Ministry of Higher Education and Scientific Research University of Diyala College of Engineering Chemical Eng. Dept.

Batteries Technology

Topics to be included

1- Batteries

- Introduction
- History
- voltaic pile
- Chemical Process
- Modern Battery Chemistry
- Battery Construction
- The ideal characteristic
- Battery choices

2- Primary Batteries

Carbon-Zinc

3- Secondary Batteries

- Lead Acid battery
- Lithium Ion

4- Fuel Cells

- What is a fuel cell
- Hydrogen as a fuel
- The Alkaline Fuel Cell
- Different Types of Fuel Cell

Batteries – an introduction

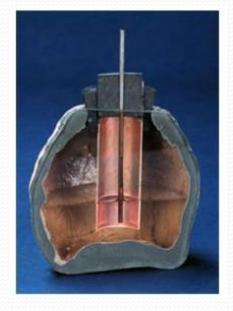
- Batteries are a sources of electrical power which rely on the reaction of chemical components within an electrochemical cell when the external circuit is completed.
- Two general classifications
 1-Primary batteries not rechargeable
 2-Secondary batteries rechargeable
- The world wide demand for batteries is enormous
- ➢ Estimated sales £50 billion in 2006.
- Huge growth in Li-Ion (Secondary) batteries.

Batteries – an introduction

- Much of the demand come from automotive industry
- Consumer batteries
- Mobile telephones, MP3 players
- TV remote control, clocks, smoke alarms, hearing aids

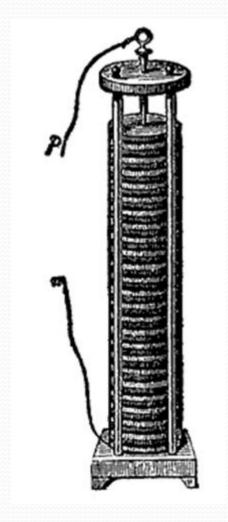
History

- It is believed that the first "battery" was dated around 250 B.C. (based on archaeological digs in Baghdad, Iraq)
- The first batteries were used for placing a thin layer of metal on jewellery.



<u>History – voltaic pile</u>

- The first modern battery was created by Alessandro Volta in 1800.
- To create his battery, he made a stack by alternating layers of zinc, blotting paper soaked in salt water, and silver.
- This arrangement was known as a voltaic pile.
- The top and bottom layers of the pile must be different metals.
- If a wire is attached to the top and bottom of the pile, a voltage and a current can be measured from the pile. The pile can be stacked as high as you like, and each layer will increase the voltage by a fixed amount.



Chemical Process

Hydrochloric acid ionises in water, to produce: H^+ and Cl^- ions. Zinc is more active than hydrogen and atoms leave the Zinc electrode to form zinc ions (Zn^{++}) . This leaves two electrons (negative charge) on the electrode. The Hydrogen ions move to the copper and take two electrons, leaving a positive charge. Hydrogen gas is given off. A potential difference (voltage) is produced between the Copper and Zinc electrodes. *Electrodes*

The point or surface where the electrochemical process takes place

- ions released
- electron flow occurs

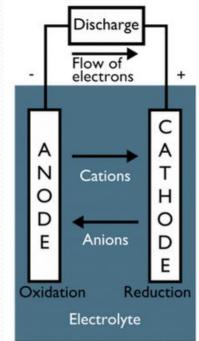
Two electrodes required:

- one produces positive ions
- one produces negative ions

Anode

Where oxidation (loss of electrons) takes place Negative electrode (while discharging) *Cathode*

Where reduction (addition of electrons) takes place Positive electrode (while discharging)

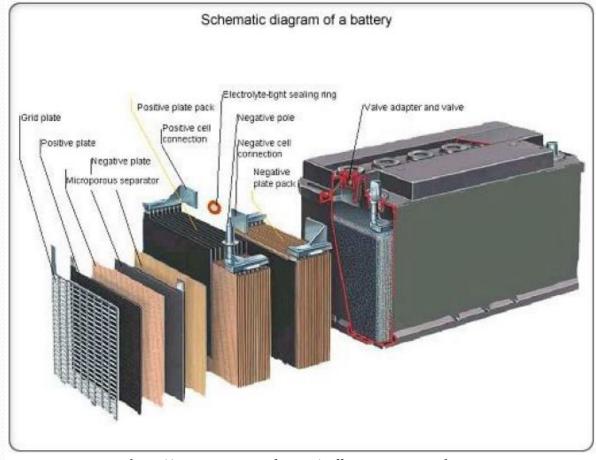


http://storage4.eu/2013/03/rechargeablebattery-diagram-convention/

Battery Construction

<u>Prismatic</u> (example is Lead Acid)

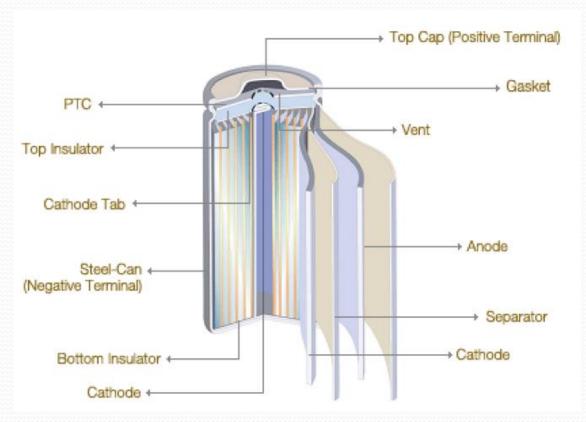
- Alternating layers of electrodes and electrolytes.
- Allows the design of complex electrodes.



Battery Construction

<u>Spiral Wound</u> (low cost domestic batteries)

- A thin sandwich of electrolytes (usually paste) between two thin metal electrodes.
- Then rolled into a spiral.
- Produces a cylindrical shape.



http://www.mpoweruk.com/cell_construction.htm



Capacity

• Total energy storage ability of the battery (Ampere Hours)

Capacity Retention

• The fraction of the full capacity available after storage for a period of time.

<u>Capacity – Energy</u>

The capacity can be measured in Watt-Hours and it is called Energy. (Watts are Volt-Amperes).

Energy density

- Energy density: It is a measurement of energy stored per kilogram of mass.
- The ratio of energy to mass (watt hour/kg).
- The higher the energy density the lighter a battery can be for the same application:-- Mobile Phone
- Laptops

C rate (or hourly rate)

• A (maximum) discharge rate that will deliver the specified hours of service to a given cut off voltage.

Battery choices

- No one battery design is perfect for every application. Choosing one requires compromise.
- it's important to prioritize the list of requirements.
- Decide which ones absolutely necessary and which you can compromise on.

Parameters to Consider

- *Voltage*: Normal voltage during discharge, maximum and minimum permissible voltages, discharge curve profile
- *Duty cycle*: Conditions the battery experiences during use. Type of discharge and current drain, e.g., continuous, intermittent, continuous with pulses, etc.
- *Temperature*: In storage and in use. Temperatures that are too high or too low can greatly reduce battery capacity.
- *Service life*: Defined either in calendar time or, for secondary cells, possible number of discharge/charge cycles, depending on the battery application. Service life depends on battery design and operational conditions, i.e., the stress put on a battery.

- *Physical restrictions*: These include dimensions, weight, terminals, etc.
- *Maintenance and resupply*: Ease of battery acquisition, replacement, charging facilities, disposal.
- Cost: Initial cost, operating cost, use of expensive materials
- *Safety and reliability*: Failure rates, freedom from outgassing or leakage; use of toxic components; operation under hazardous conditions; environmentally safe.
- *Internal resistance*: Batteries capable of a high-rate discharge must have a low internal resistance.

Primary Cell

- The chemical process that releases electrons is not reversible.
- Battery is disposed of when discharged.

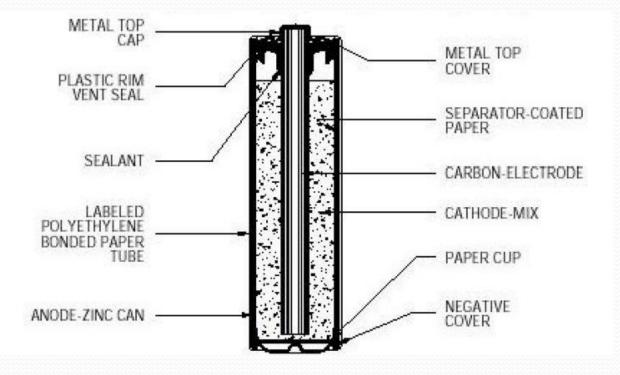
<u>Advantages</u>

- Medium shelf life.
- High energy densities (although at low discharge rates)
- Low maintenance.
- Easy to use.

Primary Cell Chemical

- Zinc-Carbon
- Alkaline battery (Duracell)
- Lithium-iodide battery (pacemakers)
- Zinc-mercury oxide battery (hearing-aids)
- Silver-zinc battery (aeronautical applications).
- Zinc-air battery (specialist)

Practical Zinc-Carbon battery



http://data.energizer.com/PDFs/carbonzinc_appman.pdf

Chemical Reaction

In a dry cell, the outer zinc container is the negative terminal. The

$$\operatorname{Zn}(s) \to \operatorname{Zn}^{2+}(aq) + 2 e^{-}$$

A graphite rod surrounded by a powder containing manganese(IV) oxide is the positive terminal. The manganese dioxide is mixed with carbon powder to increase the conductivity. The reaction is as follows:

$2\mathrm{MnO}_2(s) + \mathrm{H}_2(g) \rightarrow \mathrm{Mn}_2\mathrm{O}_3(s) + \mathrm{H}_2\mathrm{O}(l)$

The H₂ comes from the NH₄⁺(*aq*): $2NH_4^+(aq) + 2 e^- \rightarrow H_2(g) + 2NH_3(aq)$ and the NH₃ combines with the Zn²⁺.

Chemical Reaction

In this half-reaction, the manganese is reduced from an oxidation state of (+4) to (+3).

There are other possible side-reactions, but the overall reaction in a zinc-carbon cell can be represented as:

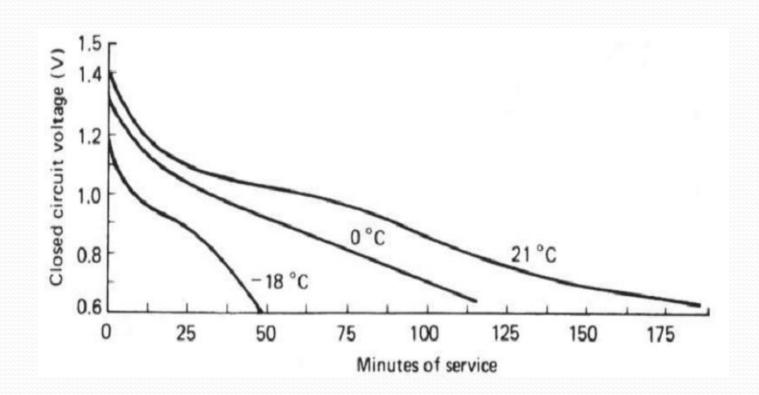
 $Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Mn_2O_3(s) + Zn(NH_3)_2^{2+}(aq) + H_2O(l)$

The battery has an e.m.f of about 1.5 V.

Example (Zinc Carbon Primary Cell AA) Current (mA) Time (h) Energy delivered 3 350 1.05 Ah 15 40 0.60 Ah 30 15 0.45 Ah

Extra losses are caused by the internal resistance and dendrite growth

Typical Carbon-Zinc Discharge Curve



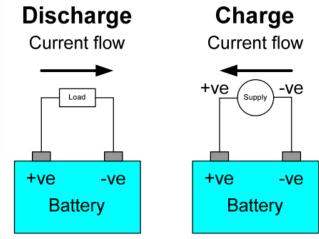
Secondary Cells Topics

- Lead Acid battery
- Nickel Cadmium
- Nickel Metal Hydride
- Lithium Ion
- Lithium Polymer
- Summary

Secondary Cells

- The chemical processes that releases electrons is reversible by injecting electrons back into the battery.
- Charging voltage must be greater than the charged battery voltage.
- Charge current has to be limited.





Advantages of Secondary Cells

- Can be used as primary cells then recharged externally. However, voltages and capacity are usually lower.
- Can be used as energy storage devices such as in an automobile.

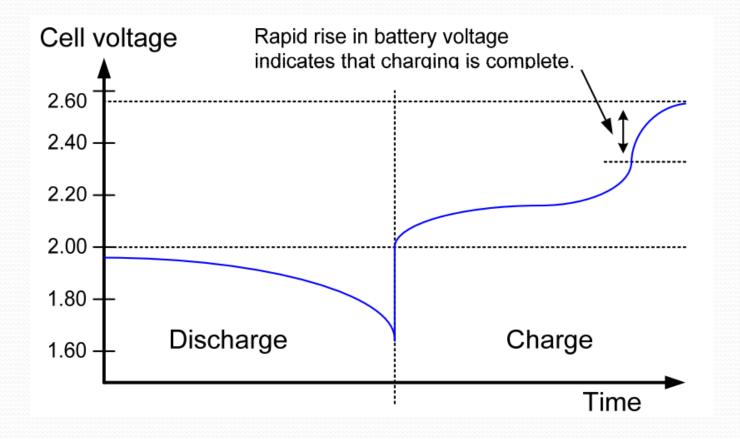
The ideal characteristic

- Constant open circuit cell voltage.
- Constant loaded cell voltage.
- Sudden drop when the energy is exhausted.

Typical cell characteristic

- Decreasing initial cell voltage with higher discharge currents.
- Total energy delivered is reduced at higher currents.
- For very long discharges (effectively open circuit) the chemicals deteriorate, limiting shelf life.

Discharge and Charge Characteristics(Lead-Acid Cell)



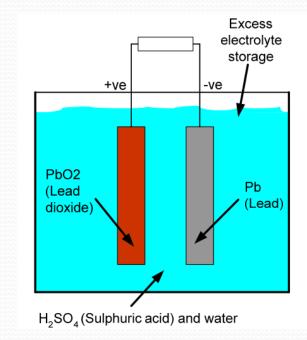
Lead Acid Battery

Chemical Reactions

- Sulphuric acid ionises in water
- $H_2SO_4 \longrightarrow 2H^+ + SO_4^{--}$
- The SO₄⁻⁻ ions combine with both electrodes.
- $Pb + SO_4^{--} \longrightarrow PbSO_4 + 2e^{-}$

with the electrons being deposited on the negative electrode.

- $PbO_2 + SO_4^{--} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$
- Electrons are absorbed from the positive electrode
- Lead sulphate (PbSO₄) is deposited on both electrodes and acts a polarising agent.



Specific Gravity

- The sulphuric acid is depleted by this process with inert PbSO4 (Lead sulphate) deposited on both electrodes.
- Eventually the battery is unable to supply current and is discharged.
- Specific gravity identifies the amount of sulphuric acid remaining.

High performance cell

- Specific gravity (Fully charged) = 1.28
- Specific gravity (Discharged) = 1.15
- The specific gravity is linearly related to the percentage charge.

100% = 1.28 and 0% = 1.15 So 50% = 1.22

Lithium Ion Batteries

- Lithium ion batteries are an excellent source of high energy power in a variety of portable devices.
- Light weight with a high cell voltage.
- Contribute to weight and size reduction in portable products.

Battery Chemistry

• <u>Positive Electrode</u>

- Lithium Cobalt Oxide
- (or Lithium Manganese Oxide which is cheaper and safer but not as efficient)
- <u>Negative Electrode</u>
- Highly crystallised carbon (graphite)
- Electrolyte fluid
- Organic solvent (optimised for carbon)
- Typically a non-aqueous Lithium salt

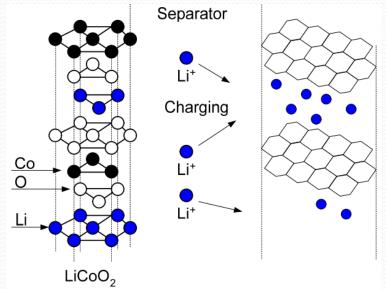


Battery Chemistry

Positive Electrode LiCoO₂ \rightarrow Li-x CoO₂ +xLi⁺ + xe⁻

Negative Electrode C + xLi⁺ + xe⁻ \rightarrow CLix

- Charging ionises the Li in the LiCoO 2 which are then inserted into the graphite layers. Discharge is the reverse process.
- A porous plastic separator is used to keep the two electrodes apart.



<u>Lithium Ion Batteries</u>

• A lithium-ion battery in use typically lasts between 2-3 years. The capacity loss manifests itself in increased internal resistance caused by oxidation. Eventually, the cell resistance reaches a point where the pack can no longer deliver the stored energy although the battery may still have ample charge.

• For this reason, an aged battery can be kept longer in applications that draw low current as opposed to a function that demands heavy loads.

• Increasing internal resistance with cycle life and age is typical for cobalt-based lithium-ion, a system that is used for cell phones, cameras and laptops because of high energy density.

Fuel Cells

- What is a fuel cell
- Hydrogen as a fuel
- The Alkaline Fuel Cell
- Different Types of Fuel Cell
- Applications
- Example Technology



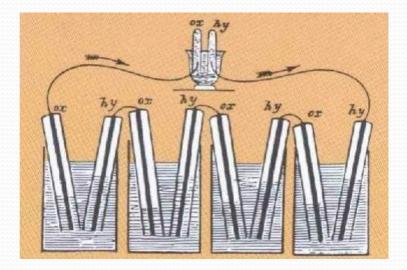
A *fuel cell* produces electricity from fuel and an oxidant, which react in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate virtually continuously as long as the necessary flows are maintaineds as long as fuel and air are supplied

<u>History</u>

 \bullet 1839 Sir William Grove – credited with first electrochemical H 2 /O 2 reaction to create energy.

Grove's Device

Oxygen and hydrogen in the tubes over the lower reservoirs react in sulphuric acid solution to form water. That is the energy producing chemical reaction. The electrons produced electrolyze water to oxygen and hydrogen in the upper tube that was actually used as a voltmeter.



- This scheme was published by Grove in one of the first accounts of an operating fuel cell in Philos. Mag., Ser. 3, 1839, 14, 127.
- He proved that the fuel cell worked, but there was no practical use for them at that time so the invention slumbered for more than 130 years.

- 1950s Thomas Bacon fuel cell stack
- 1950s-now Alkaline fuel cells in space program
- 1970s first stationary power applications
- 1990s-now transportation and other applications under development
- 2006 commercial sales for communications backup power systems

Chemistry of Hydrogen

- It is the most plentiful and simplest element gas existing.
- Some other characteristics:
- It is odourless
- Taste less
- Colourless
- Very light.
- However it has a very high energy density. (Three times the energy found in contemporary fuel sources).
- Mostly found combined with other elements, such as carbon in the case of hydrocarbons and oxygen in the case of water (H2O).

Some Benefits

- It can be harnessed from almost any compound it is found This can be done in pollution free ways such as electrolysis, solar or wind power.
- It is clean in nature as an energy carrier.

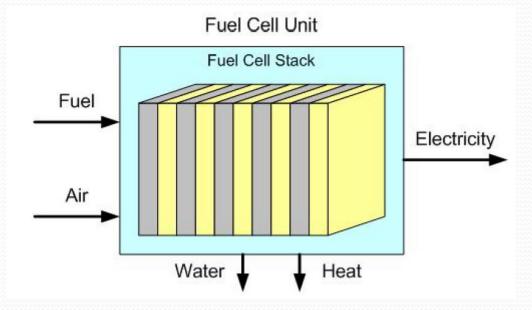
<u>Safety</u>

• In terms of safety it must be handled like any other fuel we know – that is to say careful and proper handling is required.



Fuel Cells

- The chemical action of a fuel cell is similar to that of a battery. The major difference being that it does not run down or require recharging. As long as fuel is supplied, energy will continue to be generated in the form of heat and electricity.
- There are several different types of fuel cell but they are all based around a central design.
- It basically, consists of two electrodes, the anode and cathode same as found in a battery. The electrodes are contained within an electrolyte. Two fuels oxygen and hydrogen pass over the electrodes one over each to produce energy in the form of heat, water and electricity.



<u>Alkaline Fuel Cell</u>

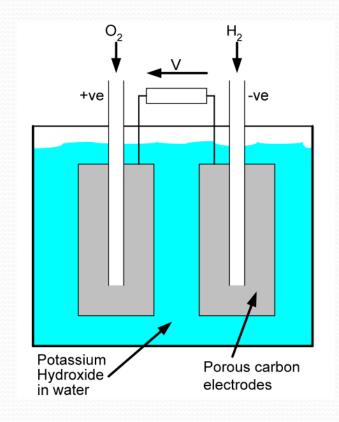
Similar chemical reaction to a battery, chemical reaction releases electrons at the electrodes

Operation

Potassium Hydroxide in water produces ions KOH \rightarrow K⁺ + OH⁻

At the positive electrode, with oxygen: $O_2 + 2H_2O + 4e^- \rightarrow 4 OH^-$

At the negative electrode with hydrogen: $2H_2 + 4 OH^- \rightarrow 4H_2O + 4e^-$



Process

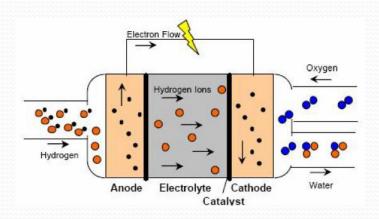
• Oxygen is channelled through into the cathode, while hydrogen is channelled through the anode. The hydrogen is cracked most times with the aid of a catalyst into its constituent – a proton and an electron. They take diverse routes to get to the cathode. While the proton travels through the electrolyte, the electron travels through the external circuit/load to produce electric current before getting the cathode.

Approximate energy distribution

- 60% emitted as heat vaporising the water
- 40% available as electricity
- $V_{nominal}$ = 1.0V
- Energy density = 100 Whkg⁻¹

(although efficiencies can be much higher)

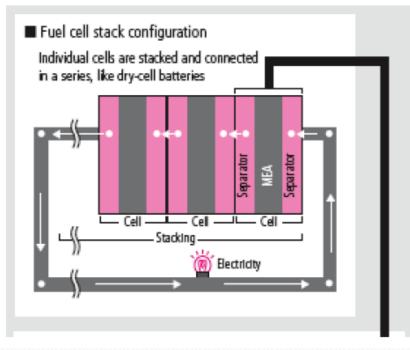
• Every fuel cell has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which accelerates the reactions at the electrodes.



Fuel Cell Voltage

Single Cell produce 0.7V - 1.0V20 cells in series to produce 14V - 20V





http://www.honda.com/newsandviews/article.aspx?id=4353

<u>Types of Fuel Cells</u>

- There are different types of fuel cells depending on the type of electrolyte being employed. Examples include:
- Alkaline Fuel Cells
- Direct Methanol Fuel Cells
- Molten Carbonate Fuel Cells
- Phosphoric Acid Fuel Cells
- Proton Exchange Membrane Fuel Cells
- Solid Oxide Fuel Cells
- Regenerative Fuel Cells

Alkaline Fuel Cells (AFC)

• The alkaline fuel cell uses an alkaline electrolyte such as potassium hydroxide. It was originally used by NASA on space missions. NASA space shuttles use Alkaline Fuel Cells.

Benefits

Fuel cells offer a combination of wide ranging benefits when compared to other generating technologies.

• Energy Security

- No dependence on oil as a source of fuel for energy generation.
- Security of supply
 - Making use of hydrogen means that they can provide a secure renewable source for the future.

• Physical Security

 The modular and distributive nature of fuel cells reduces centralisation and minimises attacks on a central facility in a bid to cripple the energy infrastructure such as in a terrorist attack.

• <u>High Reliability</u>

- They can be employed as backup units for residents being supplied by the grid.

• Environment

- As the by product is water electricity and heat, it is environmentally friendly.