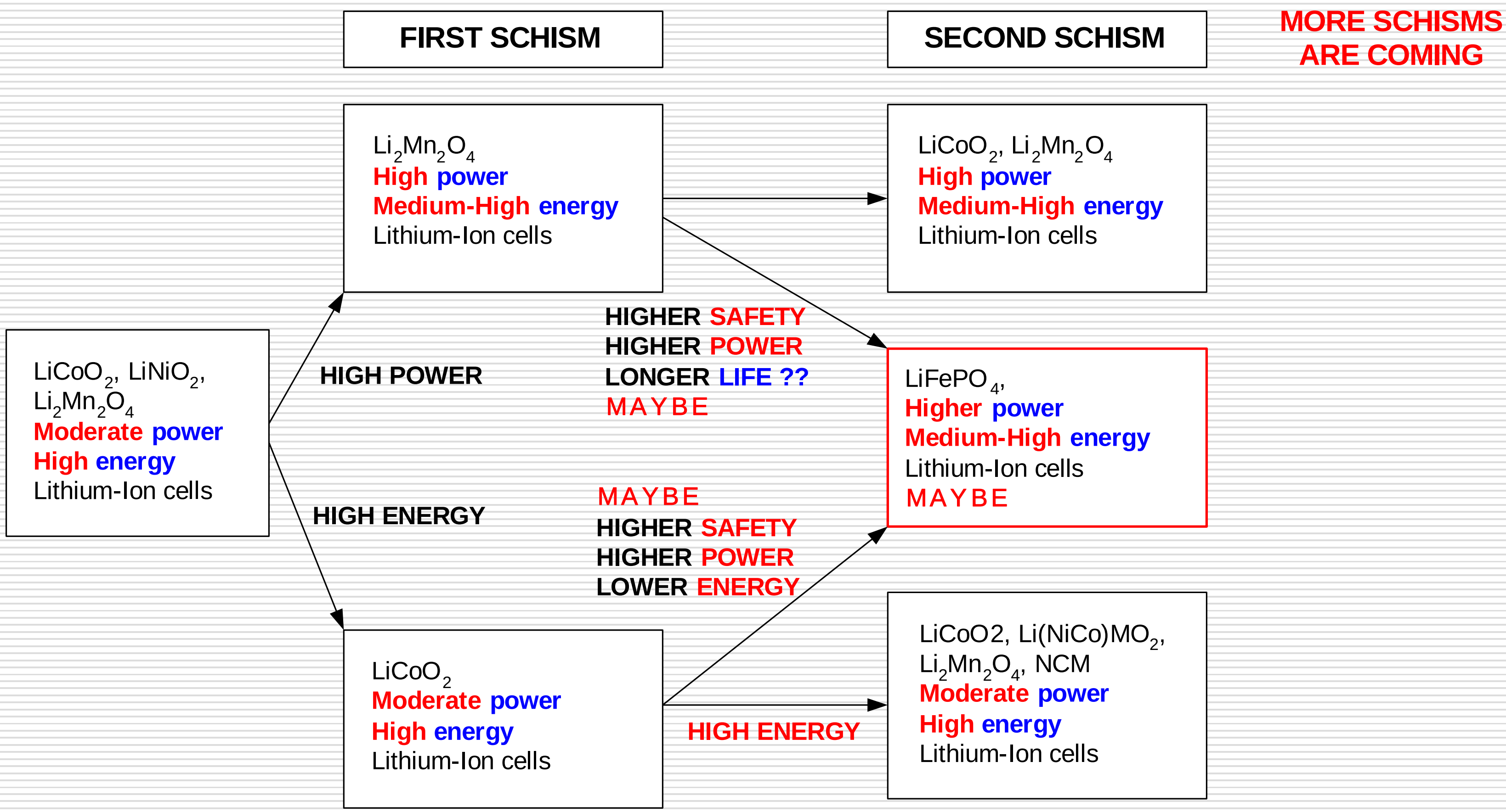
Redox Flow Batteries

- **Like other flow batteries, the power and energy ratings of VRB are independent of each other**
  - power is determined by the size of the electrodes
  - energy content is determined by the size of the electrolyte tanks
- **Shortcomings of VRB**
  - Crossover of electrolyte through membrane
  - Cost is more than 2x of Lead-acid
- **Competing technologies**
  - Polysulfide Bromide Battery (PSB)
  - Zinc Bromine Battery (ZnBr)

A Schism in Lithium-Ion Batteries

- **The driver that initially brought Lithium-Ion batteries to market was the need for higher energy density**
  - Nickel batteries, NiCd and NiMH were still able to provide higher power at a better price
  - By the late 1990s Lithium-Ion, even with their still-then high price relative to NiMH and NiCd, had replaced the Nickel chemistries in most laptops and cell phones in developed countries because of the desire for more energy, even with the increased cost
- **The *first schism* occurred when manufacturers wanted to produce high power Li-Ion batteries**

Schisms in Li-Ion technology



A Schism in Lithium-Ion Batteries

- **Evolution of the Lithium-Ion Battery has created “schisms”, i.e., variants of the cell chemistry or design that allow Lithium-Ion batteries to fill more markets**
  - More changes are likely as new higher energy anode and cathode materials are introduced
  - Sanyo also shows some of their battery development schism with their drivers being safety, capacity, power, and Cobalt reduction

High-rate Lithium-Ion

- **Lithium-Ion chemistries used in high-rate (i.e. high power) cells**
  - Initially $LiCoO_2$ and its derivatives and $LiMn_2O_4$ as cathodes, with Carbon anodes
  - Cell redesigned for current flow and heat management at the expense of energy density
  - Power tools using these chemistries in high-rate applications performed worse than expected
    - overheating and shut-down of tool operation being the major complaint
    - This is largely due to the intrinsic nature of these cathode materials

Next Generation Lithium-Ion

- **The major companies began to research cathodes containing different amounts of Cobalt, Nickel, Manganese and other elements**
  - Goal: impart different properties to the battery including increased capacity and safety, and reduced Cobalt content
- **New cathode formulations:**
  - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (a.k.a. NCA)
  - $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (a.k.a. NMC)
- **New anodes**
  - Si-Li, Sn-Li, Sn-Li-Co alloys
- **Inorganic electrolytes**

Lithium Iron Phosphate - $LiFePO_4$

- **There prime motivation for the initial study of $LiFePO_4$ was the stability of this material**
  - The P-O bond in $LiFePO_4$ is stronger than the Co-O bond in $LiCoO_2$ and its derivatives
  - The perception is that on overcharge or at elevated temperatures, Oxygen will not be released by the cathode and create a safety problem or contribute to irreversible capacity loss for the battery
- **$LiFePO_4$ in the Olivine structure is a semiconductor**
  - MIT scientists doping of the material with M^{3+}/M^{2+} into Li sites, increasing the conductivity by a factor of 10^8 to 10^9

Commercial Viability of $LiFePO_4$

- **The electrochemical viability of $LiFePO_4$ and its doped and coated derivatives depends strongly on the synthetic method used to produce it**
  - Optimization of synthetic methods, particle sizes, dopant, the degree of coating, and the complexity and cost of processing $LiFePO_4$-based electrodes are among the reasons for the delay in commercialization of this technology, not concern about the ownership of the technology.
- **Widespread adoption of batteries based on $LiFePO_4$ will represent a paradigm within the well-established Lithium-Ion industry**
  - The processing of materials to produce $LiFePO_4$ is more complicated than for other Lithium-Ion battery chemistries, and operates at a different voltage

Is There Enough Lithium?

- **Lithium Ion batteries are rapidly becoming the technology of choice for the next generation of Electric Vehicles - Hybrid, Plug In Hybrid and Battery EVs**
  - Analysis of Lithium's geological resource base shows that there is insufficient Lithium available in the Earth's crust to sustain Electric Vehicle manufacture in the volumes required, based solely on Li-Ion batteries
  - Depletion rates would exceed current oil depletion rates and switch dependency from one diminishing resource to another

Is There Enough Lithium?

- **World reserves of Lithium are estimated at 6.4 Million MT (metric tons) with a reserve base of 13.7 Million MT (2006)**
  - At present, batteries consume 21 % of Lithium
- **Today, some 60M to 80M cars are produced each year**
  - Existing Lithium-ion batteries for EVs require about 0.3kg of Lithium metal equivalent per kWh
  - The total amount of Lithium metal required to make 60M PHEVs with a small 5kWh Lithium-ion battery would therefore be 90,000 tons – *nearly 4 times current global Lithium production*

Summary

- **Old Battery chemistries like Lead-acid may find new life with high energy densities and new applications.**
- **Aside from Lithium's technical problems and cost, there may not be enough of it …**
  - *. . .* Unless recycling of Lithium batteries becomes the new source of Lithium
- **Technology changes are happening at a rapid pace**