

Batteries and Energy Storage

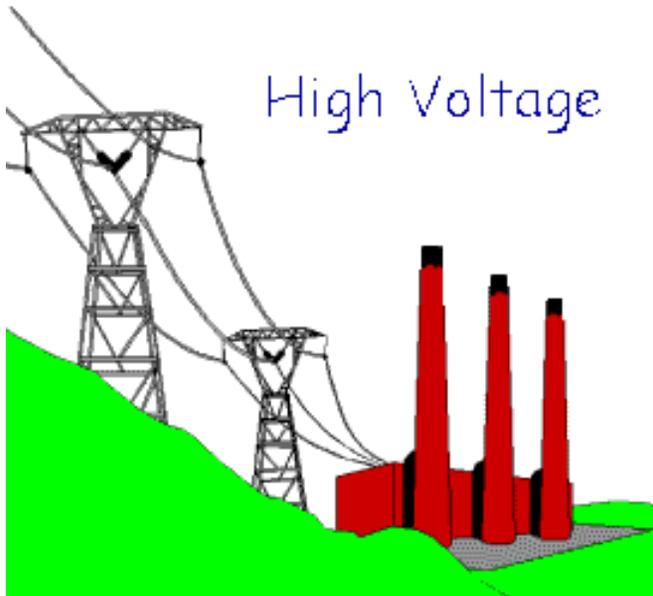
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How do we make and store electricity ?

Today, we can convert energy from many different forms into usable electricity:

- Coal
- Wood
- Nuclear fission
- Oil
- Water
- Solar
- Wind



But the main problem for electricity is how we store and transport it from the generation source

- Transmission wires
- Batteries

But how did we get here ?

For today, we'll focus on batteries for portable energy storage

In ancient times, the generation of electricity was purely accidental.

By rubbing certain materials together, static charges
can be accumulated

- Drag feet on carpet
- Pet a cat
- Take off a sweater

Ancient Greeks rubbed amber on fur to generate electricity. In fact, the word elektron comes from the greek word for amber

By the mid 1600's, static electricity could be readily generated by rubbing insulating materials together: fur/cloth, sulfur, amber, etc.

We still use this method today: Van de Graff generators

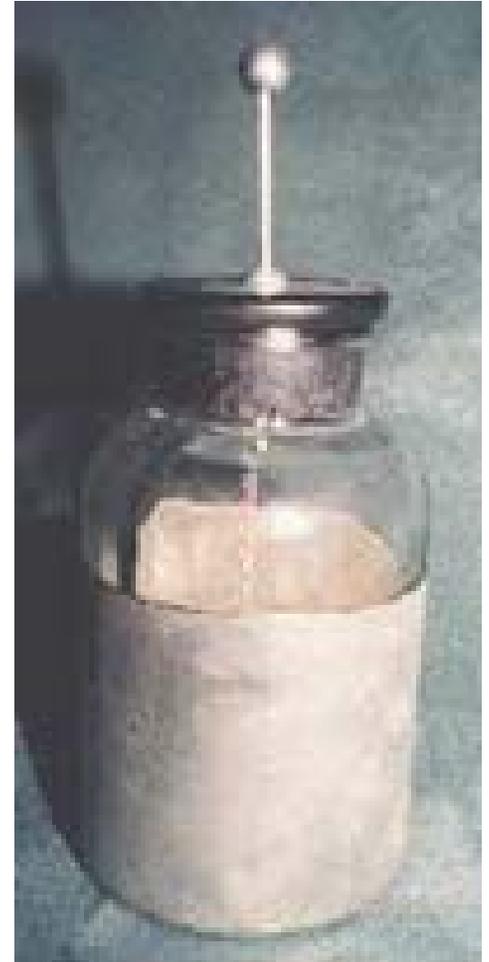
But in the 1600's, scientists did not really know much about electricity or how to use it. The spark generators were mostly used by scientists to study the nature of the sparks

In 1745, scientists (Musschenbroek and Cunaeus) noticed that one could “charge” up a glass filled with water and get a shock by touching a metal nail

Shortly thereafter, this was simplified to just metal foil wrapped around the inside and outside of a jar with a chain connecting the inner layer.

→ Leyden Jar

We know these devices as capacitors, but they work by storing charge **ELECTROSTATICALLY**



Although they still didn't know all that much about electricity, they now had methods of storing and generating electricity, but it was still a research tool (and a parlor trick)

In fact, this enabled many important experiments of the time

1746: Nollet assembled a line of 200 monks each holding the end of a wire to test if electricity can travel faster than human communication. Without warning he connected a Leyden Jar to the ends ...

1747-1753 Cavendish used Leyden Jars to discover many of the fundamental physics laws of electricity

→ Inverse square law for force, electric potential, capacitance, resistance

But Cavendish did not publish all that much and these discoveries were rediscovered years later by Faraday, Ohm, Coulomb, Maxwell

1752: Ben Franklin and his famous kite experiment

Showed that lightening is the same as electricity stored in Leyden Jar



Franklin's other main contributions to the field include the concept of current as the flow of positive charges, and the term battery

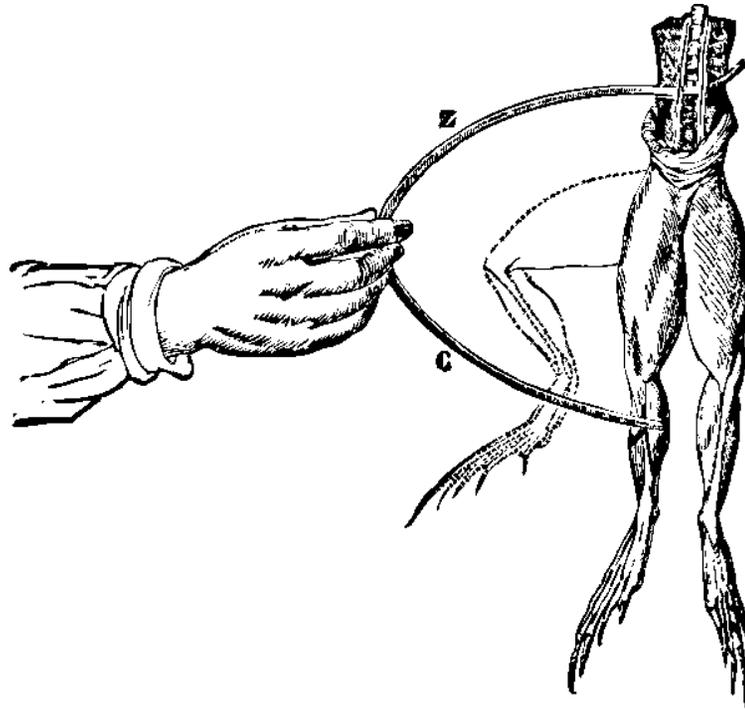
We later found out he was very wrong, but unfortunately it was too late. This is why current goes in the opposite direction of electron flow

Two disadvantages of the Leyden Jar are that it doesn't store charge all that long (This is true in general for electrostatic storage) and it doesn't store all that much energy

1786: Galvani's famous experiments on frog legs

He took two dissimilar metals (Zn, Cu) and touched them to the ends of a dead frog's leg

Surprisingly, the leg moved and Galvani attributed this to bioelectricity

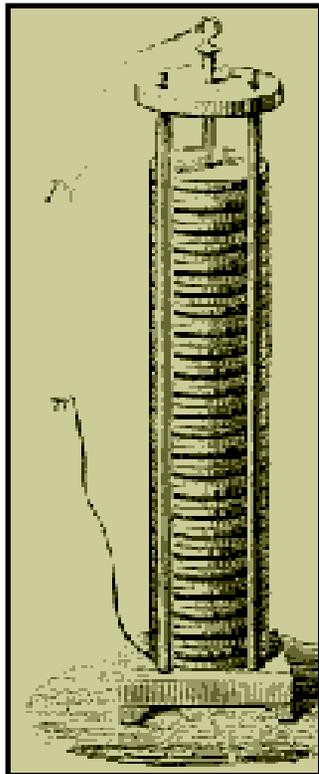


But Volta did not believe that the electricity came from the frog. He believed the electricity came from the metals

In 1799, he showed that by combining different metals that are separated by a salt or acidic solution it was possible to generate electricity

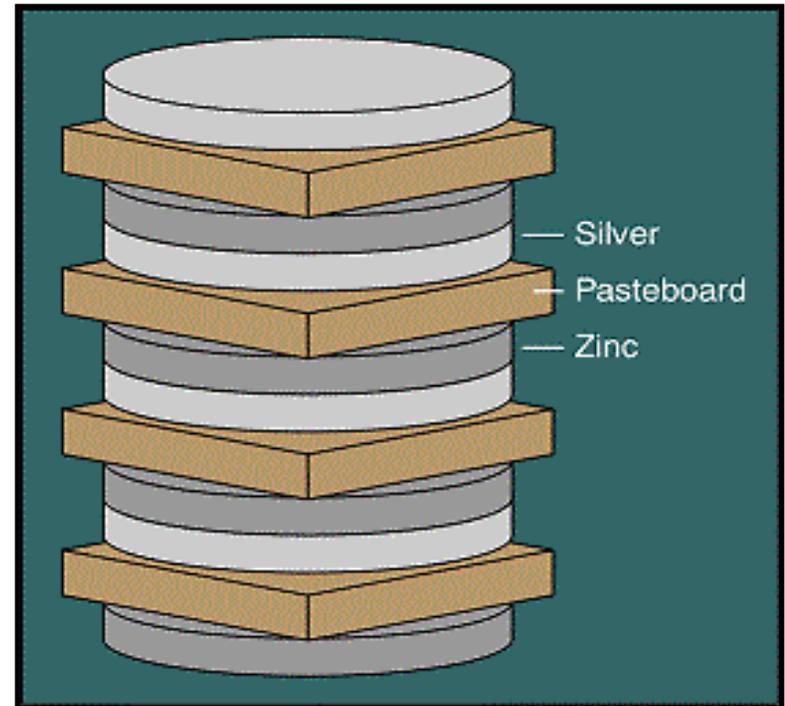
→ VOLTA PILE

Side note: Galvani died one year earlier and never knowing the answer



First commercially available battery

An enabling technology for the telegraph



How does all of this work ?

It's all electrochemistry!!

Chemical Energy is Converted to Electrical Energy Through Oxidation and Reduction reactions

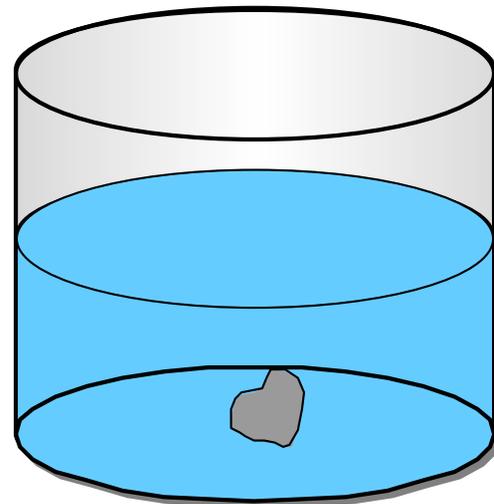
- Voltaic(Galvanic)
 - Spontaneous
 - Generates energy

→ Batteries, Fuel Cells, corrosion
- Electrolytic
 - Non-spontaneous
 - Needs energy to occur

→ Electrodeposition, electrowinning, polishing

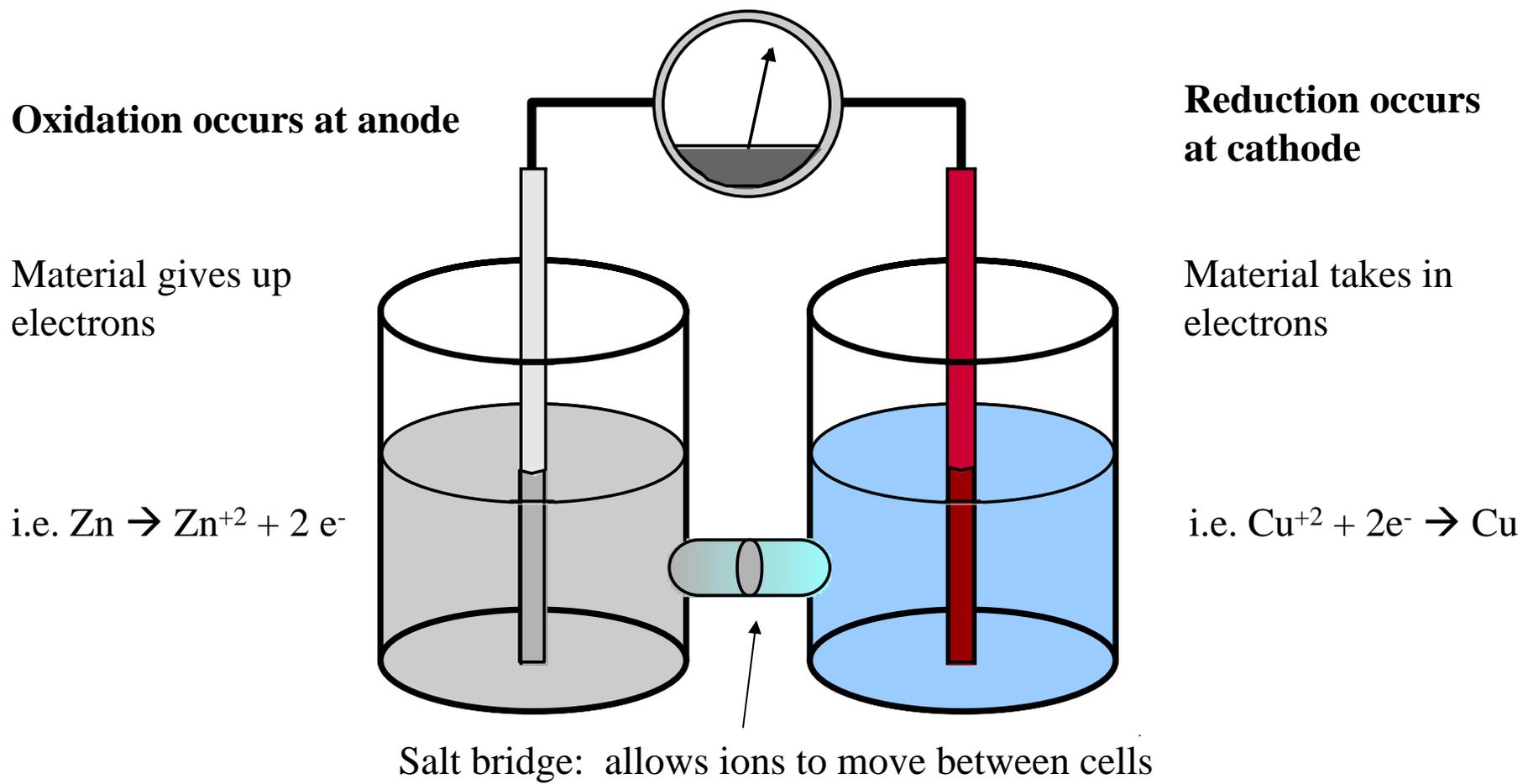
But, if reactions are spontaneous ...

... how do we harness them?



Voltaic or Galvanic Cells

Separate reactions into half-cells



Electrochemistry: chemical reactions require charge transfer

This occurs through redox reactions

Oxidation	$M \rightarrow M^{n+} + ne^{-}$	Oxidation is loss of electrons Ions dissolve into solution
Reduction	$M^{n+} + e^{-} \rightarrow M^{(n-1)+}$	Reduction gains electrons Ions deposited from solution

Oxidation occurs at the anode \rightarrow anodic reaction

Reduction occurs at the cathode \rightarrow cathodic reaction

These are called Half-Cell reactions

Both need to happen... electron is generated at the anode and must be consumed at the cathode so net charge is conserved in overall process

We need a salt bridge to complete the circuit so that the charge remains balanced \rightarrow otherwise, the charge would build up and the battery would stop working

In the process of oxidation and reduction, energy is converted from chemical into electrical

i.e. Electrons are free to run through the circuit and do work

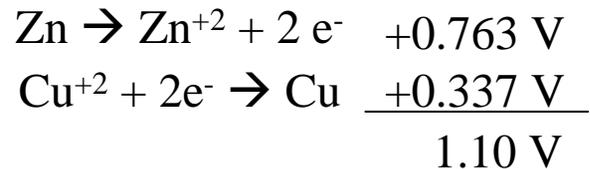
But they must go through the external wires

In previous example,

Zn can lower its energy by giving up electrons and dissolving into solution

Cu⁺ can lower its energy by capturing electron and ‘plating’ out on electrode

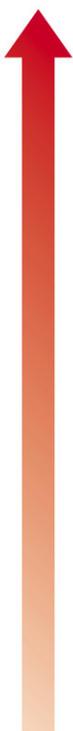
Voltage of the cell is determined by the oxidized and reduced species and related to the change in free energy



Can think of this as analogous to water flowing downhill where the voltage is the height of the hill

The important thing here is that every material has a slightly different potential

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction	E° (V)		
Stronger oxidizing agent 	$F_2(g) + 2 e^- \longrightarrow 2 F(aq)$	2.87	Weaker reducing agent 	
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78		
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51		
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36		
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33		
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23		
	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09		
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80		
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77		
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70		
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54		
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40		
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34		
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15		
		$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$		0
	Weaker oxidizing agent	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$		-0.13
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26		
	$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40		
	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45		
	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76		
	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83		
	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66		
	$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37		
	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71		
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04		

Electrochemical Energy Storage

Batteries are a compact method of producing a voltaic cell

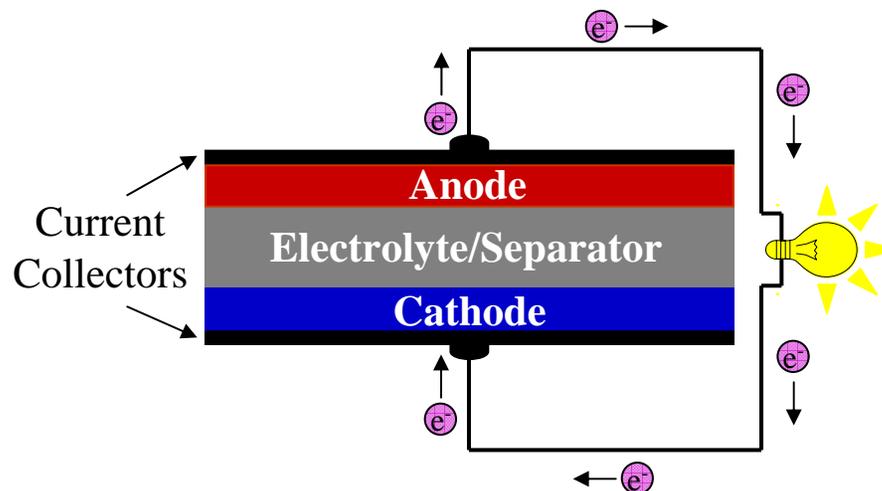
Other methods, fuel cell, photovoltaic cell, electrochemical capacitors etc.

Primary: Non-rechargeable

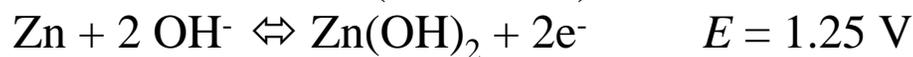
Secondary: rechargeable

Voltage → Potential difference between anode and cathode.
Related to energy of reactions

Capacity → amount of charge stored (usually given per unit mass or volume)



Anode (Oxidation):



Cathode (Reduction):



	Fuel Cell	PEC Cell
Anode	H ₂	TiO ₂
Cathode	O ₂	Metal

So this raises a potential problem with the Volta Pile

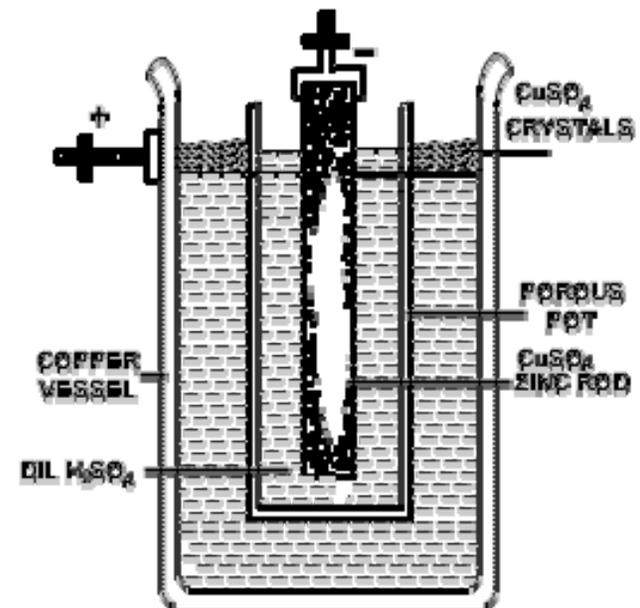
If Zn is the anode and H is the cathode, there is an evolution of hydrogen gas that could passivate the electrode or generate a large resistance to flow

Solution is to use a wet cell that has the proper ions around

(1836) Daniel Cell: Cu/Zn in sulfate solutions

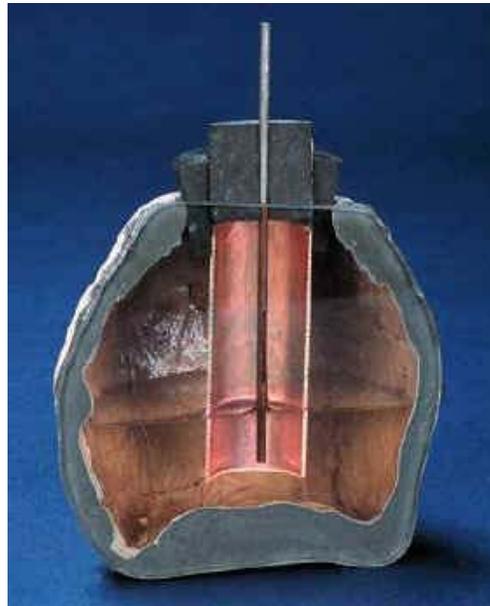
(1859) Plante: Pb/PbSO₄ cell

Wet cells have an obvious disadvantage for transport, but they do work well



But actually, a wet cell battery may have existed well before Volta
Archeologists found this clay pot in the Baghdad area in the 1930's

Carbon dating places it ~250 BC



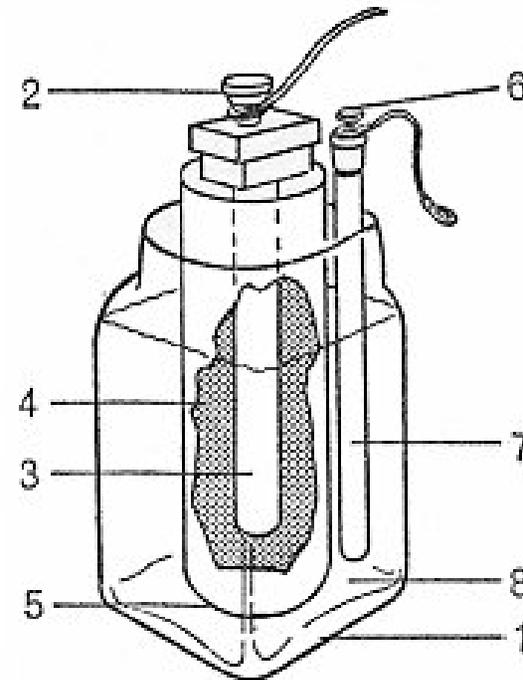
How does this work?

Leclanche in 1866 developed another kind of wet cell that had a better shelf life and was less reactive with the environment

This battery was constructed with Zn as the anode and $\text{MnO}_2 + \text{C}$ as the cathode

The cathode was mixed into a paste and placed in a porous pot

The Zn anode was immersed in a chloride electrolyte



LECLANCHÉ CELL

1. Glass jar.
2. Positive terminal.
3. Carbon rod.
4. Powdered carbon and manganese dioxide (depolarizer).
5. Porous pot.
6. Negative terminal.
7. Zinc rod.
8. Aqueous ammonium chloride solution

Very popular with the new Telegraph !!

Other variations came about as well

Different materials: Ni/Cd (Junger) 1899

Different electrolyte: Alkaline (Edison) 1911, “dry” cell
(Gassner) 1888

They all pretty much looked about the same, but some were better than others

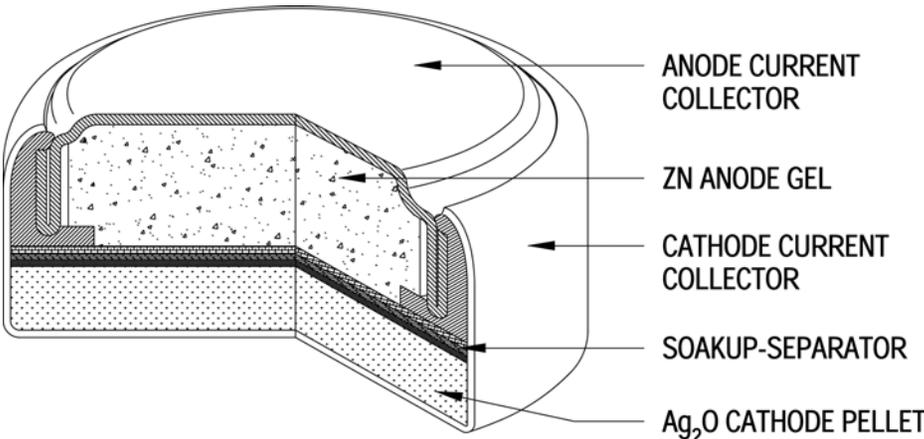
- Lifetime
- Capacity
- Marketing
- Convenience
- Rechargeability

Edison Cell
Ni/Fe in
KOH
electrolyte

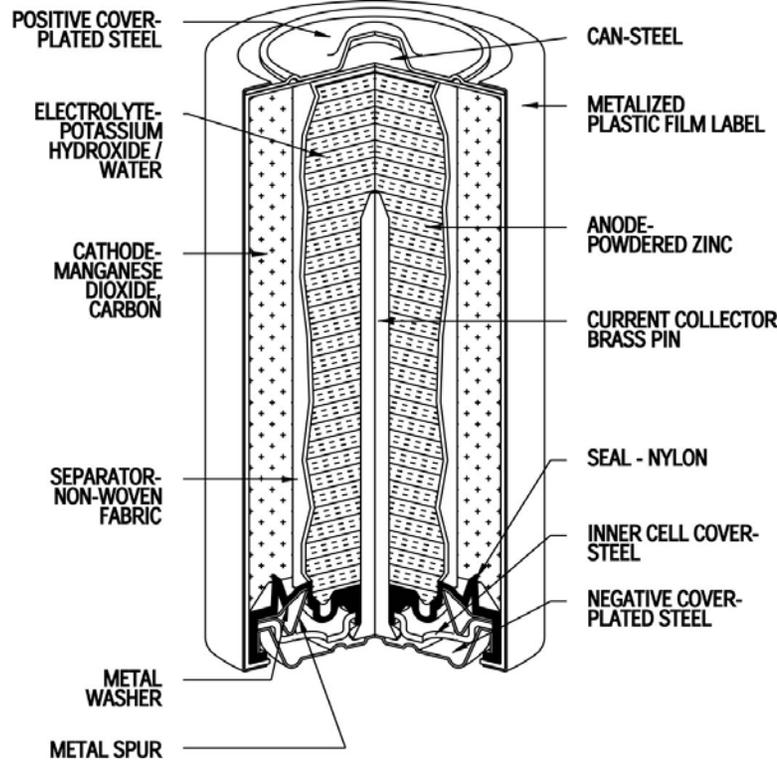
Edison was actually trying to make a battery for the Automobile, but gas engines were too good



Modern Batteries



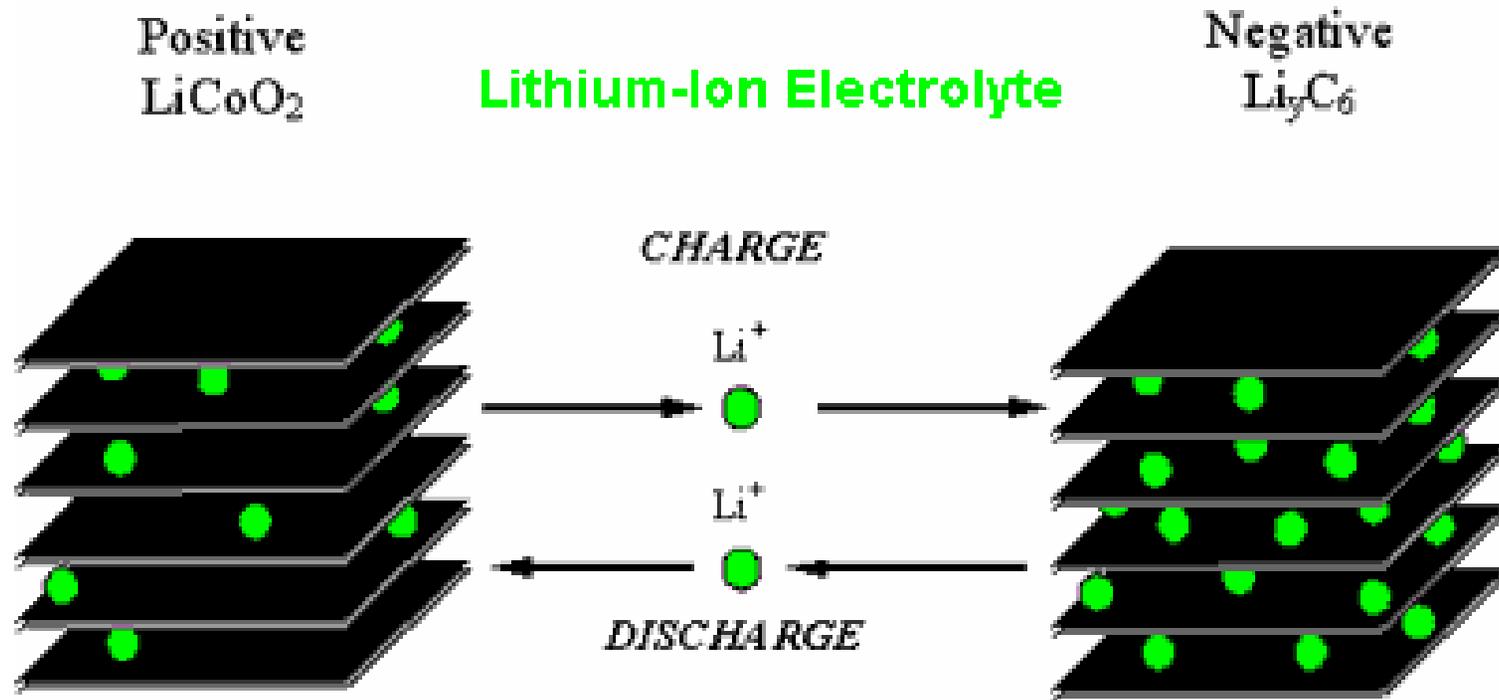
Modern Button Cell



Battery Types

Battery chemistry has not changed much since 1800's

Leclanché	1866, 1888	Zn-MnO ₂
Alkaline	1949	Zn-MnO ₂
Silver-Oxide	1950	Zn-Ag ₂ O
Rechargeable Alkaline	1978	Zn-MnO ₂
Lead-acid	1859	Pb-PbSO ₄
Ni- based		
NiCad	1899	Cd-NiOOH
Metal Hydride	1990	MH-NiOOH
Li- based		
Lithium-Iodine	1968	Li-I ₂
Lithium ion	1991	Li-LiCoO ₂
Plastic/Polymer	1995	Li-LiCoO ₂



How does a Li-ion battery work?

Li ions intercalate into the crystal structure of the electrode materials

But Li is very reactive (high V) which causes side reactions and passivation layers (solid electrolyte interphase)

➔ Critical to the proper functioning of these cells

More advanced topic

So what makes a battery rechargeable ?

In reality, as long as the electrochemical reaction is reversible, the battery should be rechargeable

However, other effects are important

- Decay of structural properties as ions move in and out of electrodes
- Growth of metal on electrodes
- Decay/contamination of electrolyte
- Cost
- Power signature

Lead-acid works well

Impedance Matching

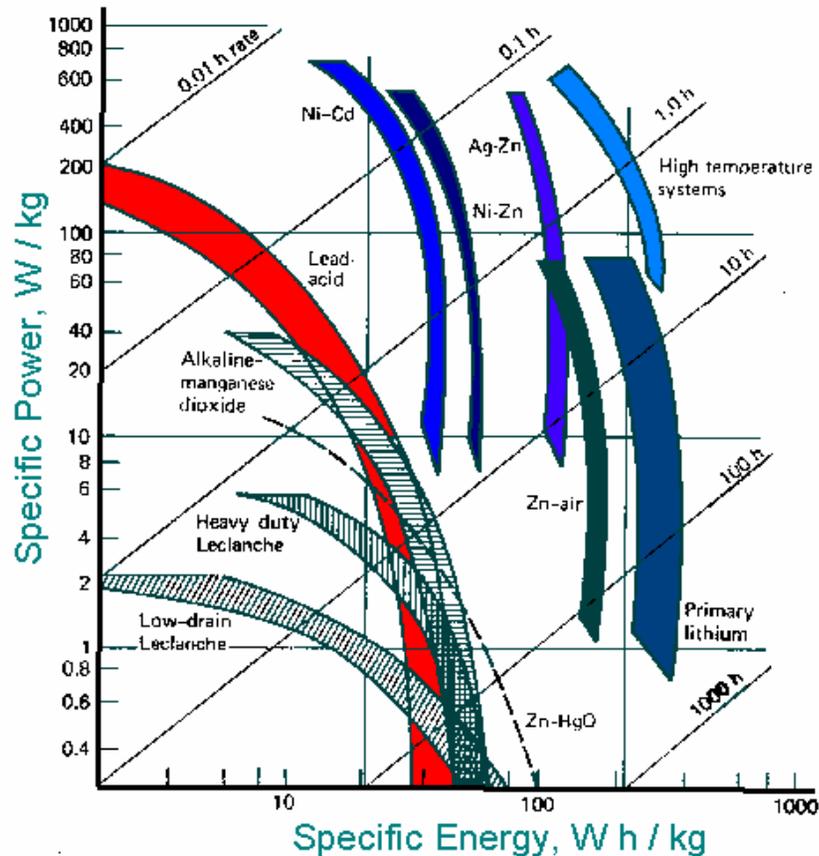
So faced with all these choices, how do we choose an appropriate power source?

The optimal power transfer to the load will occur when the impedance (resistance) is equal to the internal resistance

Can derive this from Ohm's laws

However, we would not typically run a battery at this current as it would heat up too much

Ragone relation



<http://www.powerstream.comz/ragone.gif>

Energy density \rightarrow Energy per unit area/volume
Specific Energy \rightarrow Energy per unit mass

In general, electrochemical systems always show the characteristically downward curved plots

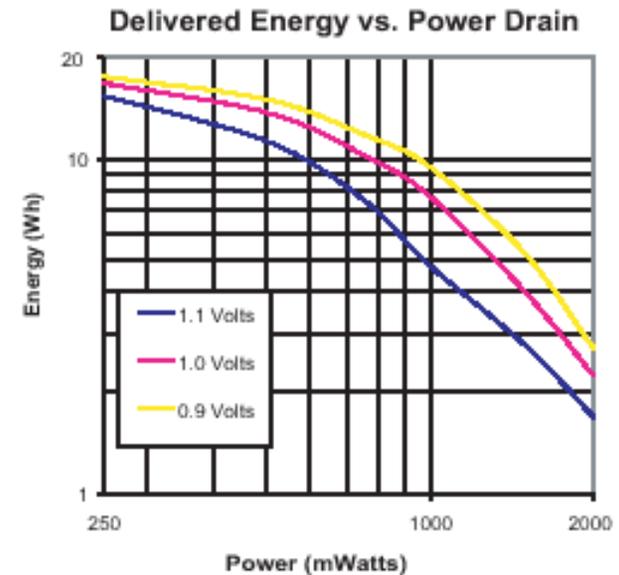
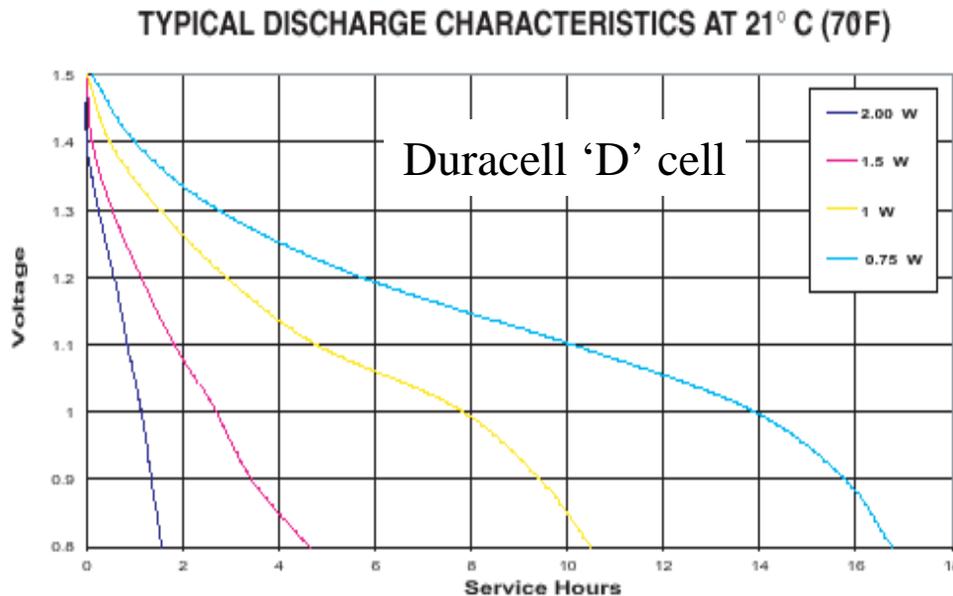
High power \rightarrow Low energy
High energy \rightarrow Low power

One might think that it is best to just push the limits of energy or power

Other issues such as total weight, size, voltage, environmental concerns can limit our selection process

Rate effects

Another major factor in optimizing energy storage is the rate at which the energy is needed



As with all batteries, there is a decrease in capacity (efficiency) as the power is increased

Main limiting factor is rate of ion movement across electrolyte

Energy demands differ from application to application

But many application for batteries do not require extended periods of high power draw

Rate effects

Although standard specs can be reported, there are a variety of important issues that ultimately affect the lifetime and performance of a battery system for a desired application

Current Drain: Different batteries respond differently to current

In general, as current is increased, the available voltage and capacity decrease

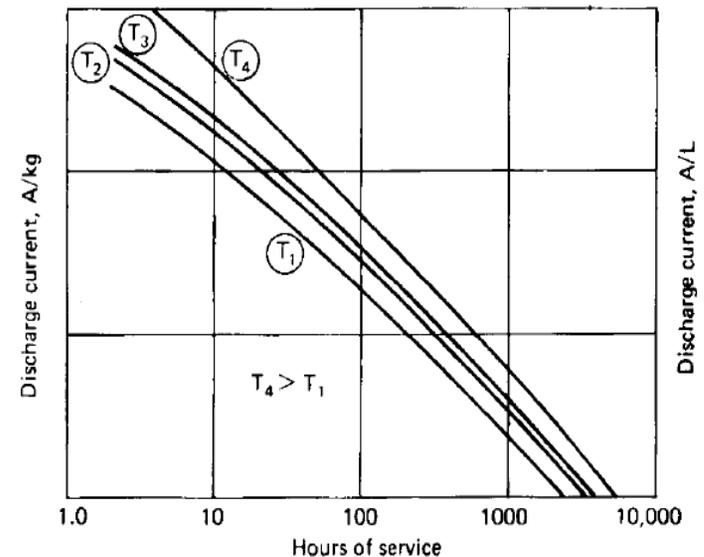
Peukert's equation:
 $I^n \times t = C$
 I is current in A
 t is time in hr
 C is rated capacity

But since C depends on rate, one must correct for this

Modified Peukert's law

$$t = \frac{H}{\left(\frac{IH}{C}\right)^n}$$

Where H is the hours for the rated capacity



Handbook of Batteries 3e, Eds Linden and Reddy

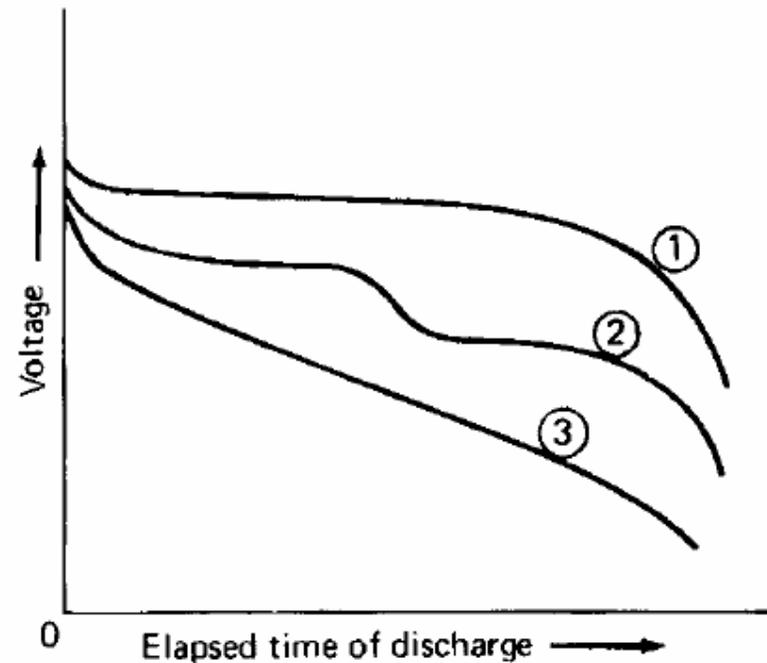
This is a significant issue for small batteries being used to power transmitters and it is non-linear

Discharge Characteristics

Different chemistries will have different voltages and different characteristic discharge curves

→ Appropriate choice will depend on application limitations

Cut-off voltage of the device is an important parameter as it will determine the actual capacity that can be used

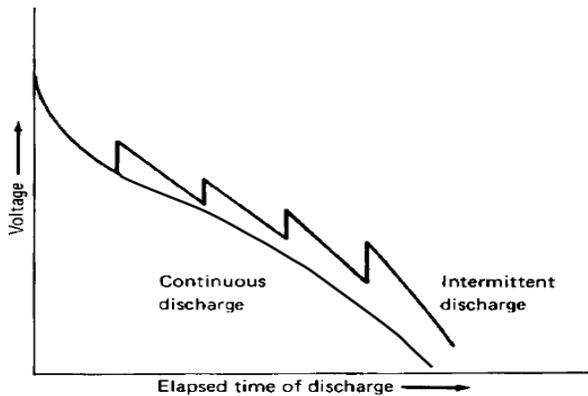


Handbook of Batteries 3e, Eds Linden and Reddy

For instance, Silver Oxide batteries have a very flat discharge at 1.5 volts compared to Li-ion batteries with a sloping curve around 3 V

Pulsed Discharges

Batteries operated in pulsed applications will last longer than constant discharge at same current



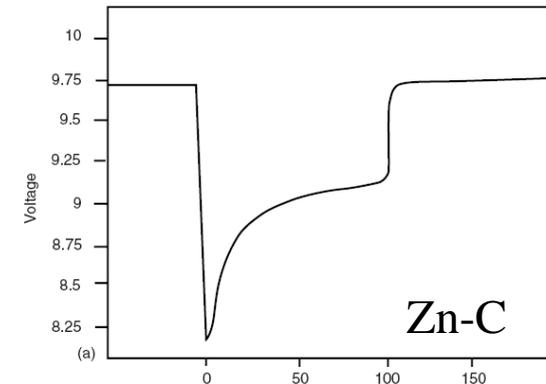
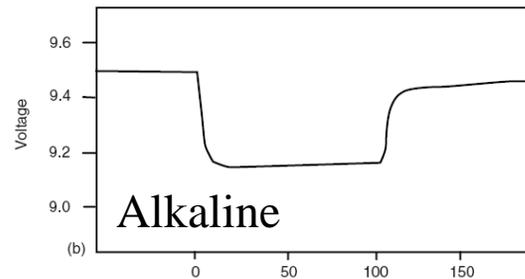
Handbook of Batteries 3e, Eds Linden and Reddy

During rest time, battery recovers voltage → more of the theoretical capacity can be used

Pulsing between high and low current (e.g. transmit/receive operations) will have a similar effect → voltage will oscillate

Voltage response to pulse will vary with chemistry

High current pulsed can lead to catastrophic failure



Factors such as maximum current and duty cycle will have a profound effect on this issue

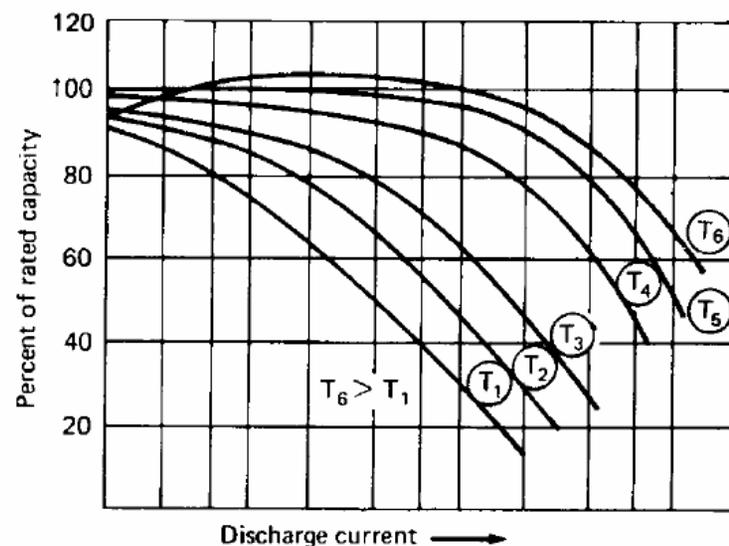
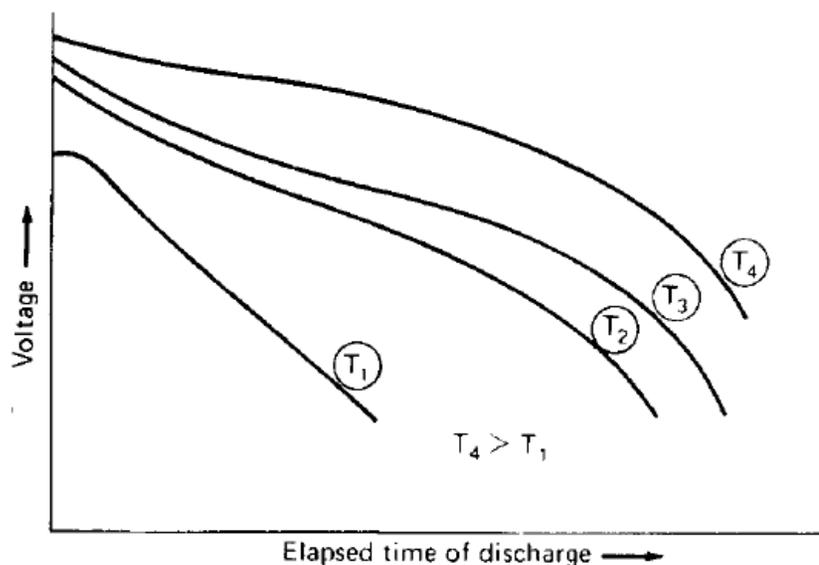
Other Considerations

We mentioned

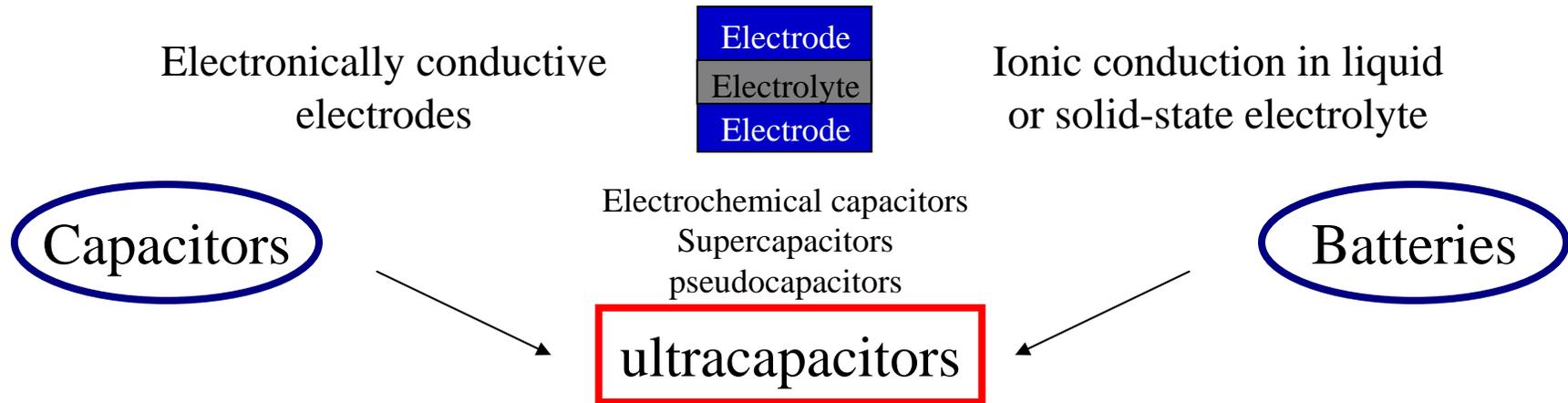
- Current drain
- Shape of discharge curve
- Pulsed operation

Other considerations include:

- Effects of temperature
- Discharge mode (constant power, current, load)
- Self discharge
- Depth of discharge (for secondary)



Supercapacitors



An ultracapacitor has properties of both battery and capacitor

It has a high power density and can be cycled like a capacitor

But it also has a significant energy density like a battery

First ultracapacitor was patented in 1957 using porous carbon electrodes

Different Flavors: carbon, transition metal oxides

Double Layer: Charge stored in double layer at interface between electrolyte and electrode

Pseudocapacitance: Faradaic charge storage at electrode surface

Require high surface area electrodes to achieve large capacitance

Supercapacitors

Supercapacitors have certain advantages over traditional batteries for tracking applications

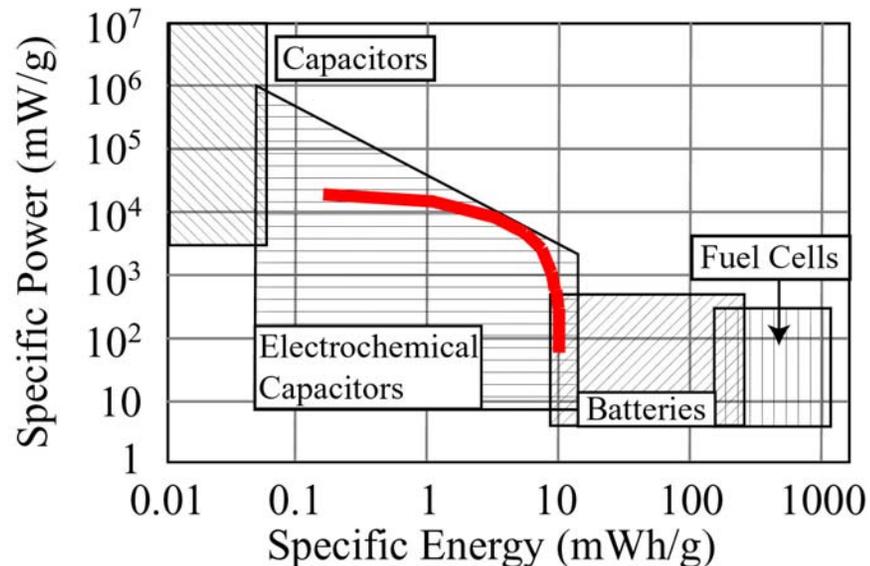
Pros

- Greater cycle life
- Better reversibility → low capacity fade
- Higher power
- Rapid charging discharging

Cons

- Lower energy density
- Shorter shelf life
- Higher self-discharge
- Cost

Red line shows
results from our work



One could envision a supercapacitor for transmitting information, but one must take care not to have too large a duty cycle or it will not sufficiently recharge

Limitations

Why can't we make a super battery that solves all the problems?

Limited energy density: There are only so many coulombs of charge we can store in the system

For instance, $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

This means for every mole of Li, I get 1 mole of electrons $\rightarrow 3.86 \text{ Ah/g}$

Limited conductivities: ions must move from one place to another

Material	Specific Energy (Wh/kg)
Hydrogen	> 30,000
Gasoline	12,200
Methanol	6400
Primary Li battery	2190 (600)
Secondary Li battery	635 (180)
Zn-air	1300 (370)
Alkaline battery	360 (150)
Pb-acid	250 (35)
Compressed air	35

Based on energy density of 'fuel'
Combustion fuels win out

However, that is not the whole story

- Mass/volume of entire system
- Economics of production

The "best" energy device depends on the applications

Materials Challenges

Reactions occur at the electrode surfaces

Need to have ions and electrons together for reactions to occur

→ We want to get as high a surface area as possible

However Electrons must still be able to get outside the cell

→ Electron resistance cannot be too high

Energy of the reactions also depend on the surface properties

e.g. Nanoparticles behave differently than bulk materials

Separator must be robust and allow rapid transfer of ions

Fundamental materials properties need to be understood

Basic materials properties
Transport in porous materials
Interfacial properties