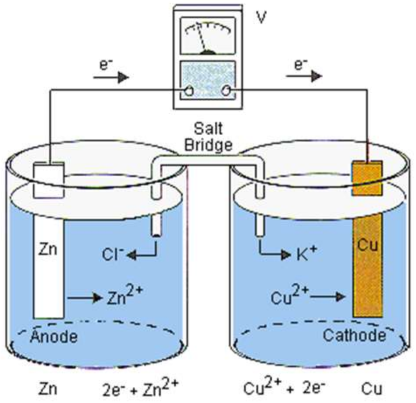
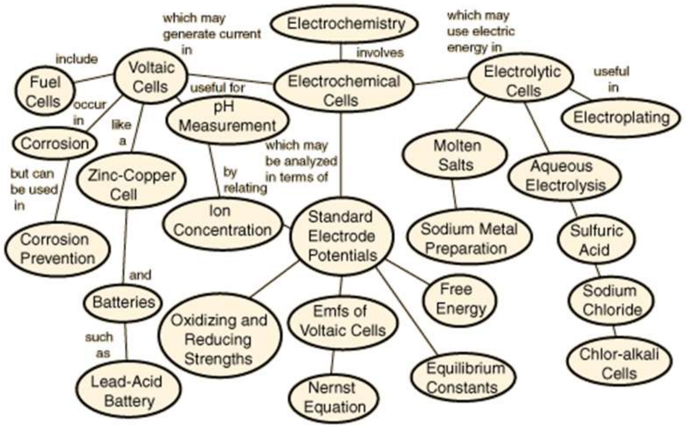
Electrochemistry & Batteries





Lecture - Learning Objectives

At the end of this lecture you should be able to:

- Understand the difference between the heat engine and the electrical approach based systems

- Understand the basic principles of electrochemistry.

- Understand the redox reactions related to battery technology

Heat engine vs. electrical power

- Electrical power's (EP) efficiency is based on the following derivation:

1st law of thermodynamics: $U = Q - W$

$W = Q - \text{U}$

Our efficiency can be defined like this.

$$\eta_{EP} \equiv \frac{-W}{\Delta H}$$

In conversion of electrical energy we don't really have a PV of the electron, thus the PV is effectively 0, and U=ΔH

$$U = \Delta H - PV$$

$$\eta_{EP} = \frac{\Delta H - Q}{\Delta H}$$

In reality W can not be 100% efficient. From the 1st law…

2nd law of thermodynamics: $T\Delta S = Q$

$$\eta_{EP} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} = \frac{\Delta G}{\Delta H}$$

Electrical power production

$$\eta_{EP} = 1 - \frac{T\Delta S}{\Delta H} = \frac{\Delta G}{\Delta H}$$

- This relation scales the opposite way with temperature compared to the Carnot efficiency.
- Hydroelectric can theoretically get 99% energy conversion efficiency. In reality they get 85-90% due to mechanical losses.
- Electrifying all of society could cut our energy demands by ~35-50% - very rough estimate.

Quantitative advantage of electrochemistry

- Take the reaction below:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

- We can:
  - Burn the hydrogen with oxygen to form water and get energy
  - Electrochemically convert (use ΔG) it to get water and energy

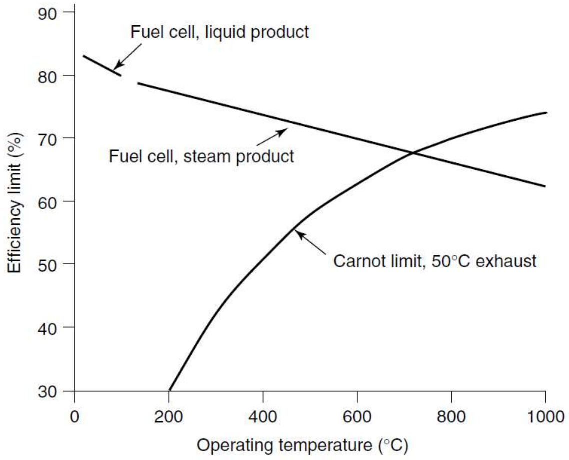
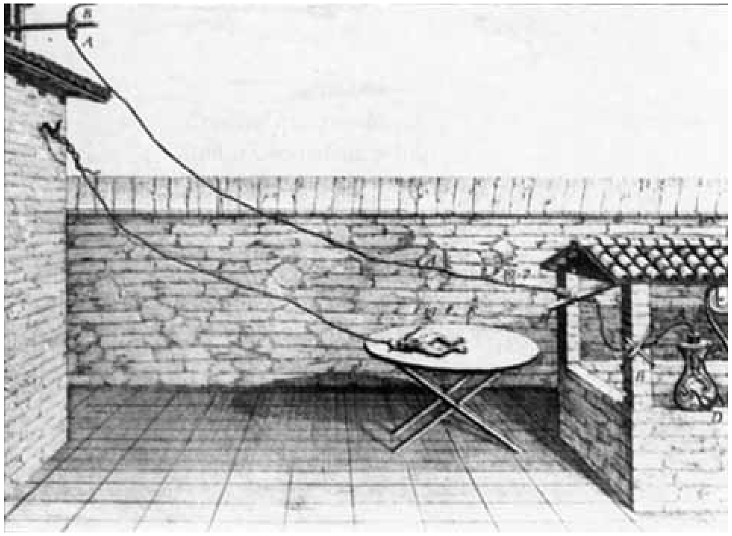


Figure 2.4 Maximum H_2 fuel cell efficiency at standard pressure, with reference to higher heating value. The Carnot limit is shown for comparison, with a 50°C exhaust temperature.

$$\eta_{Carnot} = \frac{T_h - T_c}{T_h}$$

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

History of Electrochemistry



Galvani's test on frog legs

- In 1791 Luigi Galvani first linked chemical reactions with electrical current.
  - He was interested in biochemical reactions and discovered electrochemical reactions from animal tissue.
- In 1800 William Nicholson and John Ritter were able to electrolyze water into H_2 and O_2.
- In 1800, Alessandro Volta developed the first battery with Cu and Zn.
- In 1839 William Grove made a fuel cell in which he produced current by reacting H_2 with O_2 to make water.

Uses of Electrochemistry

- There are 2 major types of electrochemistry
  - Galvanic : This is where chemical reactions force an electrical current
  - Electrolytic: This is where electrical currents force a chemical reaction

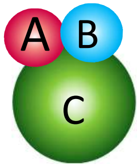
- Batteries:
  - Run galvanically when discharging
  - Run electrolytically when charging

- Molecular fuels (such as hydrogen)
  - Fuel cells operate galvanically
  - Electrolyzers operate electrolytically

- Other uses
  - Galvanic- our nervous system, corrosion
  - Electrolytic- electroplating

Electrochemistry vs. Regular Reaction

- In a regular reaction both A and B are in intimate contact with each other (or contact with a catalyst C).

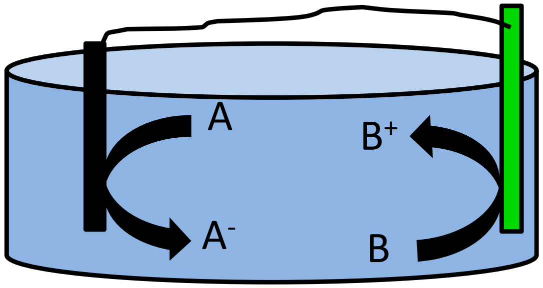


- Below is a generic electrochemcial reaction:

Charged Discharged

$$A + B \rightarrow A^{-} + B^{+}$$

- In an electrochemical reaction A and B can be very far apart, but connected by a wire.



Terminology

Oxidation reaction: The reaction in which an electron is removed.

Reduction reaction: The reaction in which an electron is added

Anode: This is the electrode where oxidation occurs.

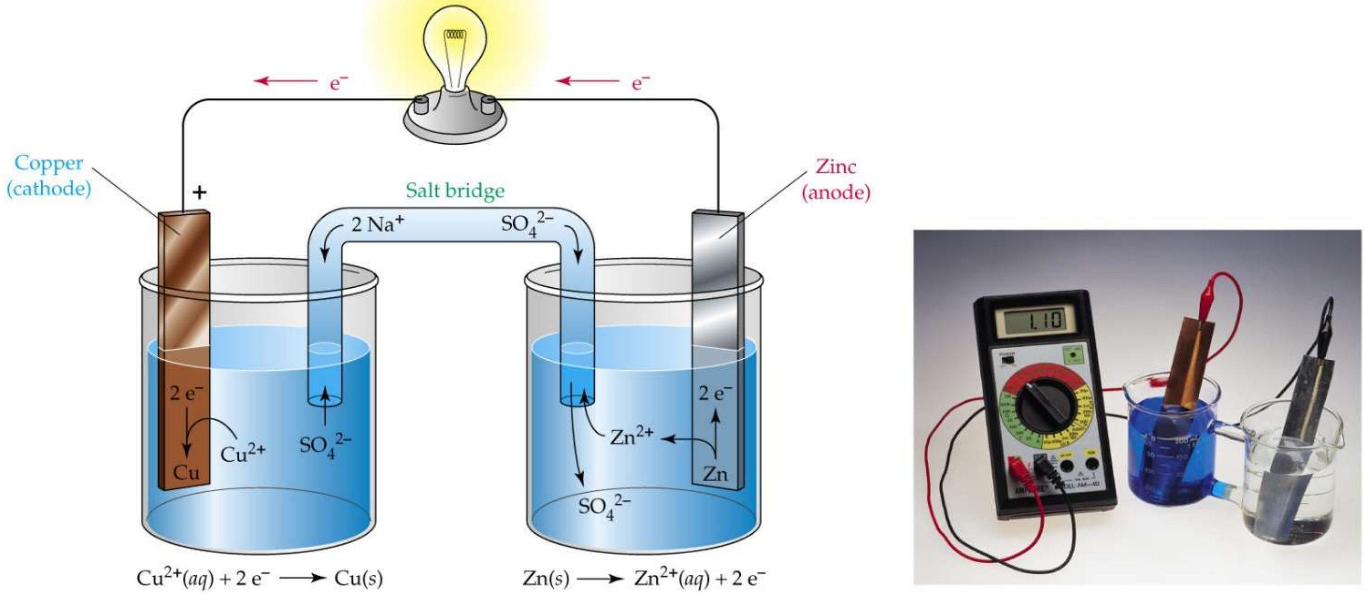
Cathode: This is the electrode where reduction occurs.

Useful Mnemonic:

OIL RIG (**O**xidation **I**s **L**osing electrons; **R**eduction **I**s **G**aining electrons)

Overall Reaction

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$



(a)

(b)

$E_{Cu2+/Cu}$=0.34 V

$E_{Zn/Zn2+}$= -0.76 V

Basics

- Most of electrochemistry is just thermodynamics divided by Faraday's constant.

$$\Delta E = \frac{-\Delta G}{nF}$$

G = Gibbs Free Energy
F = Faraday's Constant (96,485 C/mol e^-)
E = Potential
n= # of electrons in the reaction

- Just like Gibbs free energy is a relative term, so is the potential.
- For our Cu/Zn reaction, we have the following.

(i.e. Products – Reactants)

$$\Delta E = \frac{\left({G_f}^{Cu} + {G_f}^{Zn^{2+}} - {G_f}^{Cu^{2+}} - {G_f}^{Zn}\right)}{nF}$$

- Gibbs fee energy of formation (G_f) can be found in reference books. For all pure elements (i.e. Cu, Zn, O_2 ,H_2), this is defined as 0.

Exercise

- Assume you had the following reaction instead:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

- Theoretically how much energy could you get from 1 mol of H_2?
- How much hydrogen would you need to power an average laptop (60W) for 1 hour?
- What would be the theoretical potential of this reaction?

$$\Delta E = \frac{-\Delta \mathrm{G}}{nF}$$

F = Faraday's Constant (96,485 C/mol e^-)

Gibbs Free energy of H_2O is -237 kJ/mol

Exercise

- Assume you had the following reaction instead:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

H_2 Fuel cell reaction →

← Electrolysis

- Theoretically how much energy could you get from 1 mol of H_2?

Answer: 237 KJ (Since H_2 and O_2 both have G_f=0)

- How much hydrogen would you need to power an average laptop (60W) for 1 hour?

Answer: 60W for 1hour = 60 W for 3600S =216 kJ, thus 237 kJ/ 216 kJ = 0.9 mol H_2

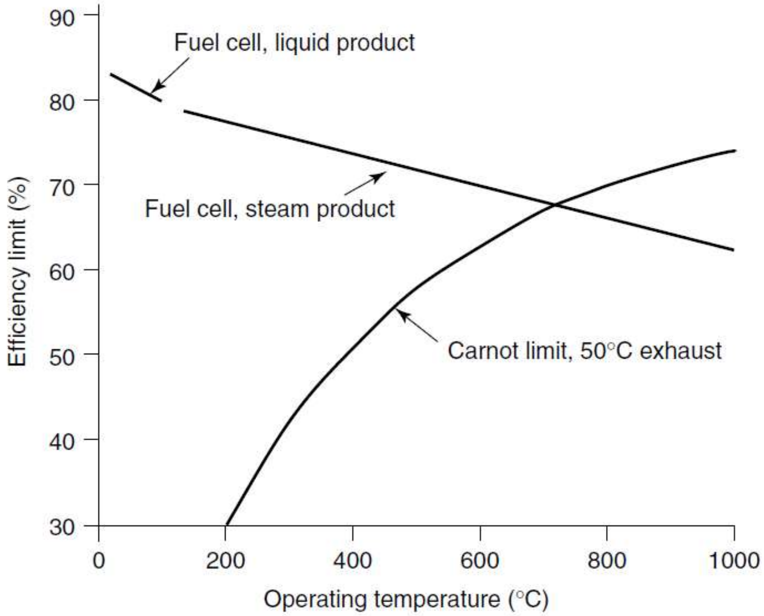
- What would be the theoretical potential of this reaction?

$$\Delta E = \frac{\Delta \mathrm{G}}{nF} = \frac{G_f(H_2O) - G_f(O_2) - G_f(H_2)}{2 \times 96{,}485} = \frac{237{,}000 - 0 - 0}{2 \times 96{,}485} = 1.23\ \mathrm{V}$$

Hydrogen fuel cell efficiency

- From earlier we defined electrical efficiency as $\eta = \frac{\Delta G}{\Delta H}$
- Since H_2 and O_2 both are elements, their G_f, & H_f = 0 thus this is all about the H_2O. For H_2O:
  - G^f=-237 KJ/mol,
  - H^f=-286 KJ/mol (called Higher Heating Value- (HHV))

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H} = \frac{237\ kJ/mol}{286\ kJ/mol}\ or\ \frac{1.23\ V}{1.48\ V} = 83\%$$



‘Back to the’ Basics

- Most of electrochemistry is just thermodynamics divided by Faraday’s constant.

$$\Delta E = \frac{-\Delta \mathrm{G}}{nF}$$

G = Gibbs Free Energy
F = Faraday’s Constant (96,485 C/mol e^-)
E = Potential
n= # of electrons in the reaction

- Just like Gibbs free energy is a relative term, so is the potential.
- For our Cu/Zn reaction, we have the following.

$$\Delta E = \frac{-\left(G_f{}^{Cu} + G_f{}^{Zn^{2+}} - G_f{}^{Cu^{2+}} - G_f{}^{Zn}\right)}{nF}$$

This is useful since each ‘half’ reaction occurs at a different electrode.

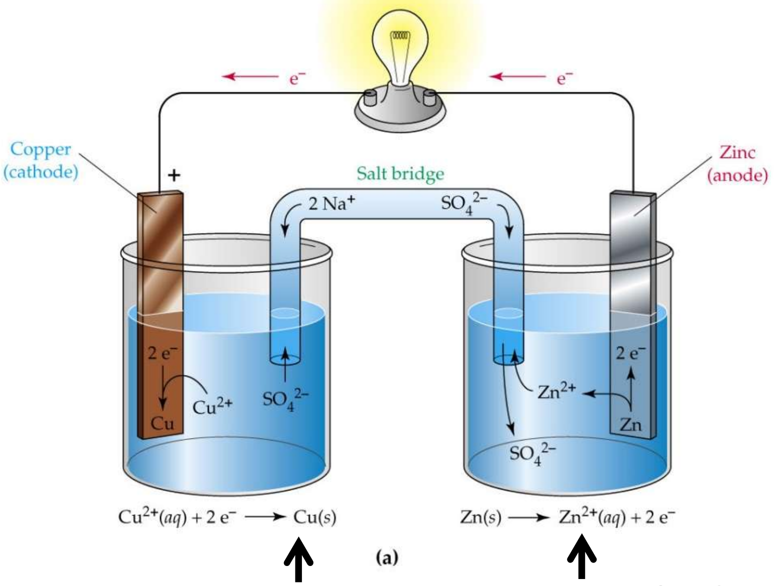
$$\Delta E = \frac{-\left(G_f{}^{Cu} - G_f{}^{Cu^{2+}}\right) - \left(G_f{}^{Zn} - G_f{}^{Zn^{2+}}\right)}{nF} = E^{Cu/Cu^{2+}} - E^{Zn/Zn^{2+}}$$

Breaking a Reaction down

Overall Reaction

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

- The overall reaction is really just a combination of the ‘Cu side’ and the ‘Zn side’ reaction



$E_{Cu2+/Cu}$=0.34 V $E_{Zn/Zn2+}$=-0.76 V

$$\Delta E = E^{Cu/Cu^{2+}} - E^{Zn/Zn^{2+}}$$

Half Reactions

- Rather than have an entire reaction like this:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

- We can write 2 equivalent 'half-reactions'. One for the reduction reaction and one for the oxidation reaction.

Reduction (Cathode): $Cu^{2+} + 2e^{-} \rightarrow Cu$ $\quad E^{Cu/Cu^{2+}} = 0.34\,V$

Oxidation (Anode): $\underline{Zn \rightarrow Zn^{2+} + 2e^{-}}$ $\quad E^{Zn/Zn^{2+}} = -0.76\,V$

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

- In our half reactions we have electron and can also have protons (i.e. acid) or hydroxide ions (i.e. base)

Half Reactions

- The keys to writing half reactions are as followed:

1) The anode reaction + cathode reaction need to equal the overall reaction.

2) All the atoms and charges on the left side of a half reaction need to balance the right side.

3) All the species on both sides need to be stable entities (in the electrolyte).

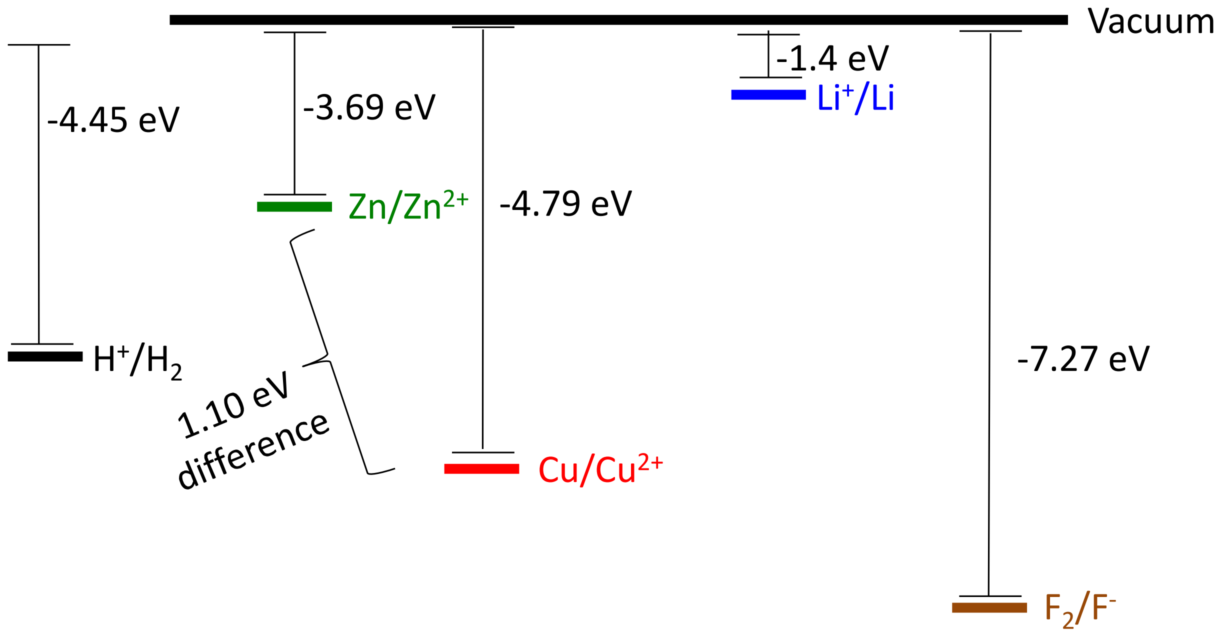
Anode Reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode Reaction: $2e^- + 2H^+ + \frac{1}{2}O_2 \rightarrow H_2O$

Overall Reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Redox Potentials

- In electrochemistry we have 2 ‘half reactions’, which are completely seperate from each other from an energy standpoint.
- Thus it would be nice to relate each half reaction to a constant standard to easily switch out half reactions.



Reference electrode-NHE

- Our reference can be anything, but it should be something useful

- This can be field dependent. Batteries, use Li/Li$^+$, whereas most other field use the hydrogen half reaction

$$H_2 \leftrightarrow 2H^+ + 2e^-$$

- A normal hydrogen electrode (NHE) is defined when the hydrogen gas is at 1 atm and the acid is 1M H$^+$.

Sidenote- There is also a term called standard hydrogen electrode (SHE), which is often used interchangeably with NHE. The actual difference is an SHE use 1bar pressure and NHE uses 1 atm pressure.

Changing Concentrations

- The redox potential is the potential where we have 50% reactant and 50% product.

$$H_2 \leftrightarrow 2H^+ + 2e^-$$

- For the hydrogen reaction this means our equilibrium constant is 1 at the redox potential.

$$K = \frac{[H^+]^2}{[H_2]} = 1$$

- What if we change the concentration of H^+?

$$G = -RTln(K)$$

$$nF\Delta E = -RTln\left(\frac{[H^+]^2}{[H_2]}\right)_{Ref} + RTln\left(\frac{[H^+]^2}{[H_2]}\right)$$

Reference case

Changed conditions

Nernst Equation

$$\Delta E = -\frac{RT}{nF} ln\left(\frac{Products}{Reactants}\right)$$

$$nF\Delta E = -RTln\left(\frac{[H^+]^2}{[H_2]}\right)_{Ref} + RTln\left(\frac{[H^+]^2}{[H_2]}\right)$$

Assume we have a change in H^+, but no change in H_2 concentration

$$E_{new} = E_{initial} + \frac{2RT}{nF} ln[H^+]_{Ref} - \frac{2RT}{nF} ln[H^+]$$

n=2… This term will almost always match the power of the product (thus canceling out)

$$E_{new} = E_{initial} + \underbrace{\frac{RT}{2.303F}}_{\text{59 mV at room temperature}} log[\Delta H^+]$$

$$E_{new} = E_{initial} - \underbrace{59mV * pH}_{\text{Called ‘Nernstian Shift’}}$$

Nernstian Shift

- The Nernst Equation and its effect on potential is highly useful in analyzing situations
- This shows the effect of varying concentration or pressures in terms of voltage
- Alternatively changes in potential can be used as a probe to monitor changes in operating conditions. (i.e. pH meters)

$$\Delta E = -\Delta \frac{RT}{nF} ln\left(\frac{Products}{Reactants}\right)$$

For reaction involving H^{+} *@ 25C*

$$E_{new} = E_{initial} - 59mV * pH$$

Concept Check

Which one(s) of these half reactions is a function of pH:

a) . $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

b) . $4NaCl + O_2 + H_2O + 4e^- \rightarrow 4NaOH + 4Cl^-$

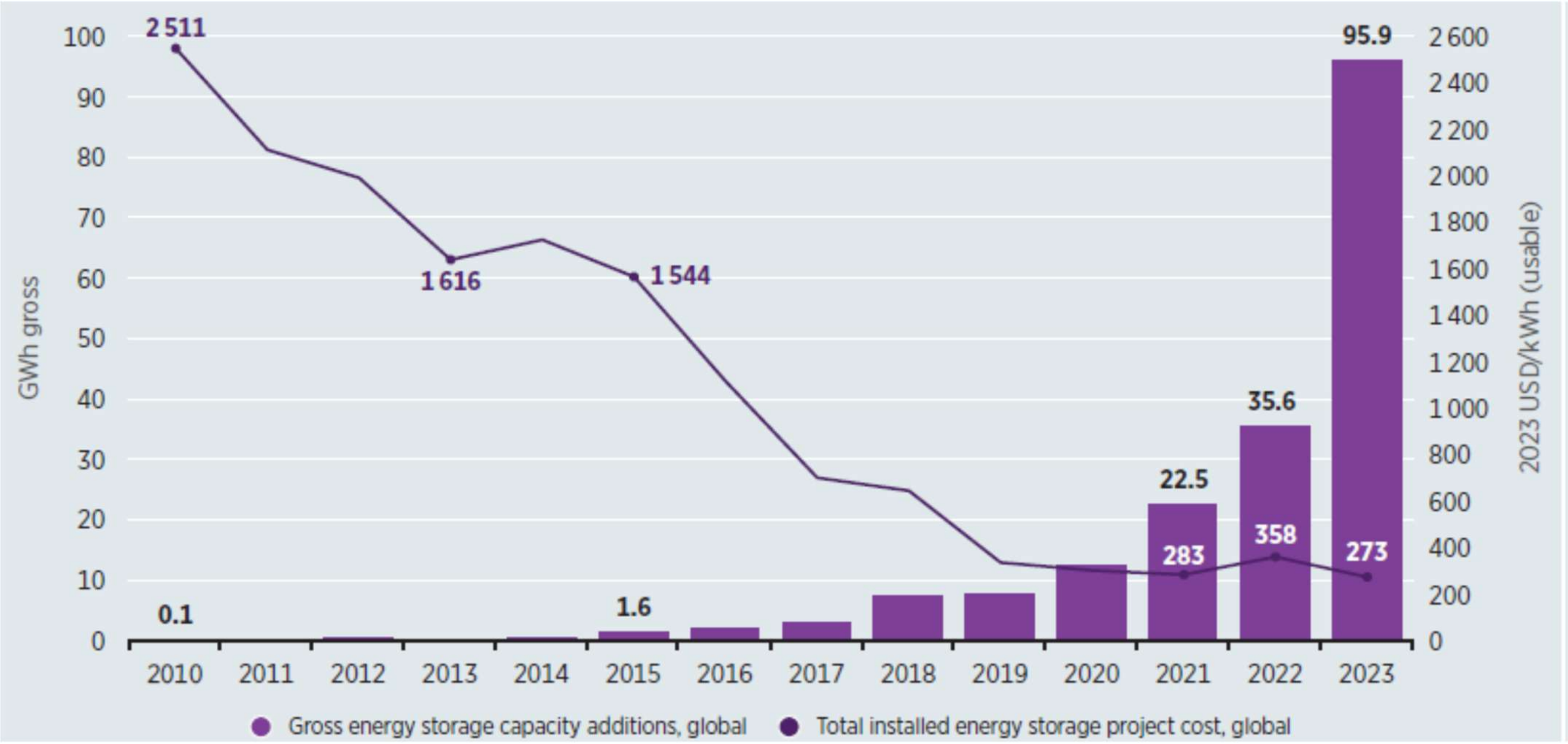
c) . $H_2SO_4 + 2e^- \rightarrow H_2 + 4{SO_4}^-$

d) . $AgCl + e^- \rightarrow Ag + Cl^-$

Batteries

Economics

- Price goes down, demand goes up



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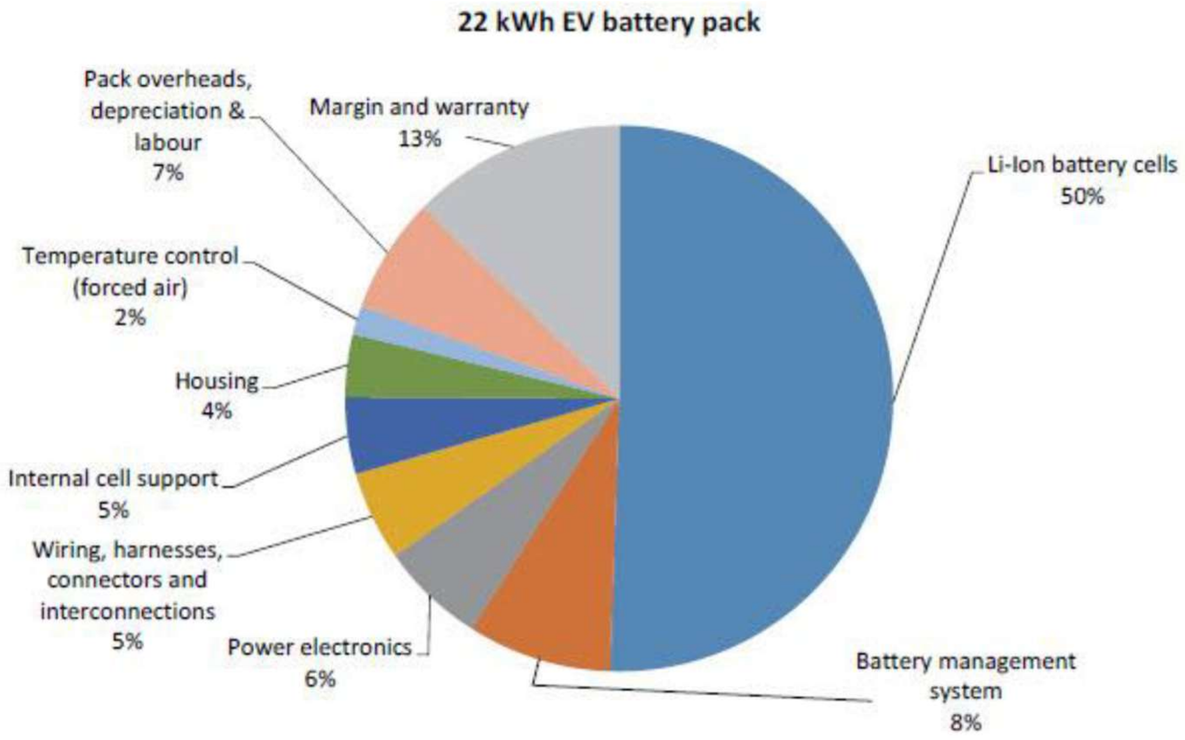
Economics in Electrical Vehicles

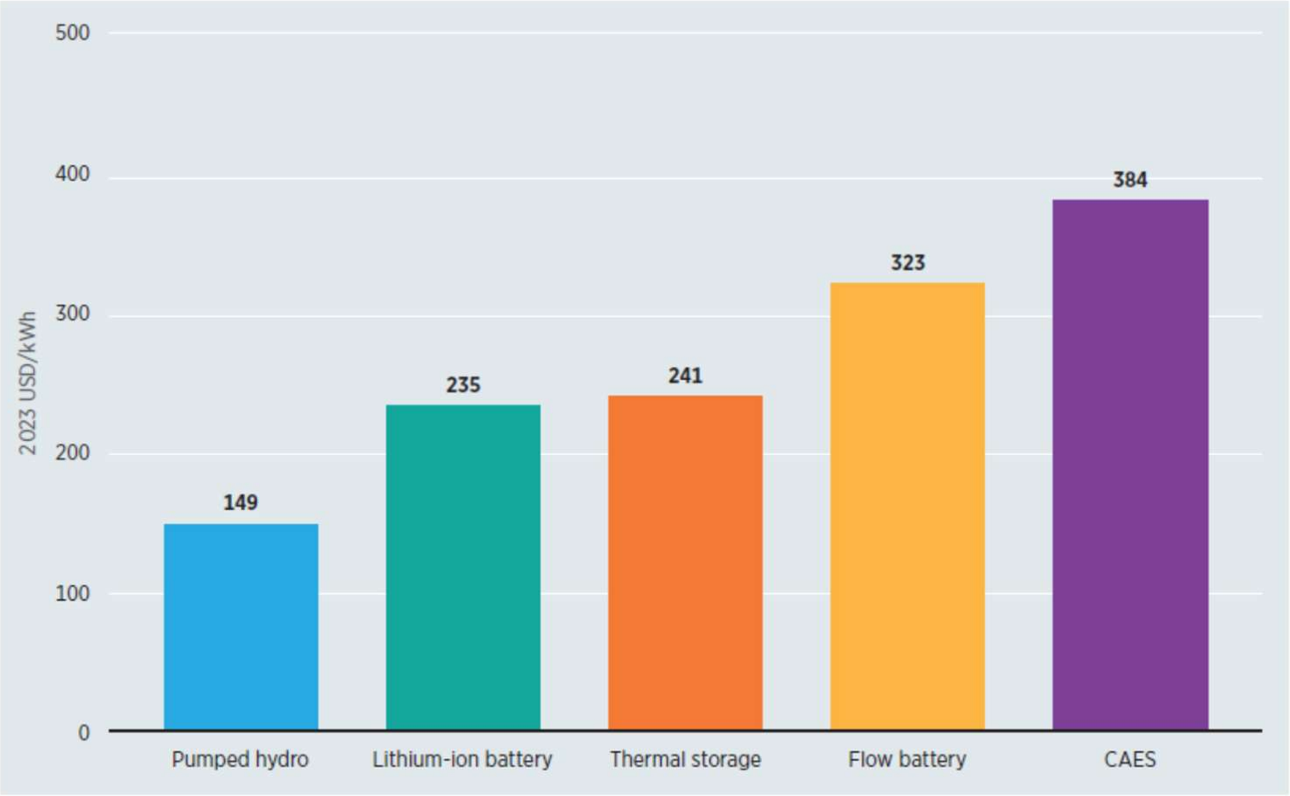
- There is more to a battery cost than just the cell.



Reference: doi:[10.2991/ahe.k.210202.005](10.2991/ahe.k.210202.005)

Economics

- Even for long-term storage, Li-ion batteries look quite good



Source: AURORA(2022, 2023); BNEF (2024b); DESNZ (2023).
Note: CAES = Compressed Air Energy Storage; kWh = kilowatt hour.

IRENA Renewable Power Generation, 2023

Basic Principles

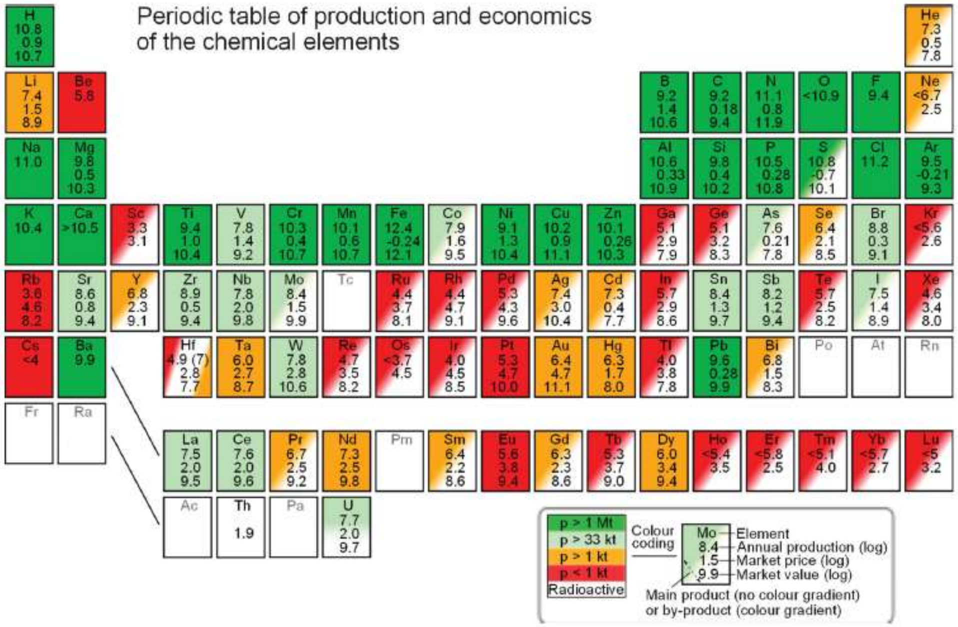
- Both energy and power are important.

$$E = P \times t$$

$$P = V \times i$$

E = Energy
P = Power
t = Time
V = Voltage
i = current

- We can use Peter Vesborg's paper to look at materials cost.



Periodic table of production and economics of the chemical elements

H 10.8 0.9 10.7																	He 7.3 0.5 7.8
Li 7.4 1.5 8.9	Be 5.8											B 9.2 1.4 10.6	C 9.2 0.18 9.4	N 11.1 0.8 11.9	O <10.9	F 9.4	Ne <6.7 2.5
Na 11.0	Mg 9.8 0.5 10.3											Al 10.6 0.33 10.9	Si 9.8 0.4 10.2	P 10.5 0.28 10.8	S 10.8 -0.7 10.1	Cl 11.2	Ar 9.5 -0.21 9.3
K 10.4	Ca >10.5	Sc 3.3 3.1	Ti 9.4 1.0 10.4	V 7.8 1.4 9.2	Cr 10.3 0.4 10.7	Mn 10.1 0.6 10.7	Fe 12.4 -0.24 12.1	Co 7.9 1.6 9.5	Ni 9.1 1.3 10.4	Cu 10.2 0.9 11.1	Zn 10.1 0.26 10.3	Ga 5.1 2.9 7.9	Ge 5.1 3.2 8.3	As 7.6 0.21 7.8	Se 6.4 2.1 8.5	Br 8.8 0.3 9.1	Kr <5.6 2.6
Rb 3.6 4.6 8.2	Sr 8.6 0.8 9.4	Y 6.8 2.3 9.1	Zr 8.9 0.5 9.4	Nb 7.8 2.0 9.8	Mo 8.4 1.5 9.9	Tc	Ru 4.4 3.7 8.1	Rh 4.4 4.7 9.1	Pd 5.3 4.3 9.6	Ag 7.4 3.0 10.4	Cd 7.3 0.4 7.7	In 5.7 2.9 8.6	Sn 8.4 1.3 9.7	Sb 8.2 1.2 9.4	Te 5.7 2.5 8.2	I 7.5 1.4 8.9	Xe 4.6 3.4 8.0
Cs <4	Ba 9.9		Hf 4.9 (7) 2.8 7.7	Ta 6.0 2.7 8.7	W 7.8 2.8 10.6	Re 4.7 3.5 8.2	Os <3.7 4.5	Ir 4.0 4.5 8.5	Pt 5.3 4.7 10.0	Au 6.4 4.7 11.1	Hg 6.3 1.7 8.0	Tl 4.0 3.8 7.8	Pb 9.6 0.28 9.9	Bi 6.8 1.5 8.3	Po	At	Rn
Fr	Ra																
			La 7.5 2.0 9.5	Ce 7.6 2.0 9.6	Pr 6.7 2.5 9.2	Nd 7.3 2.5 9.8	Pm	Sm 6.4 2.2 8.6	Eu 5.6 3.8 9.4	Gd 6.3 2.3 8.6	Tb 5.3 3.7 9.0	Dy 6.0 3.4 9.4	Ho <5.4 3.5	Er <5.8 2.5	Tm <5.1 4.0	Yb <5.7 2.7	Lu <5 3.2
			Ac	Th 1.9	Pa	U 7.7 2.0 9.7											

Colour coding
🟩 p > 1 Mt
🟩 p > 33 kt
🟧 p > 1 kt
🟥 p < 1 kt
☐ Radioactive

Mo — Element
8.4 — Annual production (log)
1.5 — Market price (log)
9.9 — Market value (log)
Main product (no colour gradient) or by-product (colour gradient)

Maximize Voltage

- Find an oxidation and reduction reaction with a large difference in potential.

Conductivity issues

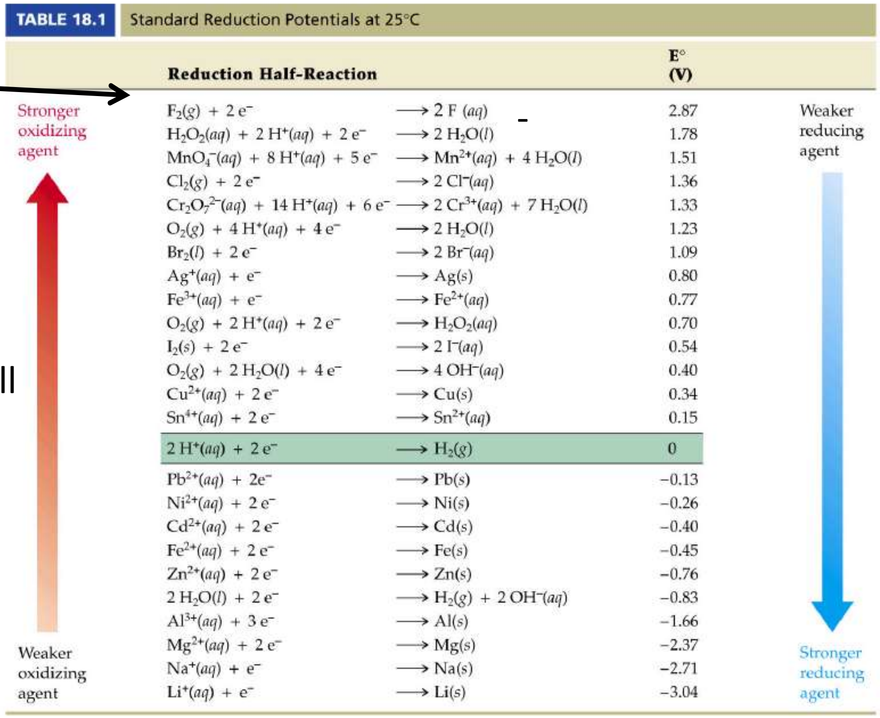


TABLE 18.1 Standard Reduction Potentials at 25°C

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

- Image from Prentice-Hall publishing

- About 500 redox potentials can be found in CRC Handbook

Concept Check

What battery will have the highest potential? (Refer to standard reduction potential of species graph):

a) . $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

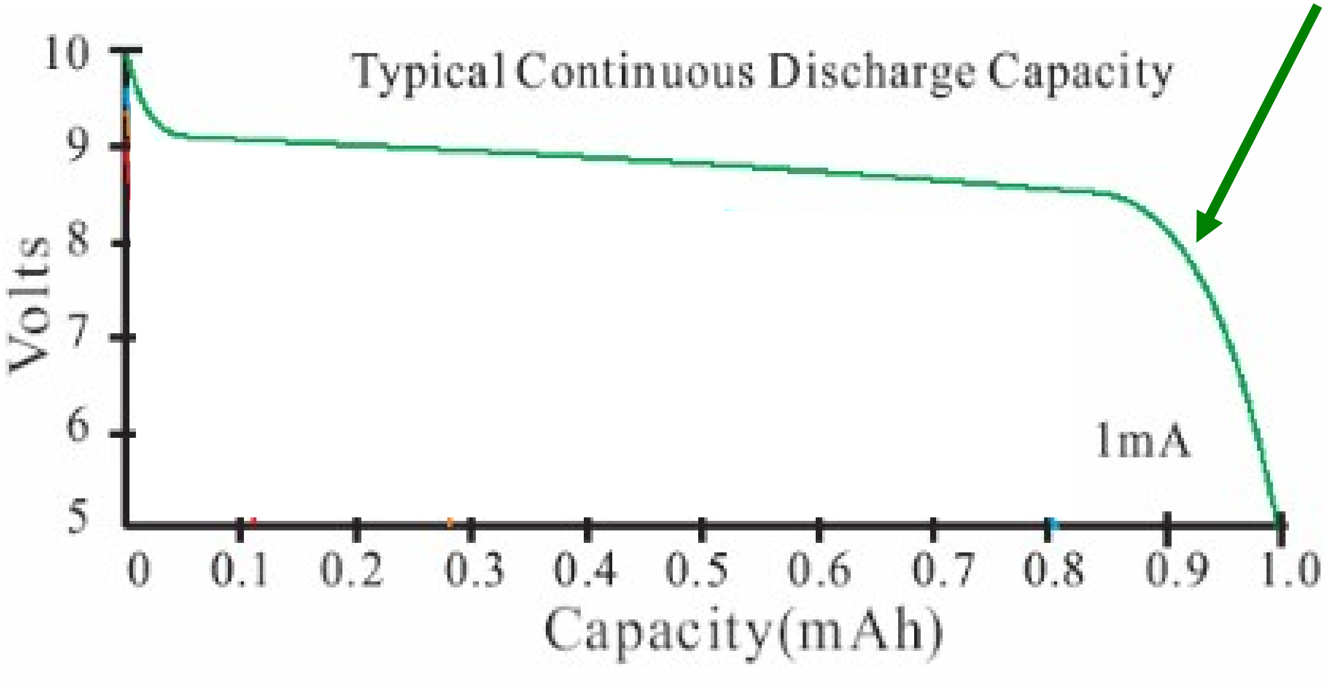
b) . $2Ag^{+} + Pb \leftrightarrow Ag + Pb^{2+}$

c) . $2NaCl \leftrightarrow Na + Cl_2$

d) . $O_2 + H_2 \leftrightarrow H_2O$

Voltage vs. Current

- The key to a good battery is an easy redox reaction.
- This should lead to an i-V curve as followed:



Logarithmic decay due to Nernstian shift

Types of Batteries

- Batteries can be group into 2 types:

- **Primary Batteries** (non-rechargeable)- Examples are:
  - Typcially Alkaline batteries (typical 9V, AAA, AA, C, D)
  - Aluminum batteries
  - Carbon fluoride batteries

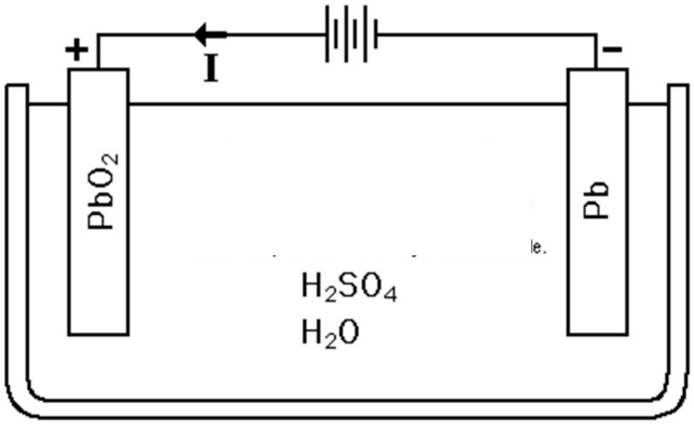
- **Secondary Batteries** (rechargeable)- Examples are:
  - Lead-Acid batteries
  - Nickel-Cadmium batteries
  - Lithium ion batteries

- Since we are focused on sustainability we will only focus on secondary batteries.

Lead Acid

- These are the typical car batteries in internal combustion cars.

$$\begin{array}{rl} \text{Anode:} & \mathrm{Pb} + H_2SO_4 \quad \rightarrow \mathrm{Pb}SO_4 + 2H^+ + 2e^- \\ \text{Cathode:} & \mathrm{Pb}O_2 + H_2SO_4 \quad +2H^+ + 2e^- \rightarrow \mathrm{Pb}SO_4 + 2H_2O \\ \hline & \mathrm{Pb} + \mathrm{Pb}O_2 + 2H_2SO_4 \rightarrow 2\mathrm{Pb}SO_4 + 2H_2O \end{array}$$



Lead Acid

- How much charge/kg can you obtain from these devices? Answer in C/Kg

- Given these devices have an open circuit voltage of 2.1 V, how much Energy/kg can these devices theoretically hold? Answer in kJ/kg

Anode: $\mathrm{Pb} + H_2SO_4{}^- \rightarrow \mathrm{Pb}SO_4 + 2H^+ + 2e^-$

Cathode: $\mathrm{Pb}O_2 + H_2SO_4{}^- + 2H^+ + 2e^- \rightarrow \mathrm{Pb}SO_4 + 2H_2O$

$$\mathrm{Pb} + \mathrm{Pb}O_2 + 2H_2SO_4 \rightarrow 2\mathrm{Pb}SO_4 + 2H_2O$$

Molecular weight Pb= 207 g/gmol
Molecular weight of H_2SO_4=98 g/mol
Molecular weight of an oxygen atom = 16 g/mol
Faraday's constant = 96,485 C/mol e-

Lead Acid

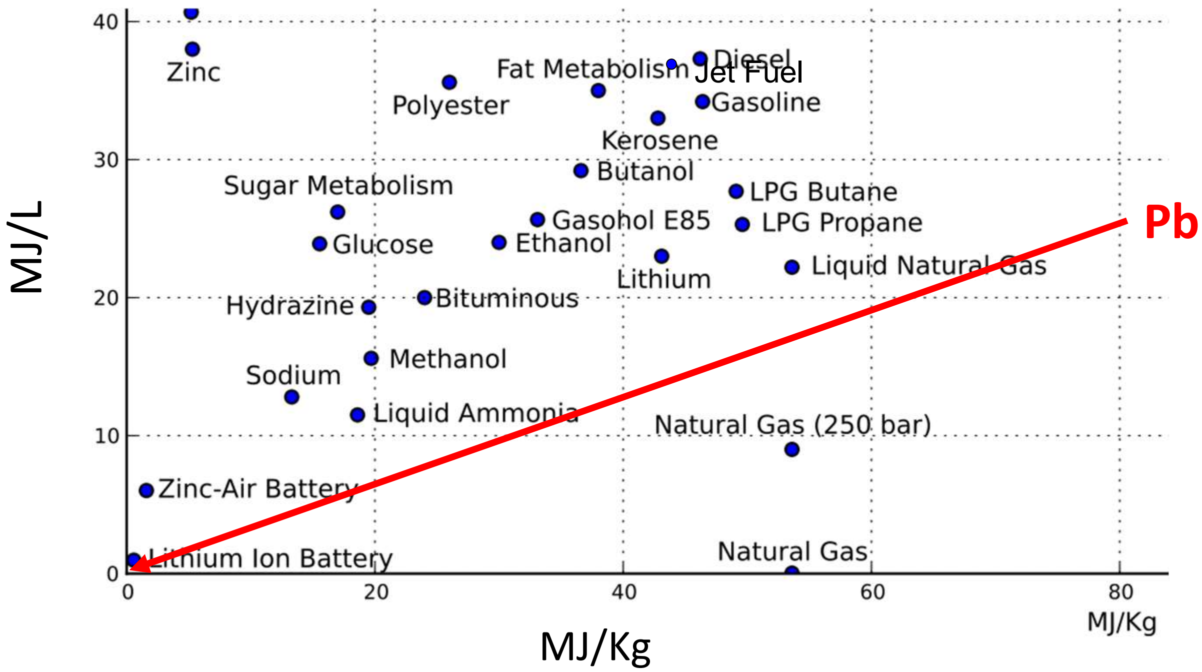
- How much charge/kg can you obtain from these devices?
  - Mol. Weight of $PbSO_4$ + H_2O= 323 g/mol
  - 1kg = 3.1 mol $PbSO_4$ and 3.1 mol H_2O
  - You need 2 atoms of Pb for every 2 e- transferred,
  - 3.1 mol Pb = 3.1 mol e-
  - 1 mol e- = 96,485 C (Faraday's constant.)
  - Thus we have 299,000 Coulumbs/Kg.

- Given these devices have an open circuit voltage of 2.1 V, how much Energy/Kg can these devices theoretically hold?
  - Energy= Columbs x Voltage = 299,000x 2.1 = 628 KJ/Kg .
  - or 628 / (207 g/g-mol Pb / 323 g/gmol total) = 980 KJ/Kg Pb.

- Dilution of the acid makes this value lower for real devices (typically about 140 kJ/kg).

Will we burn things in a sustainable society?

- Airplanes and boats almost certainly will need the energy density from molecules not batteries.



Pb acid Battery

● Hydrogen

140 MJ/kg,
10 MJ/L

Lead Acid

- The open circuit voltage is about 2.1 V.
- Durability- 1200 cycles (5 years in a car). Tesla's have Pb acid batteries in them as a starter battery (until 2021).
- Auto industry uses 1 million tons of lead for batteries and an extra ~7% is used/lost in the mining/manufacturing process of batteries.
- Deactivation mechanism- $PbSO_4$ crystallizes and becomes compact preventing it's ability to react.
- Corrosion issues from the acid, and potential explosions from electrolysis (H_2 + O_2) are other issues with this.

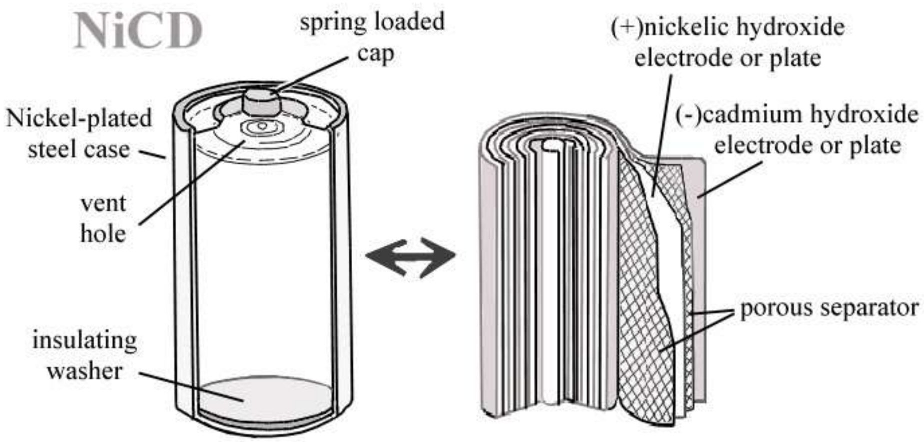
NiCd

- NiCd was traditionally used as rechargeable batteries

Anode: $\mathrm{Cd} + OH^{-} \rightarrow \mathrm{Cd}(OH)_2 + 2e^{-}$

Cathode: $\underline{2\mathrm{NiO}(OH) + 2H_2O + 2e^{-} \rightarrow 2\mathrm{Ni}(OH)_2 + 2OH^{-}}$

$$2\mathrm{NiO}(OH) + \mathrm{Cd} + 2H_2O \rightarrow 2Ni(OH)_2 + \mathrm{Cd}(OH)_2$$



- Open Circuit Voltage = 1.2 V.
- Energy density = 140 kJ/kg.
- Durability = 2000 cycles
- Issue = Cd is toxic

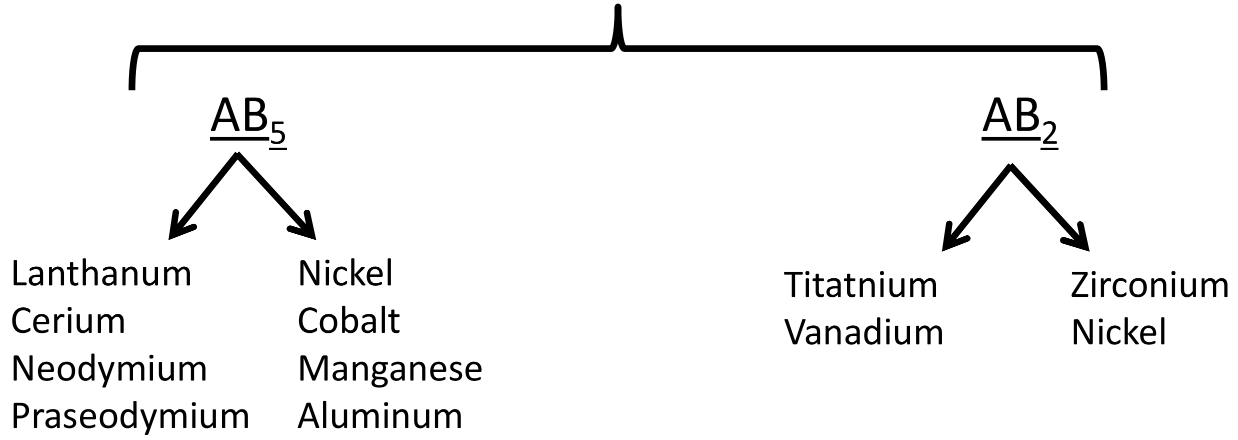
Ni Metal Hydride

- These are replacing NiCd electrodes becuase the reactions are quite similar.

Cathode: $H_2O + M + e^- \rightarrow OH^- + \mathrm{MH}$

Anode: $\mathrm{Ni}(OH)_2 + 2OH^- \rightarrow 2\mathrm{NiO}(OH) + H_2O + e^-$

$$\mathrm{Ni}(OH)_2 + \mathrm{M} \rightarrow \mathrm{NiO}(OH) + \mathrm{MH}$$



M = Metals (or Metal Composites)

AB$_5$

Lanthanum
Cerium
Neodymium
Praseodymium

Nickel
Cobalt
Manganese
Aluminum

AB$_2$

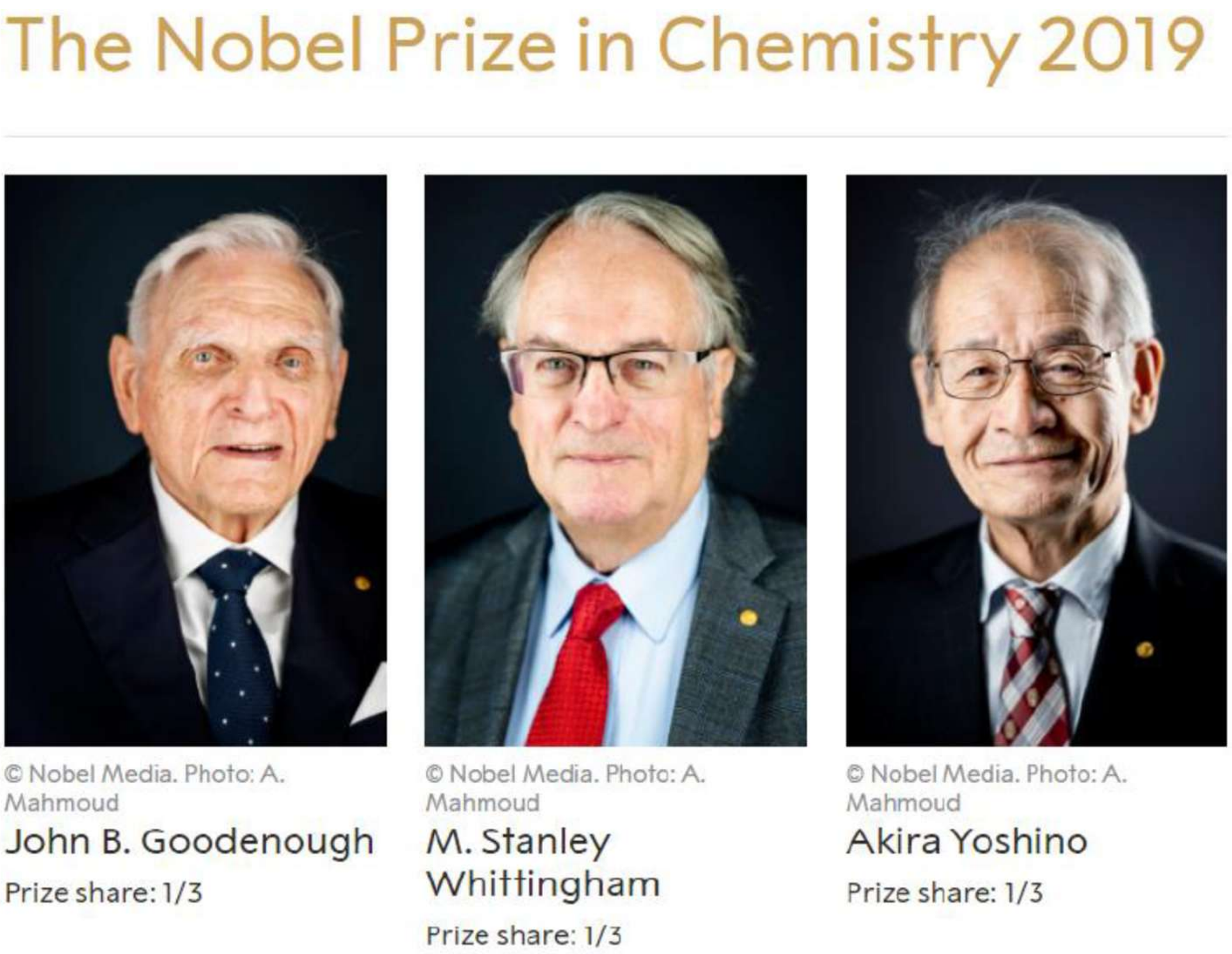
Titatnium
Vanadium

Zirconium
Nickel

Nickel Metal Hydride

- The specific energy is 360 kJ/kg. This is 3 times higher than NiCd.
- The open circuit voltage is about 1.2 V.
- Durability- 500- 2000 cycles or 2-5 years.
- These are used in many of the older electric cars.
- Self discharge of 20-50% per year.
- Too fast charging or allowing the battery to discharge completely can lead to permanent damage.

Toyota Prius Battery



The Nobel Prize in Chemistry 2019

© Nobel Media. Photo: A. Mahmoud

John B. Goodenough

Prize share: 1/3

© Nobel Media. Photo: A. Mahmoud

M. Stanley Whittingham

Prize share: 1/3

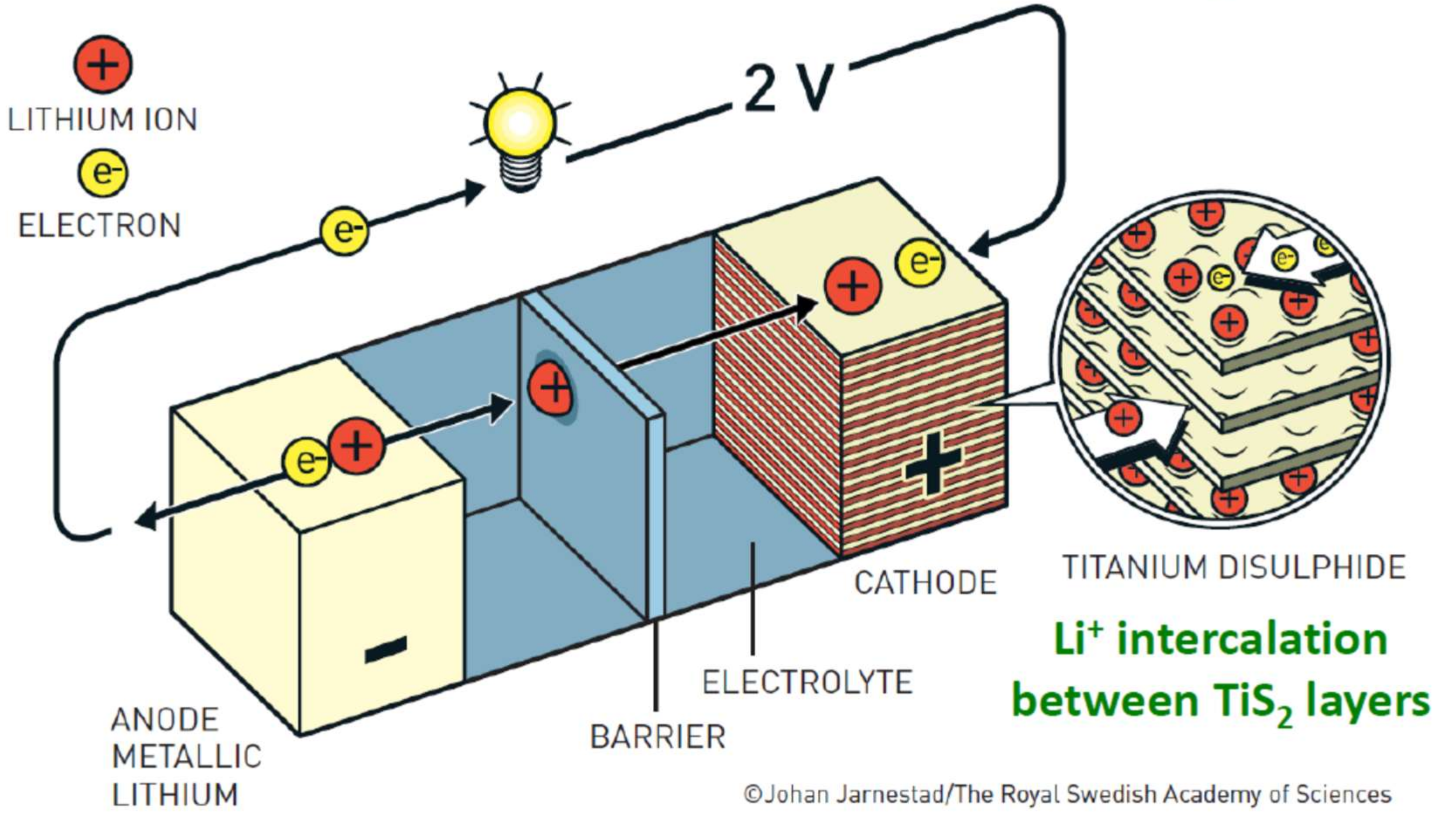
© Nobel Media. Photo: A. Mahmoud

Akira Yoshino

Prize share: 1/3

The Nobel Prize in Chemistry 2019 was awarded jointly to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries."

Cathode: $x\text{Li}^+ + x\text{e}^- + \text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2$



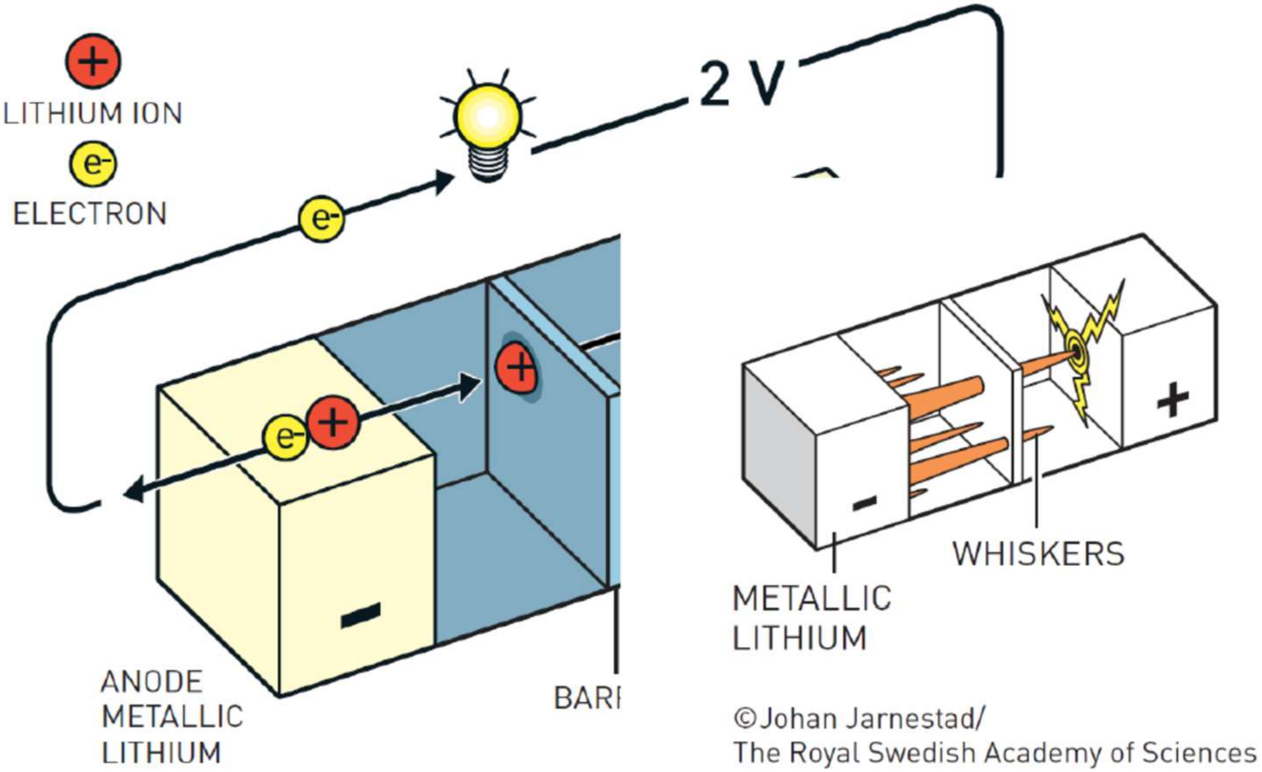
Li$^+$ intercalation between TiS$_2$ layers

©Johan Jarnestad/The Royal Swedish Academy of Sciences

Anode: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Whittingham's battery (ca. 1973)

Whiskers kill the battery (short circuit!) ☹



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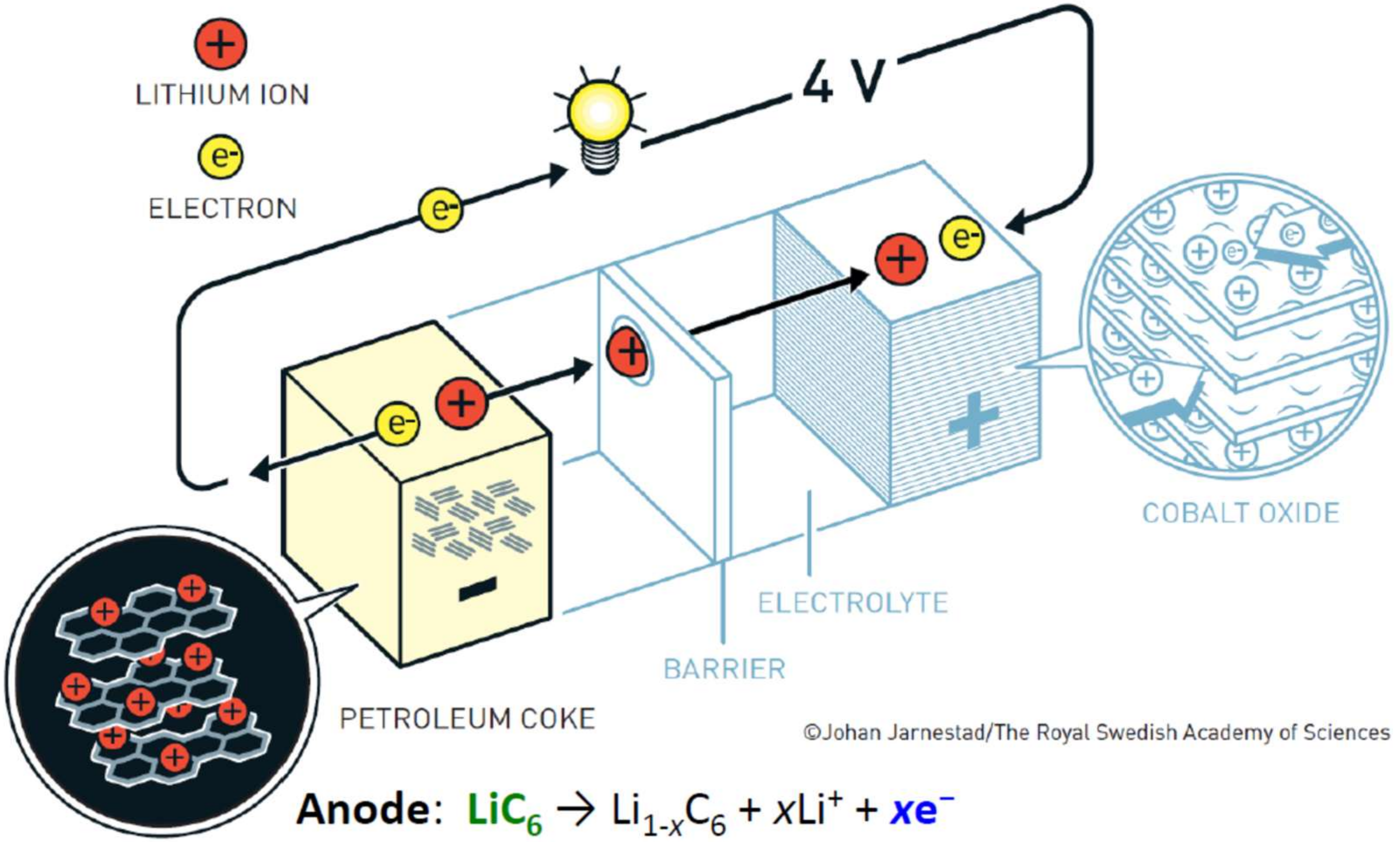
The Royal Swedish Academy of Sciences

Whittingham’s battery (ca. 1973)

Cathode: $x\mathrm{Li}^+ + \boldsymbol{xe^-} + \mathrm{CoO_2} \rightarrow \mathrm{Li}_x\mathrm{CoO_2}$



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Anode: $\mathrm{LiC_6} \rightarrow \mathrm{Li}_{1-x}\mathrm{C}_6 + x\mathrm{Li}^+ + \boldsymbol{xe^-}$

Yoshino's battery (ca. 1985)

Li-ion Batteries- Layered Materials

- In TiS_2 the Ti^{3+}/Ti^{4+} was the redox couple.
- No higher voltage redox couples could be used else it would oxidize the sulfur.
- John Goodenough realized switching from a sulfide to an oxide could allow greater voltages.
- $LiCo_2$ looks good, but since 50% its orbital overlaps with oxygen, you can only get about 50% theoretical capacity

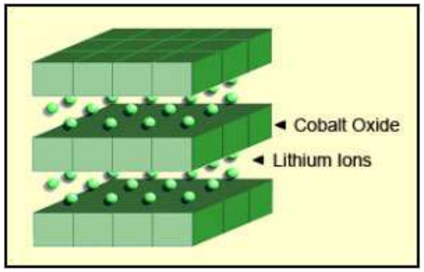


Image from BatteryUniversity.com

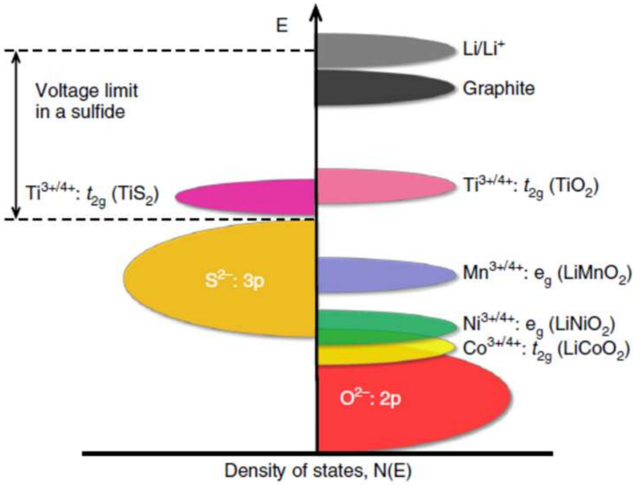


Fig. 1 Positions of the redox energies relative to the top of the anion: p bands. The top of the S^{2-}:3p band lying at a higher energy limits the cell voltage to <2.5 V with a sulfide cathode. In contrast, the top of the O^{2-}:2p band lying at a lower energy enables access to lower-lying energy bands with higher oxidation states and increases the cell voltage substantially to ~4 V.

Manthiram, Nat Com., 2020

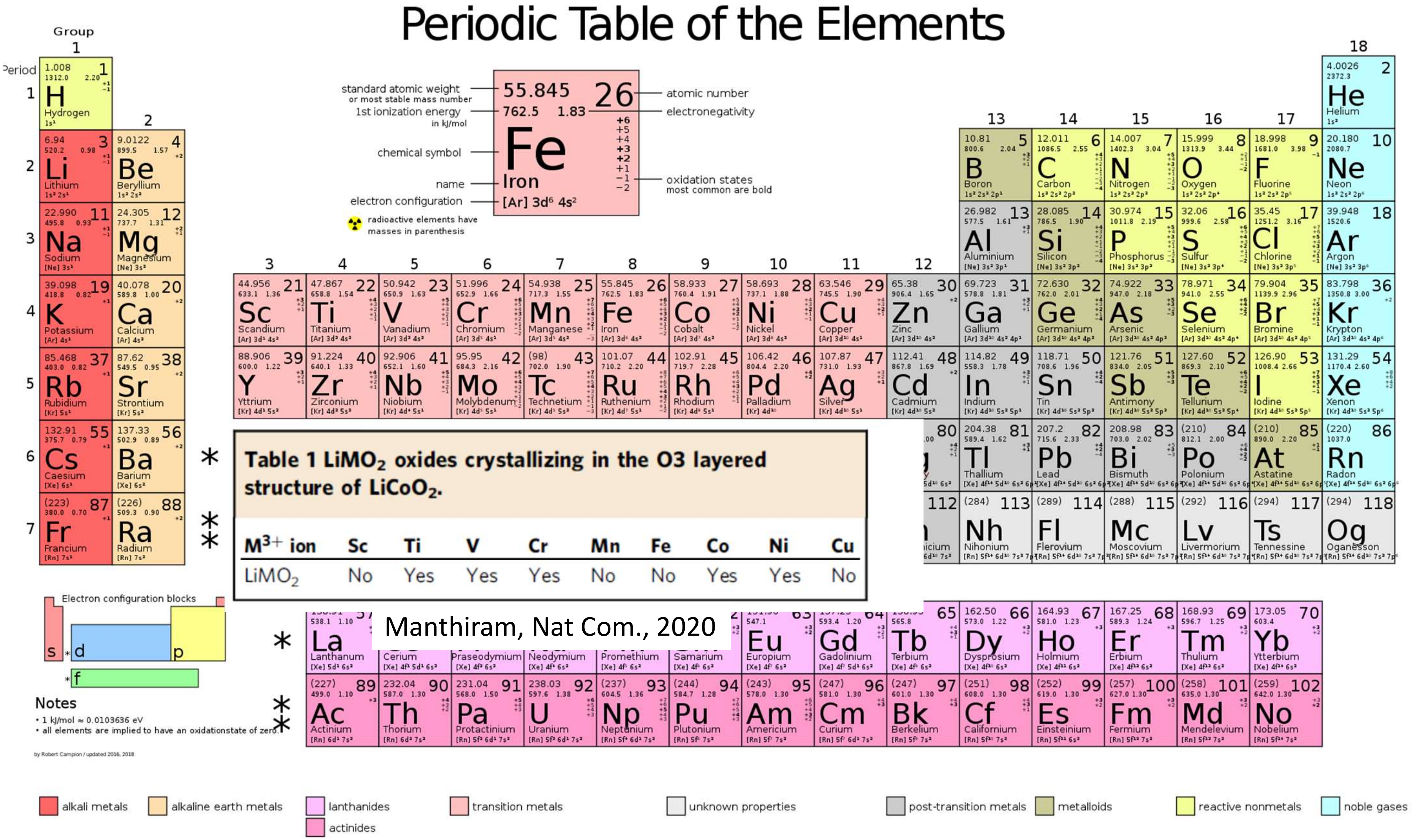


Table 1 $LiMO_2$ oxides crystallizing in the O3 layered structure of $LiCoO_2$.

M^{3+} ion	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$LiMO_2$	No	Yes	Yes	Yes	No	No	Yes	Yes	No

Manthiram, Nat Com., 2020

Li-ion Batteries- Layered Materials

- $LiNiO_2$ could be promising, but synthesizing a pure $LiNiO_2$ is quite hard due to a changing Ni redox state.
- Manganese helps stabilize the Ni, and does hurt a bit on the voltage, but is cheap
- Thus current batteries of this type are $Li\text{-}Ni_xMn_yCo_z$ with different comapnies having different x,y,z coefficients. This mixture optimizes out all needs and issues.

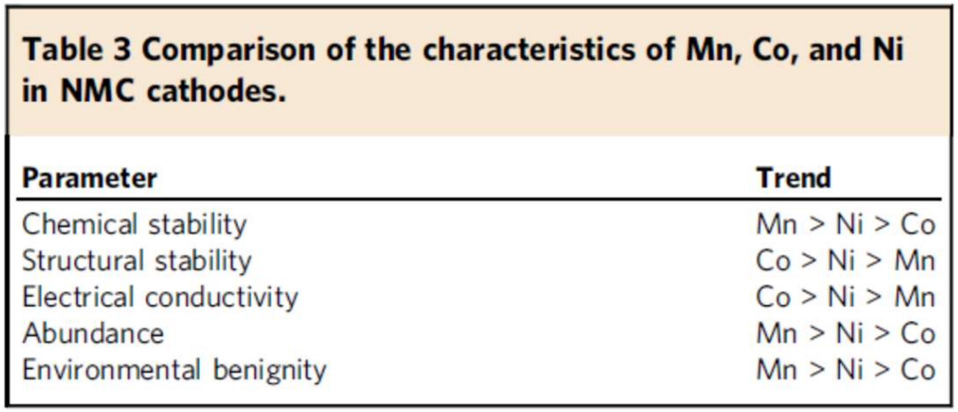


Table 3 Comparison of the characteristics of Mn, Co, and Ni in NMC cathodes.

Parameter	Trend
Chemical stability	Mn > Ni > Co
Structural stability	Co > Ni > Mn
Electrical conductivity	Co > Ni > Mn
Abundance	Mn > Ni > Co
Environmental benignity	Mn > Ni > Co

Li-ion Batteries

- The half reaction for a Li-NMC battery is shown below.

Cathode: $Li_{1-x}NiMnCoO_2 + xLi^+ + xe^- \leftrightarrow LiNiMnCoO_2$

Anode: $x\mathrm{Li}C_6 \leftrightarrow xLi^+ + xe^- + xC_6$

$$\mathrm{Li}C_6 + Li_{1-x}\,NiMnCoO_2 \leftrightarrow LiNiMnCoO_2 + xC_6$$

- C_6 is typically graphite.

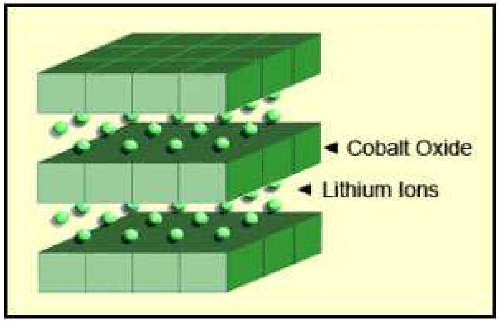
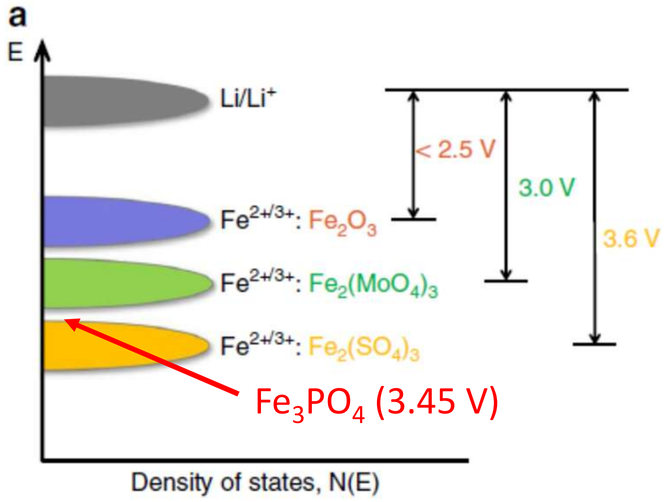


Image from BatteryUniversity.com

Li-ion Batteries- Polyanion

- In polyanions, it is the attached counterion that can change the redox potential of an element.
- The voltage is less than NMC and the volumetric energy density is also lower due to crystal structure.
- The strong oxygen binding to the counterion entails good thermal stability (i.e. durability)
- The sulfates have had low voltages (for some reason), thus we typically used phosphates.
- Iron and phosphate are both cheap, which is its best selling point



Fe_3PO_4 (3.45 V)

Lithium ion batteries

- The half reaction for a Li-$FePO_4$ battery is shown below.

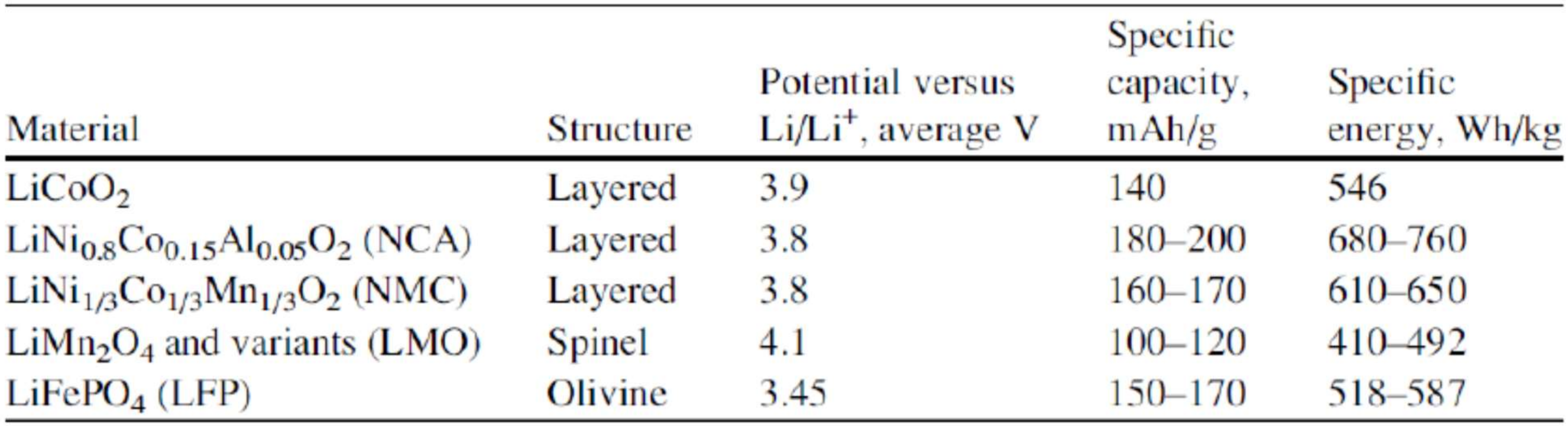
Cathode: $FePO_4 + xLi^+ + xe^- \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4$

Anode: $x\mathrm{Li}C_6 \leftrightarrow xLi^+ + xe^- + xC_6$

$$\mathrm{Li}C_6 + FePO_4 + x\mathrm{Li}C_6 \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4 + xC_6$$

Where $x_{maximum} = 0.6$

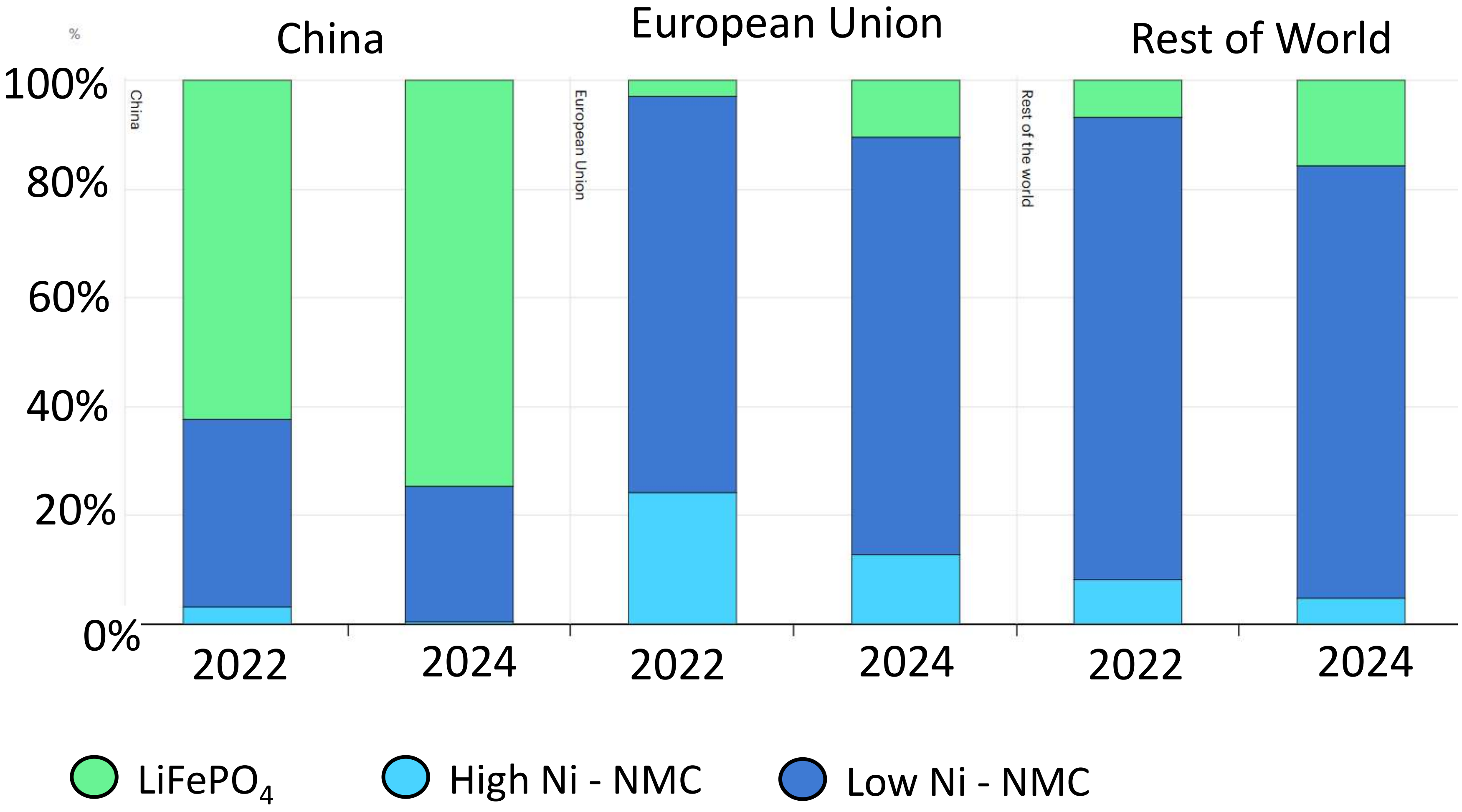
Cathode materials for Li-ion batteries



Material	Structure	Potential versus Li/Li$^+$, average V	Specific capacity, mAh/g	Specific energy, Wh/kg
$LiCoO_2$	Layered	3.9	140	546
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	Layered	3.8	180–200	680–760
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC)	Layered	3.8	160–170	610–650
$LiMn_2O_4$ and variants (LMO)	Spinel	4.1	100–120	410–492
$LiFePO_4$ (LFP)	Olivine	3.45	150–170	518–587

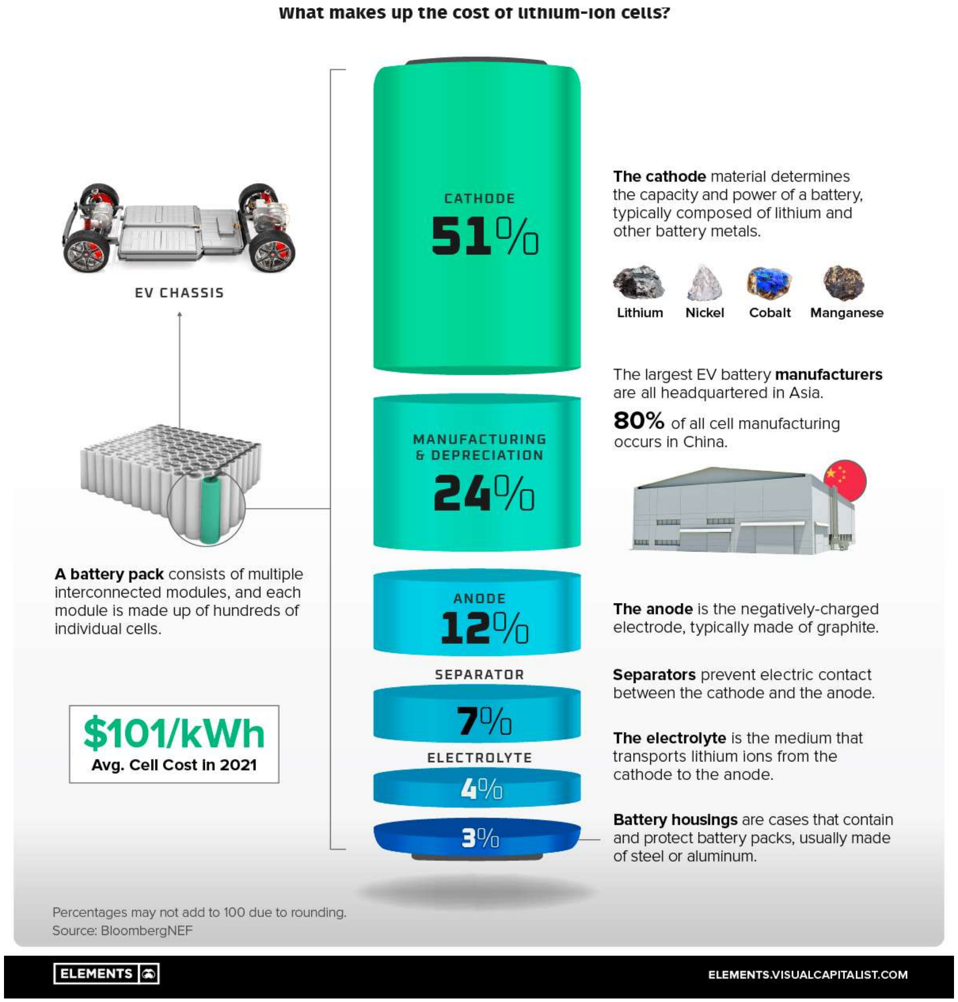
- Handheld electronics typically used $LiCoO_2$ though this is declining
- NCA is very good, but expensive. NMC is almost as good but cheaper
- Tesla uses NCA in its vehicles or LFP if produced in China, but NMC for its powerwall

Cathode materials for Li-ion batteries



Economics in Optimization

- The cathode is the most important part by far.
- China manufactures 75% of global anode graphite
- Li is mined lots of places, but mostly in South America
- Cobalt is mined in the Congo, and child labor is an issue.



What makes up the cost of lithium-ion cells?

The cathode material determines the capacity and power of a battery, typically composed of lithium and other battery metals.

The largest EV battery **manufacturers** are all headquartered in Asia.

80% of all cell manufacturing occurs in China.

A battery pack consists of multiple interconnected modules, and each module is made up of hundreds of individual cells.

$101/kWh
Avg. Cell Cost in 2021

The anode is the negatively-charged electrode, typically made of graphite.

Separators prevent electric contact between the cathode and the anode.

The electrolyte is the medium that transports lithium ions from the cathode to the anode.

Battery housings are cases that contain and protect battery packs, usually made of steel or aluminum.

Percentages may not add to 100 due to rounding.
Source: BloombergNEF

ELEMENTS
ELEMENTS.VISUALCAPITALIST.COM

Concept Check

The most important thing to get a high voltage in a battery is :

a) Charge transferred per reaction

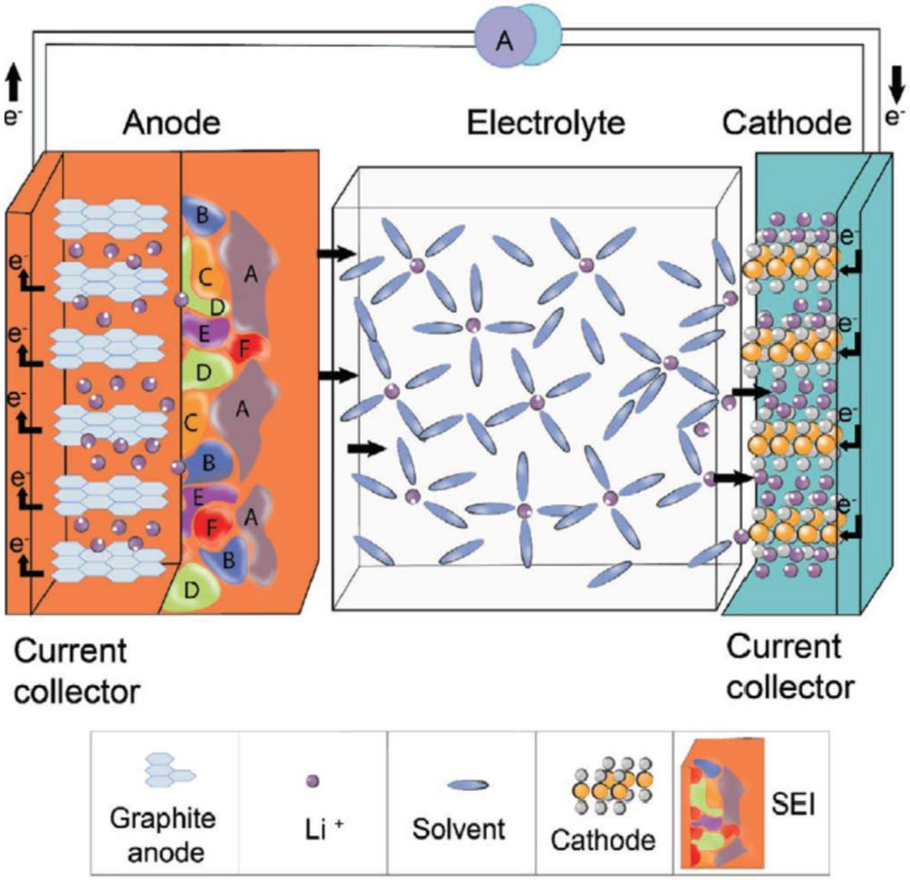
b) Molecular weight of battery redox materials

c) Having easy reaction kinetics.

d) Redox potential difference between half-reactions

Solid-Electrolyte-Interphase (SEI) Layer

- The SEI layer is basically degraded junk from the electrolyte
- The SEI block further electrolyte from oxidizing at the anode, but allows Li to pass through.
- $LiCO_3$, LiF, and LiO are near the anode side
- Organic based species are near the electrolyte side
- The SEI is very important, but it is a mess and nobody understands it.



Electrolytes

- The high voltage from batteries will split water into H_2 and O_2 so another electrolyte is needed

- Often a propylene carbonate with dimethoxy ethane with 1M $LiClO_4$ is used.

Can be explosive when mixed with organics

Flammable

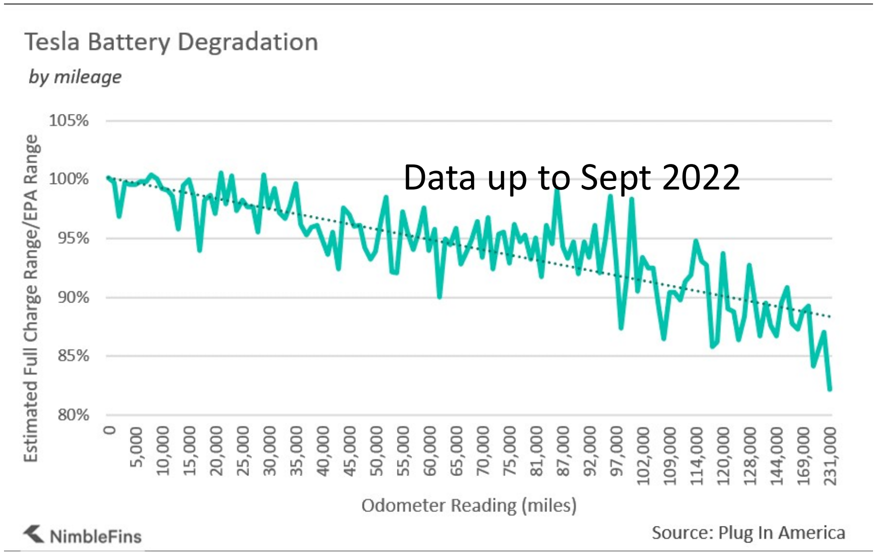
Flammable

- The quest now is to look for a solid state electrolyte and progress is being made.

Lithium Ion Battery in Cars

- Durability- 400- 1000 cycles (or even more).
- On Model S (2023) durabilty is 12% loss over 320,000 km.
- On Model 3 (2022), durability seems to indicate 5% loss over 100,000 km.

Tesla Model S Battery



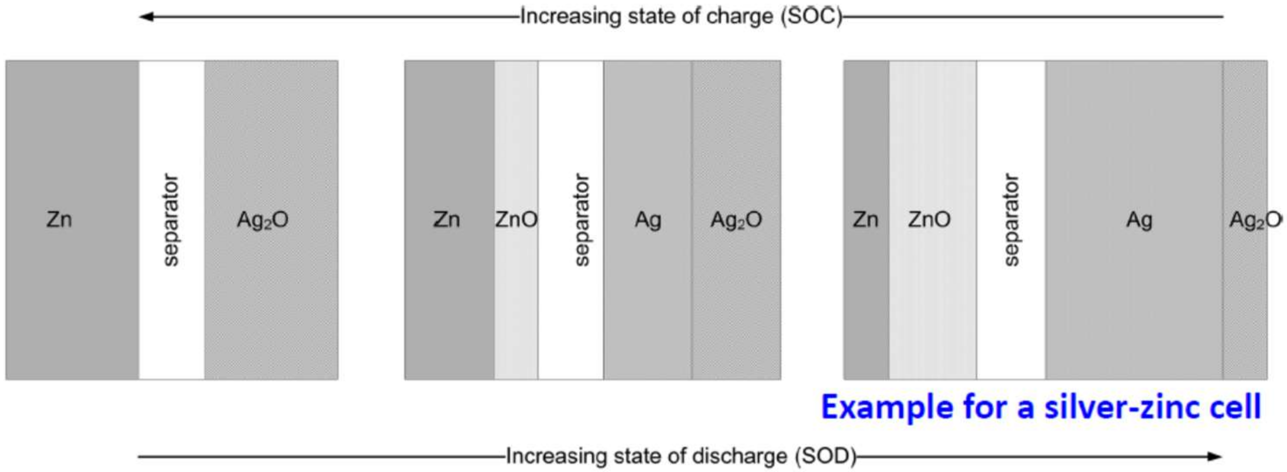
Data up to Sept 2022

Source: Plug In America

Battery performance of Tesla S

State of (dis)charge and cell voltage

- The state of charge expresses the remaining capacity (i.e. amount of unconverted active material) in the cell.



Example for a silver-zinc cell

Figure 7.4 State of charge as conversion of active material.

$$\text{State of charge} = \frac{\text{Available capacity remaining}}{\text{Total capacity}} \times 100$$

Does the cell voltage depend on the SOC/SOD?

State of (dis)charge and cell voltage

- In general, cell voltage decreases with increasing SOD
- The slopes of the curves vary depending on cell chemistry
- Most cells show a gradual linear decreases followed by a rapid change at high SOD

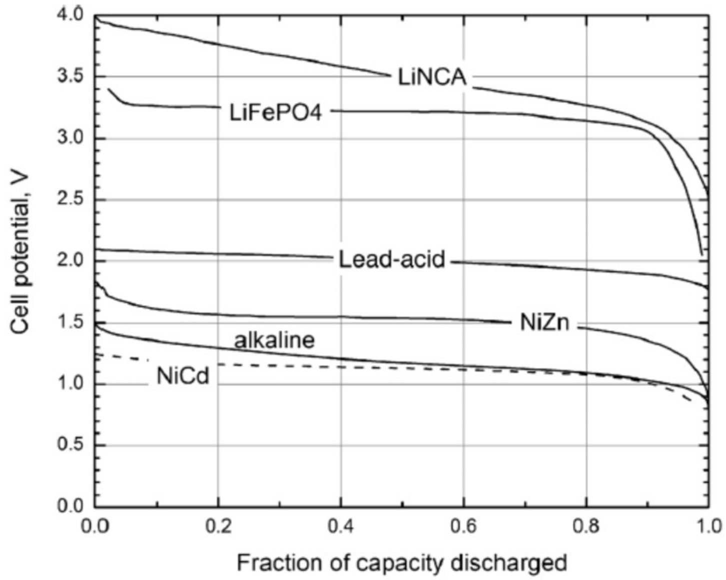
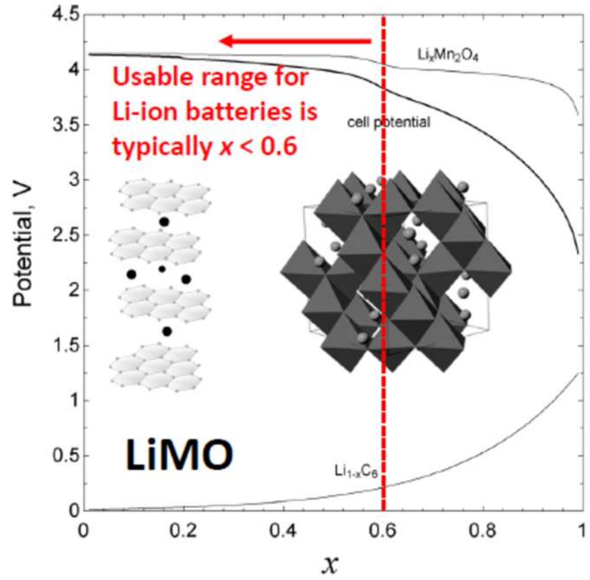


Figure 7.5 Potentials of several battery chemistries.

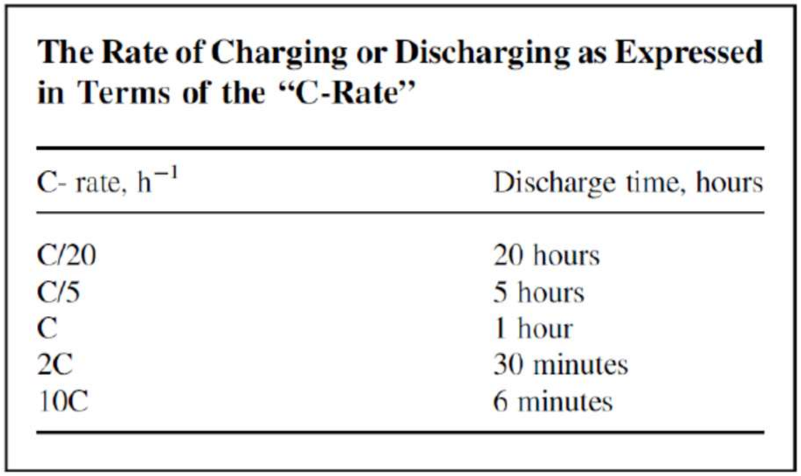


Usable range for Li-ion batteries is typically $x < 0.6$

Figure 7.6 Potential versus the fraction discharged for a lithium-ion cell. Also shown are the structural aspects of the negative electrode (a) and positive electrode (b).

The (dis)charge rate: the ”C-rate”

- Whether a current is large or small is relative to the battery’s capacity – this is taken into account by the C-rate.
- A rate of 1C draws a current [A] that is equal in magnitude to the battery’s capacity in [A*h]
- Or, in other words, a current of 1C drains the battery in 1 hour.



The Rate of Charging or Discharging as Expressed in Terms of the “C-Rate”

C- rate, h^{-1}	Discharge time, hours
C/20	20 hours
C/5	5 hours
C	1 hour
2C	30 minutes
10C	6 minutes

- Generally, the voltage that a battery can provide also depends on the C-rate

Effect of ”C-rate” on cell voltage

General expression for voltage losses in an electrochemical device

$$E_{cell}^{thermo} - E_{cell}^{actual} = \eta = \left|\eta_{ohmic}\right| + \left|\eta_{kinetic}^{anode}\right| + \left|\eta_{kinetic}^{cathode}\right| + \left|\eta_{conc.polarization}\right|$$

This difference is “polarization”

Ohmic losses

Losses from reaction kinetics

Concentration polarization

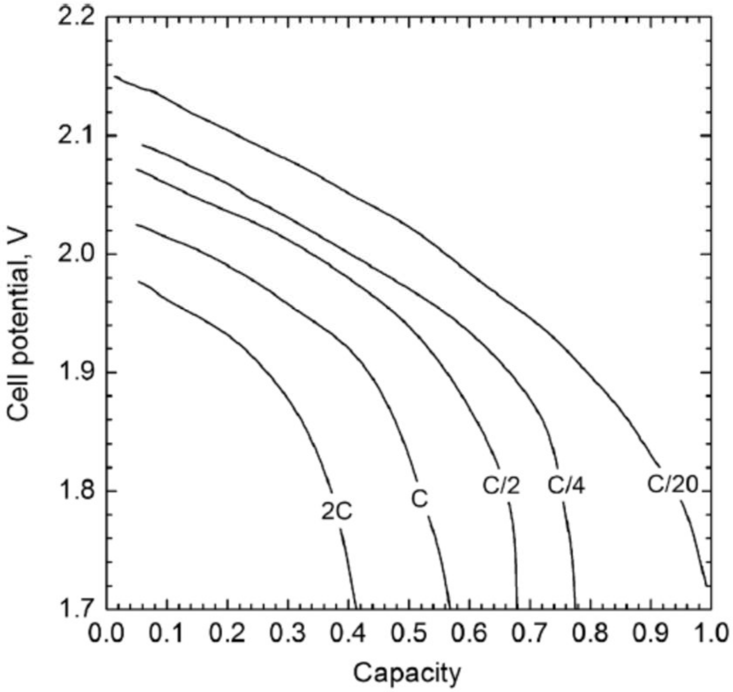


Figure 7.7 Effect of rate on potential as a function of the fractional capacity for a lead–acid cell.

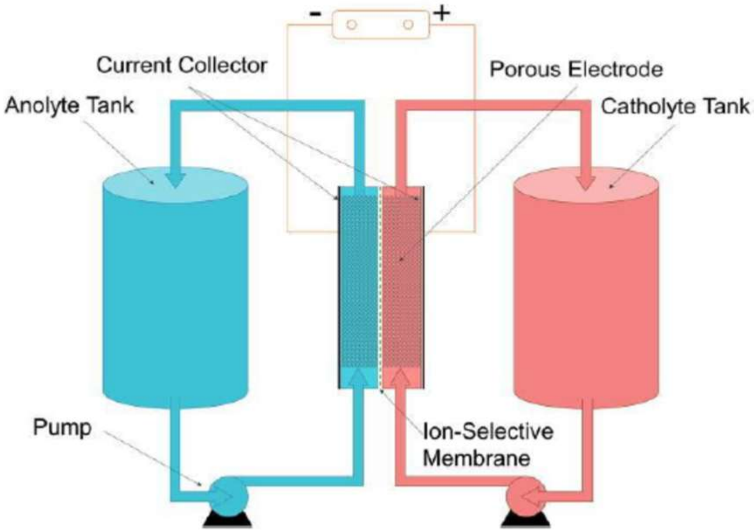
- In a well-deisgned battery ohmic losses should be a major mechanism

- Kinetic losses are small, and most significant at low currents

- Concentration polarization results from concentration gradients near the electrode

Redox Flow Batteries

- These are just like a battery, but the charged species flow into tanks



Qi and Koenig Jr., *J. Vac. Sci. Technol. B*, **2017**, 35, 040801

Vanadium RFB during discharging

Anode

$V^{2+} \rightarrow V^{3+} + e^-$ $\quad E^\circ_{anode} = -0.26\,V$ vs. SHE

Cathode

$VO^+ + e^- + 2H^+ \rightarrow VO^{2+} + H_2O$

$E^\circ_{cathode} = 0.99$ V vs. SHE

- Nominal cell voltage is 1.25 V

- Anode-Cathode contamination is mitigated, but the redox species must be relatively stable on its own.

Redox Flow Batteries

- These fill the needs of mid-range intermittent storage (6-30 hours)
- They are supposed to bemuch cheaper than normal batteries, but take up much more space.
  - Not good for mobile applications
  - Good for grid-balancing applications

Ambri

Vflow Tech

Lockheed Martin

Switched from Vanadium based
to CaSb based recently

Lecture - Learning Objectives

At the end of this lecture you should be able to:

- Understand the difference between the heat engine and electrical engines.
- Understand the basic principles of electrochemistry.
- Understand the redox reactions related to battery technology

Li ion battery

- How much charge/kg of lithium can you obtain from a $LiFePO_4$ battery? Answer in C/Kg
- Given these devices have an open circuit voltage of 3.45 V, how much Energy/kg can these devices theoretically hold? Answer in Wh/kg. Compare this to slide 51, and see how much more progress can be made theoretically.

Cathode: $FePO_4 + xLi^+ + xe^- \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4$

Anode: $\mathrm{Li}C_6 \leftrightarrow xLi^+ + xe^- + (1-x)Li\ in\ C_6$

$$\mathrm{Li}C_6 + FePO_4 \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4 + (1-x)Li + C_6$$

Where $x_{maximum} = 0.6$

Excercises

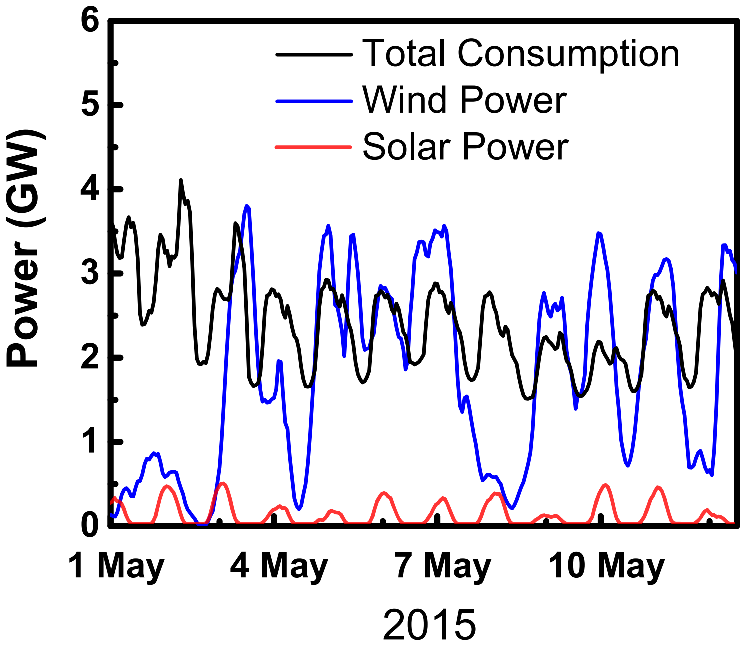
- Review the Zn/Cu electrochemical reaction. If you have 10g of Zn
  - A) What is the theoretical maximum amount of Cu you could deposit (assuming you had enough Cu^{2+})
  - B) What is the maximum theoretical amount of energy you could extract from this electrochemical reaction.

Exercises- A battery storage society

- Currently batteries cost 100$/kwh but are expected to drop to 50$/kwh in 5 years. *(2 years ago batteries cost 300$/kWh and were expected to drop to 100 $/kWh in 5 years)*
- How much would it cost to store 24 hours worth of the world's energy usage assuming 100$/kwh ?
- How does this compare to the gross world product (8 x 10^{12} $/year)

Exercises- Energy Storage- Just for Fun

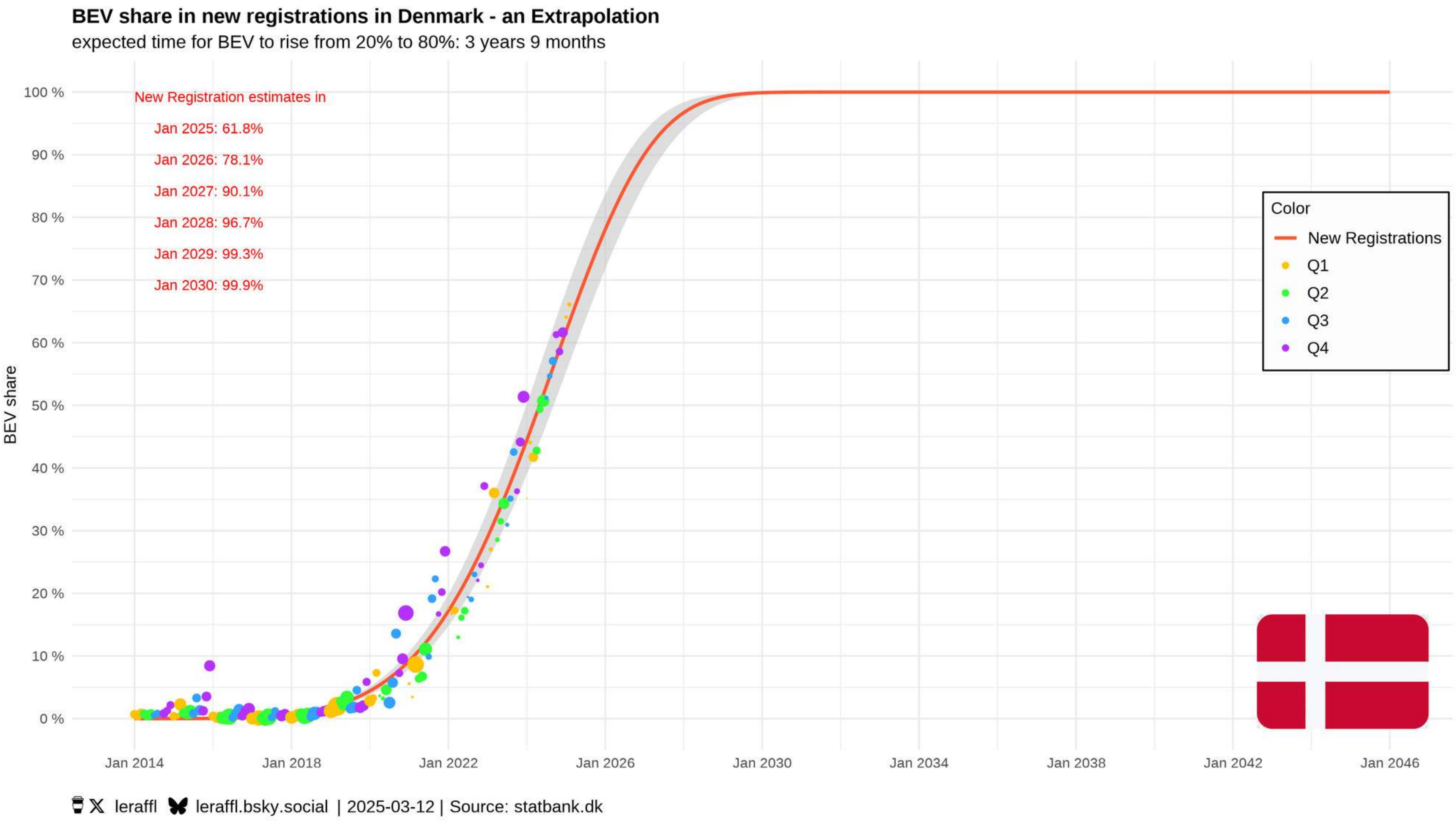
- How much do we need to store ?
  - No one really knows
  - We will try to get an order of magnitude estimate
- Denmark's electricity consumption and production can be found at [energinet.dk]() (specifically this [website]())
- By using this data you can make cool figures like the one on the right



Exercises- Energy Storage- Just for Fun

- Take the data for the last year and increase the overall wind production by a factor X and the solar by a factor of Y such that the total yearly energy consumption is met.
- When wind+solar exceeds consumption this will need to be stored , and when it is less than consumption it will need to be used from storage.
- How much storage will you need in an optimized case?
- If we assume the rest of the world is like Denmark, and only 1/6th of the total energy is electricity, we can multiply our electrical storage needs by 6 to get total energy storage needed.
- Thus if try to roughly estimate the world’s energy storage, how much would this be?

Electrical Vehicles in Denmark



BEV share in new registrations in Denmark - an Extrapolation

expected time for BEV to rise from 20% to 80%: 3 years 9 months

𝕏 leraffl 🦋 leraffl.bsky.social | 2025-03-12 | Source: statbank.dk