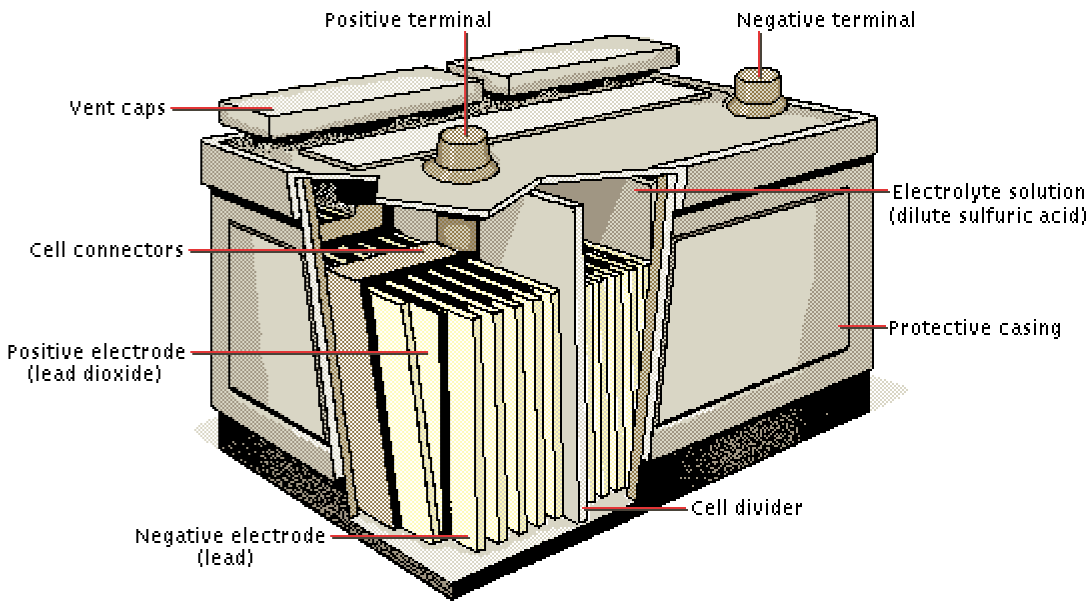
Lecture 9

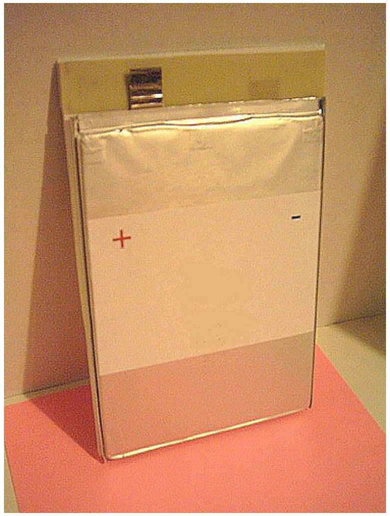
Battery Storage Devices

See online Text, PVCDROM for more detailed discussion

What is a Chemical Battery

A Chemical Battery is simply a device that allows energy to be stored in a chemical form and to be released when needed . Primary batteries only store energy and cannot be recharged. Most PV useful batteries also require that the energy can be "re-charged" by forcing the discharge reaction to be reversed and thus use rechargeable "secondary" batteries.





What is a Chemical Battery

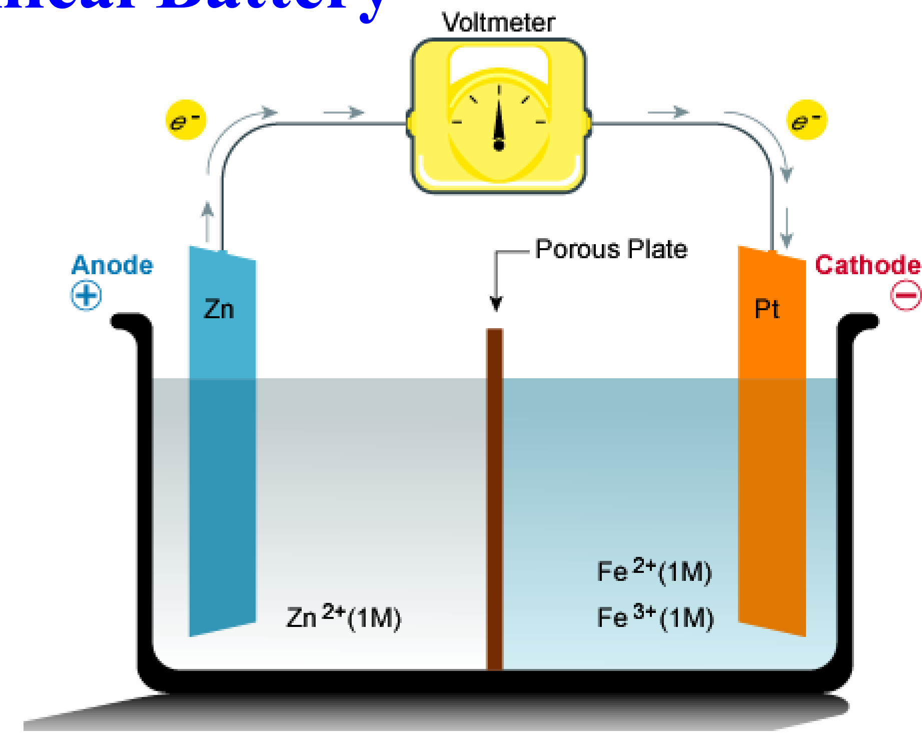
A Chemical Battery consists of at least three regions:

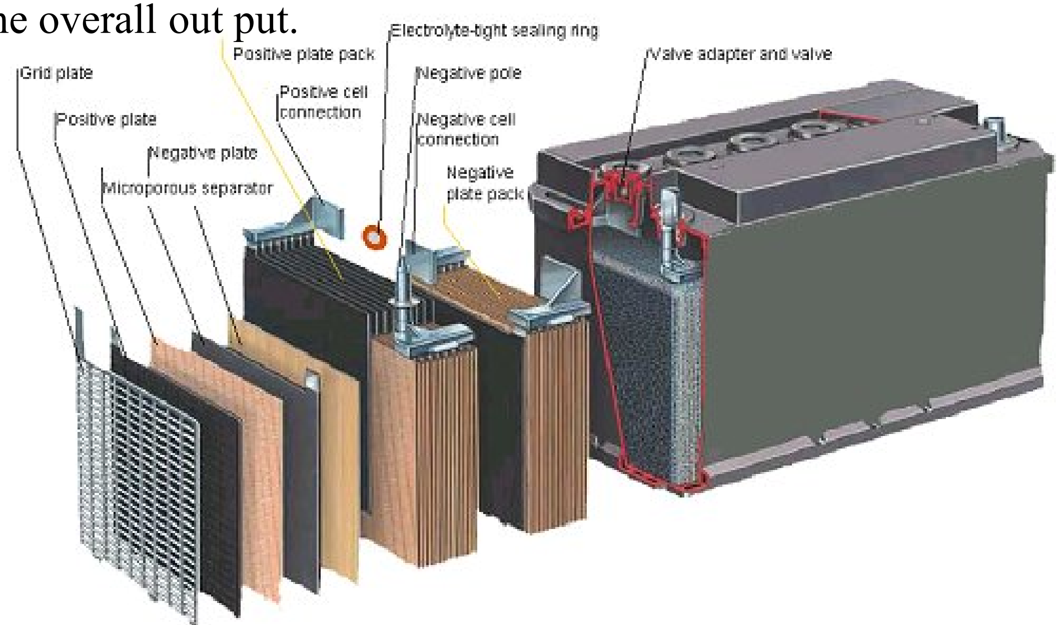
•Cathode: Negative potential lead

•Anode: Positive potential lead

•Electrolyte: A "weak barrier" that allows ions to be transferred from anode to cathode. Some batteries may have more than one electrolyte and/or the electrolyte may be solid, liquid or even gaseous or a mix of any phase.

•A battery requires mass transport to occur – which takes time limiting the overall out put.





Battery Chemistry "101" (ECE Simplified)

A Chemical Battery uses two primary reactions to reversibly store and discharge energy. These reactions are separated in space allowing a load to be connected between the points of the reaction (anode and cathode):

•Oxidation: The valence state of the reactant increases. For example:

$$Zn^0 \rightarrow Zn^{2+}(aq) + 2e^-$$

Where 2 electrons are released raising the valence of zinc from neutral (0) to doubly charged (2+) when in a solution (aqueous = aq).

•Reducing: The valence state of the reactant decreases. For example:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu^0$$

Together this set of reactions is often referred to as "Redox" reactions. An oxidation reaction must be paired with a reduction reaction, as the oxidation reaction produces the electrons required by the reduction reaction. Thus, the combined reaction of electrons leaving Zn and ending up on Cu is:

$$Cu^{2+}(aq) + Zn_{Solid}{}^0 + 2e^- \rightarrow Cu_{Solid}{}^0 + Zn^{2+}(aq) + 2e^-$$

Battery Chemistry "101" (ECE Simplified)

Electrochemical Potential:

The electrochemical potential is a measure of the potential energy difference between the average energy of the outer most electrons of the molecule (or element) in its two valence states.

The electrochemical potential has both magnitude and sign.

The lowest energy configuration for materials is for their outer shell to be fully occupied by electrons. Hence, a neutral element like lithium, Li^0 with one electron in its outer shell will have a higher energy than the element with the electron removed, Li^+. Thus in the reaction

$$Li^0 \rightarrow Li^+ + e^-$$

lithium metal has a higher energy than Li^+. The oxidation reaction has a large positive electrochemical potential, with a value of 3.04V, since the positive sign is defined such that the reaction proceeds spontaneously (assuming that there is another reaction which will accept the electron).

Battery Chemistry "101" (ECE Simplified)

Electrochemical Potential:

The total cell voltage can be found by summing up the electrochemical potential of both the oxidizing and reducing potentials. The standard potential for the cell is equal to the more positive E^0 value minus the more negative E^0 value. For example:

$$Zn^{2+}(aq) + 2e^- \Leftrightarrow Zn^0 \quad E^0 = -0.76V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu^0 \quad E^0 = +0.34V$$

By convention all ½ reaction tables are written as reduction reactions (gaining electrons). If a ½ reaction is to be used for oxidation, you must account for the proper sign (already negative in the tables indicating it is an oxidation type reaction). Thus,

$$Cu^{2+}(aq) + Zn_{Solid}{}^{0} + 2e^- \rightarrow Cu_{Solid}{}^{0} + Zn^{2+}(aq) + 2e^-$$

must account for the Zinc being oxidized and thus the cell voltage is, +0.34 V − (−0.76 V) = 1.10 V.

Also note the value of electrochemical potential used here is the standard potential defined as the electrochemical potential at 25 degrees C and at one atmosphere pressure and solutions of 1 Molar (1 mol/liter). If the actual conditions change, for example when the electrolyte becomes depleted below 1 Molar, the battery voltage will drop.

Battery Chemistry "101" (ECE Simplified)

Lead /Sulfuric Acid Battery example: Both anode and cathode are lead but one undergoes oxidation and the other undergoes reduction. When charging the battery:

Anode (oxidizes):

$$PbSO_4(s) + 5H_2O(l) \leftrightarrow PbO_2(s) + 3H_3O^+(aq) + HSO_4^-(aq) + 2e^- \quad \epsilon^o = 1.685 \text{ V}$$

Cathode (reduces):

$$PbSO_4(s) + H_3O^+(aq) + 2e^- \leftrightarrow Pb(s) + HSO_4^-(aq) + H_2O(l) \quad \epsilon^o = -0.356 \text{ V}$$

Resulting in a cell voltage of 1.685-(-0.356)V=2.04V per cell. Hence a 6 cell series connection is needed for a 12 V battery.

Battery Figures of Merit

Cell Voltage – the resulting potential of the combined double ½ reactions.

Battery Capacity - fundamental unit of battery capacity is coulombs (C) but this is normally re-written as Amp-hrs (Ah) (amps = C/time, so Ah = C/time(sec) x time (hrs))

Energy Capacity - Ah×Battery Voltage

Energy Density - Ah/Kg   Important in portable applications more so than in PV

Cut-Off Voltage - The minimum battery voltage for which the battery can be discharged. Below this value, permanent damage may be done to the battery.

Battery State of Charge (BSOC) – The fraction of the total energy or battery capacity that has been used over the total available from the battery.

Depth of Discharge (DOD) - The fraction of energy that can be withdrawn from the battery without significant devaluation of the lifetime of the battery.

Specific Energy Density - The capacity of the battery divided by the weight of the battery, in Wh/kg

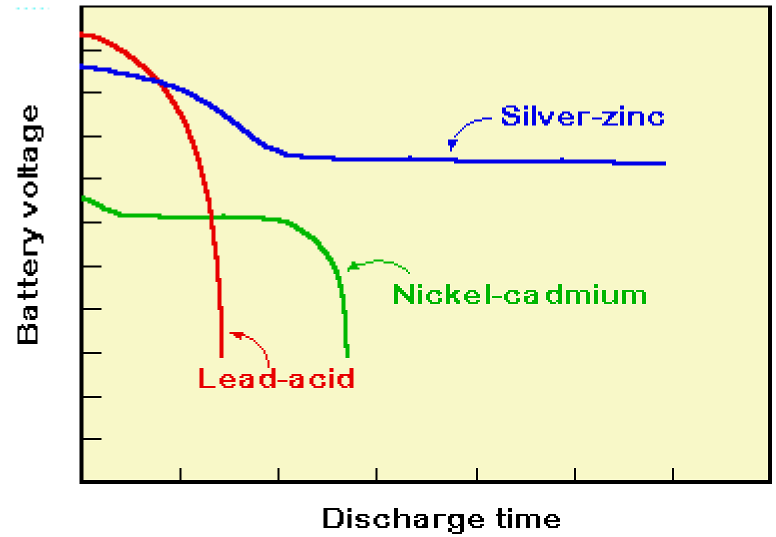
Volumetric Energy Density - The capacity of the battery divided by the volume, in Wh/m^3 (or Whr/litre)

Internal Series Resistance - Internal series resistance of a battery limits the maximum discharge current of the battery. Important mostly for high instantaneous loads.

Battery Charging and Discharging

Changes in battery voltage as it discharges, while not what we want can be used to monitor the state of charge of the battery.

To measure the BSOC, measure the voltage of the battery and compare this to the voltage of a fully charged battery. This is subject to errors due to the battery voltage depending on temperature.



<u>Charging and Discharging Rates</u>

The charging rate, in Amps, is given in the amount of charge added the battery per unit time (i.e., Coulombs/sec, which is the unit of Amps). More commonly charging / discharging rate is determined by the amount of time it takes to fully discharge the battery (in theory).

The charge and discharge current of a battery is measured in C-rate. Most portable batteries are rated at 1C whereas some lead acid batteries may be 0.05C or intended to be discharged in 20 hours.

Example: This means that a 1000mAh battery would provide 1000mA for one hour if discharged at 1C rate. The same battery discharged at 0.5C would provide 500mA for two hours. At 2C, the 1000mAh battery would deliver 2000mA for 30 minutes.

Sometimes you will see a battery rated as C_{20}=1000mAh and indicates a 20 hour intended discharge time.

Battery Charging and Discharging

Since the chemistry supplying the current is temperature driven (chemical reaction rates increase with temperature, increased temperature increases capacity BUT at the cost of battery lifetime.

Capacity often decreases as discharge rate increases since there is not enough time to "re-supply" the electrons through the normal chemical reaction (chemical reaction is too slow to keep up with current demand).

Battery Charging and Discharging

Precautions:

Battery Damage
Different battery chemistries dictate different charging and discharging limits.

Examples:
Nickel cadmium batteries should be nearly completely discharged before charging

Lithium – Ion and Lead acid batteries should never be fully discharged.

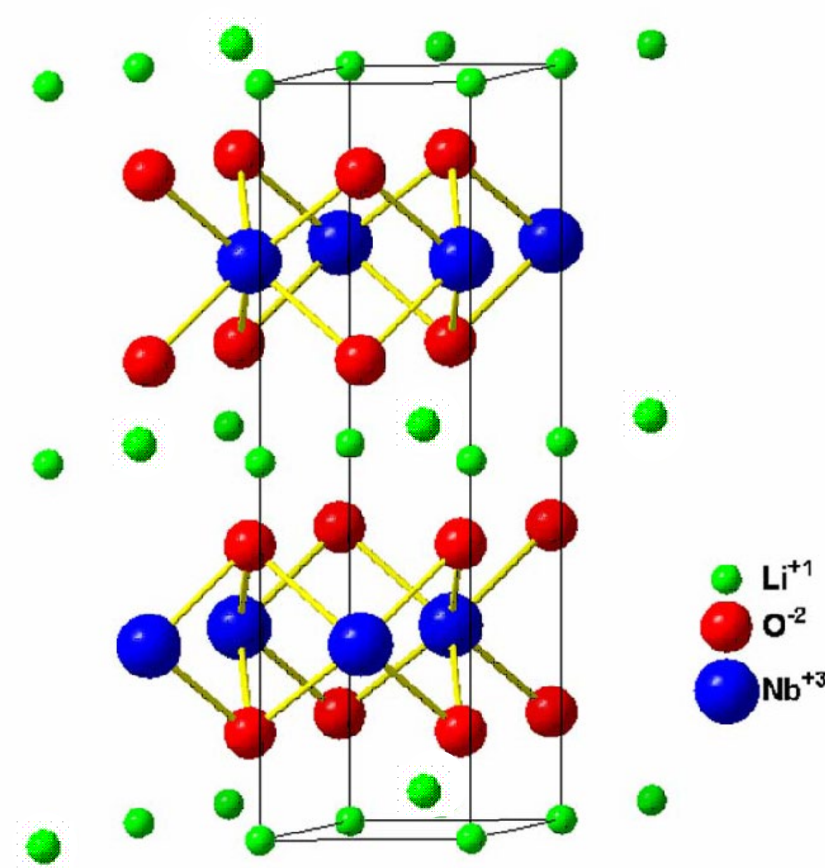
Fire or Explosion Danger
Some Batteries can explode if over charged or overheated.
Lead acid batteries can break down water to produce explosive hydrogen/oxygen mixtures if charged at too high a voltage

Li-ion batteries have carbon and oxygen containing materials that can ignite if overheated (charging or discharging). Many modern batteries have charge/discharge limiters (fuses) as safety precautions. US military does not supply Li-Ion batteries for infantry due to shrapnel damage induced ignition (instead they use the safer but less capacity Li-Polymer batteries).

Battery Design

Many Modern batteries are based on Li because the Li reduction ½ reaction has a very large standard electrochemical potential of over 3 V. This means that large single cell voltages can result (>4V).

Additionally the crystal structure of some Li compounds makes for easy intercalation / de-intercalation (addition and removal of Li). Consider $LiCoO_2$ below which is used for ~90+% of modern Li – ion batteries (cathode).



The Lithium can be easily removed and replaced from the planes it is found in resulting in high ion mobility. Additionally, up to 50% of the Li can be removed from the structure without the crystal "falling apart" making Li – ion batteries have a high capacity.

Even more advanced structures like $LiFePO_4$ have "ion channels" that allow for even easier movement of Li.

Types of Batteries

Lead Acid:
- Most common for PV because they are cheap!
- Widely available
- Long Lifetime
- Low Energy Density
- Limited Depth of Discharge
- Can explode if not properly charged

Various Nickel Cadmium and Nickel Metal Hydrides
- Not typically used for PV

Li – Ion Batteries (Including the related Li-Polymer Batteries)
- King of all batteries!
- Expensive!
- Highest Volumetric and Specific Energy Densities
- Very robust
- Mucho research into cost reductions and improvements – is likely the future

Adding energy storage ~triples the cost of a PV installation so you best really need the batteries! Better approach Smart Grid.