Electrochemical Energy Storage

(how is this different from chemical energy storage)

A. Batteries

- stores energy in chemical compounds

B. "Super" Capacitors

- stores energy in double-layer of charge

C. Fuel Cells

- extracts energy from chemical (like battery), but fuel is added from the outside

d. Water Electrolysis

→ store electrical energy via chemical compounds

A Batteries

Primary → disposable after one use

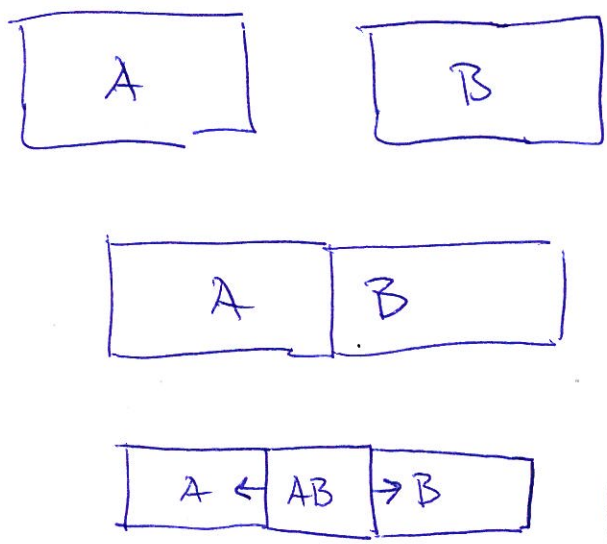
Secondary → rechargeable

A ① How does a battery work?

· imagine first a <u>chemical reaction</u>

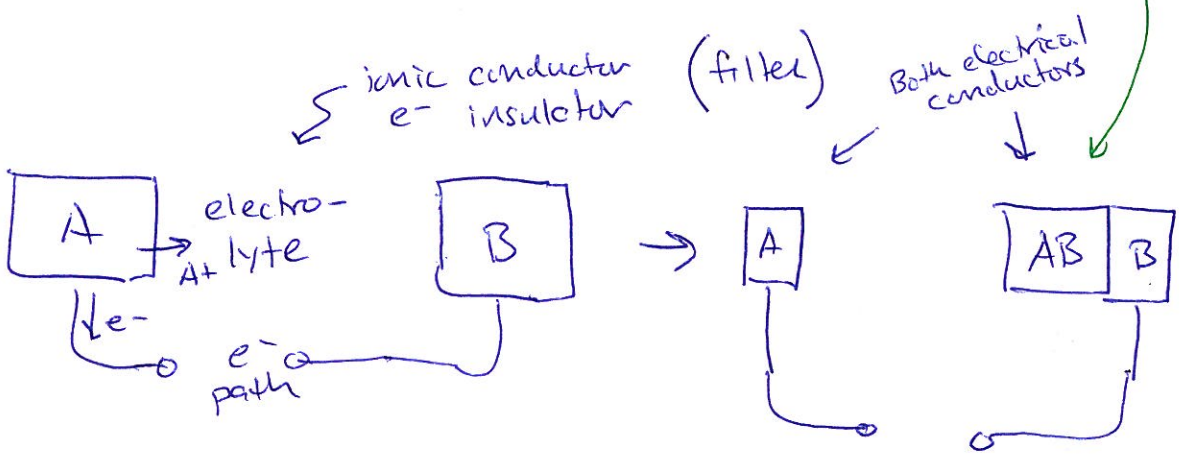
· $A + B \rightleftarrows AB$ formation reaction

$$\Delta G_r^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants})$$



reaction requires the interdiffusion of A and B

② electrochemical mechanism



Batteries composed of 3 parts

1. negative electrode (anode) (A in the example)

during the electrochemical reaction provides e^- to the external circuit (hence oxidizes species in the cell)

2. positive electrode (cathode)

→ takes e^- during discharge to do reduction in the cell

3. electrolyte (medium for ion transfer)

- over rxn requires e^- and ions

- if circuit open, no e^- can flow

  - chemical driving force (ΔG_r) is balanced by the electrostatic potential ($-nFE$) so that μ is constant everywhere.

this voltage, $E = \frac{-\Delta G_r}{nF}$, can do electrical work in an external circuit, if the ions can move freely inside the battery.

→ (Add notes on ~~tag~~ names of electrodes)

(3) Types of Reactions in Batteries

a. formation Reaction:

$$A + B \rightarrow AB$$

Ex. Li - Sb Battery (at 350°C) → Show phase diagram

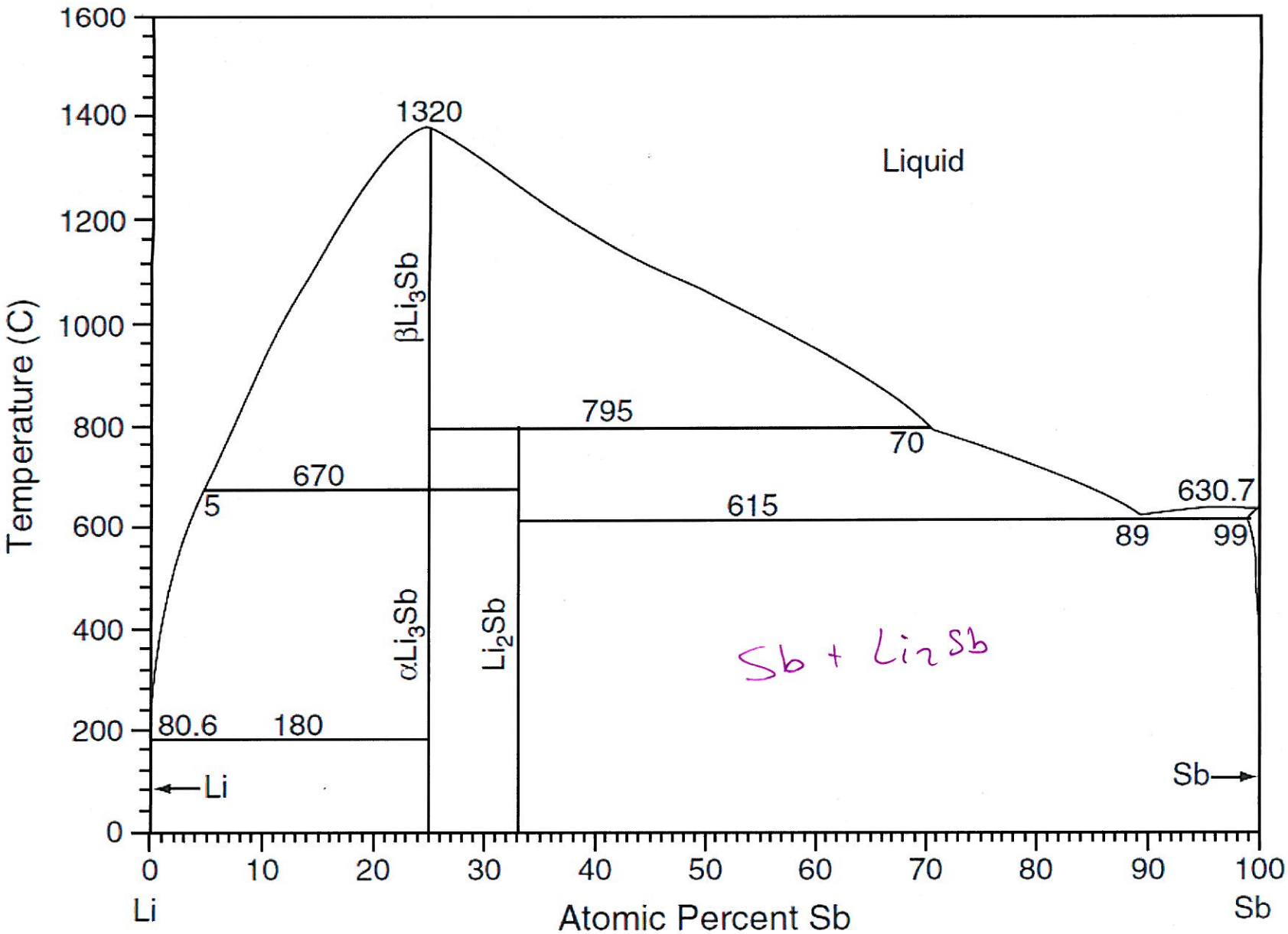


Fig. 1.3 Equilibrium phase diagram of the lithium - antimony system

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b. Displacement Reactions

$$A + BX \rightarrow AX + B$$

for example

$$Li + Cu_2O \rightarrow Li_2O + Cu$$

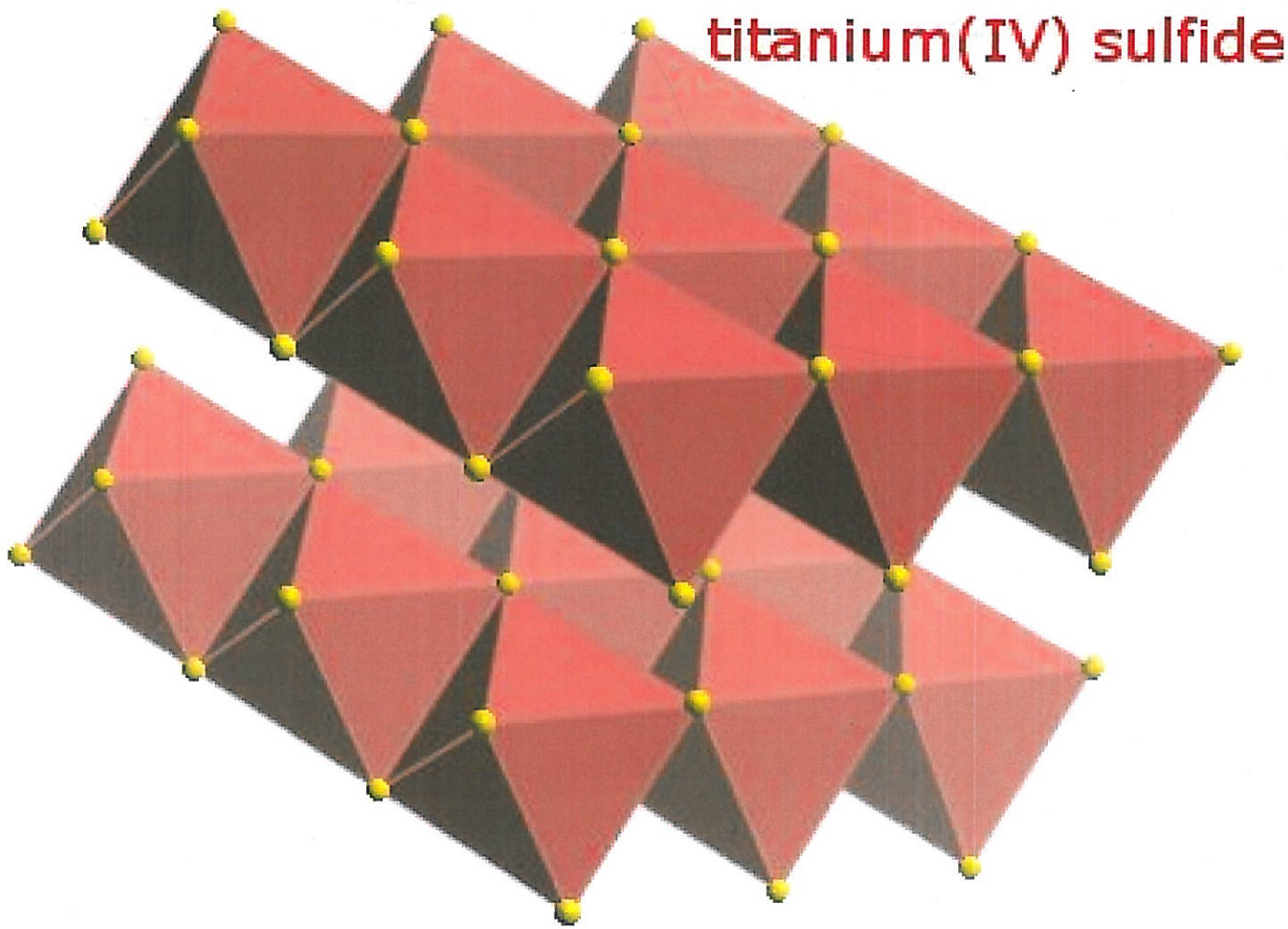
ΔG_r is negative, driven by strong reducing power of Li (M).

c. insertion reactions → basic crystal structure stays the same, ions and electrons move in / out of "channels" (intercalation reactions)

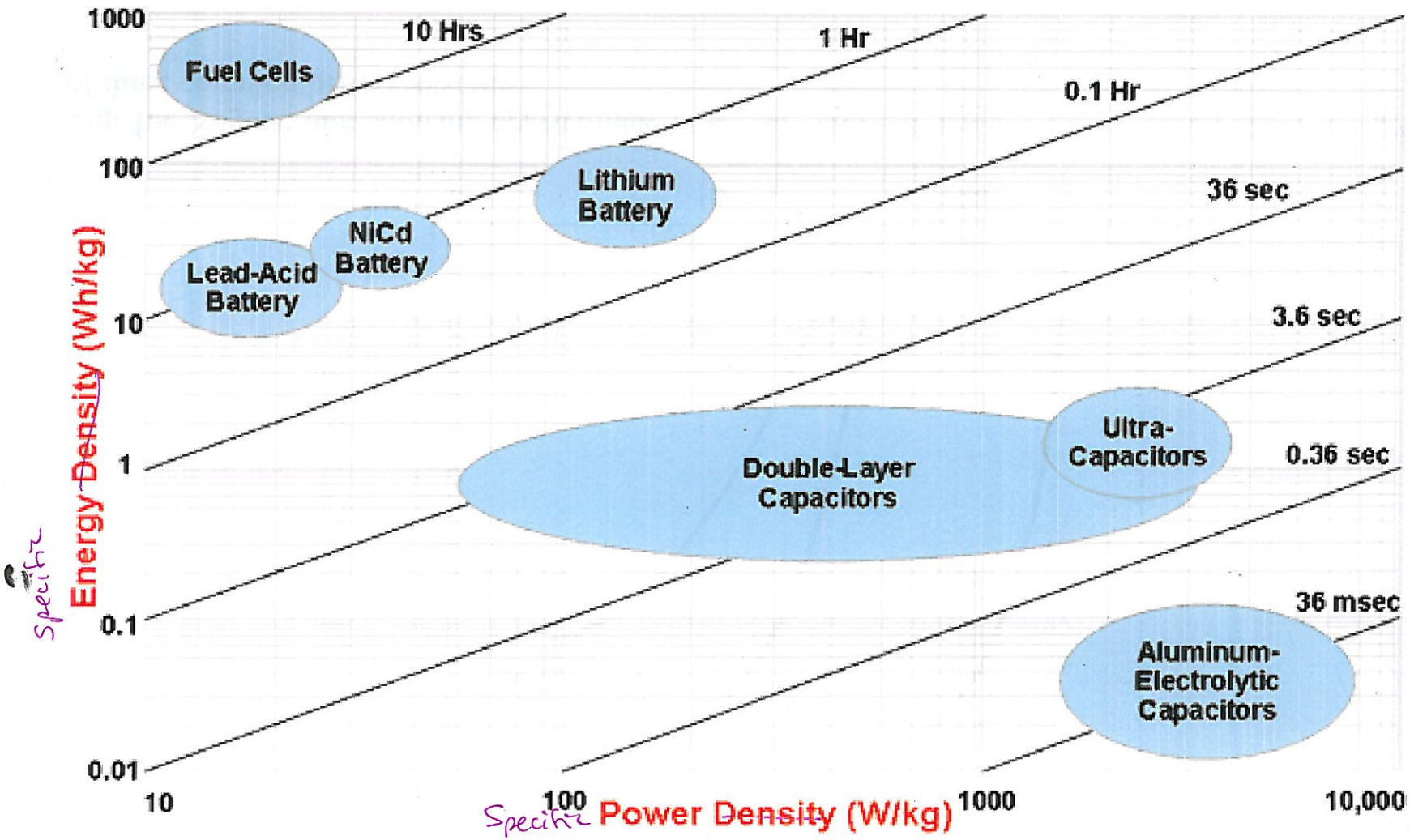
$$xA + BX = A_xBX$$

$$xLi + TiS_2 \rightarrow Li_xTiS_2$$

(show structure of TiS_2 on projector



Layered structure, Ti located at the center of the octahedra. Li intercalates in-between the sheets, while crystal structure stays relatively constant.



Source US Defence Logistics Agency

Practical Parameters

i. specific energy (Wh/kg)

ii. specific power (W/kg)

iii. energy density (Wh/L)

iv. power density (W/L)

> will compare parameters for various chemistries soon.

v. cycle life → # of cycles before battery degrades.

What determines these values for a given battery system?

A. Maximum Theoretical Specific Energy (MTSE)

$$x A + R \rightarrow A_x R \qquad (1e^-/x)$$

if $\underline{E}$ is the average voltage generated

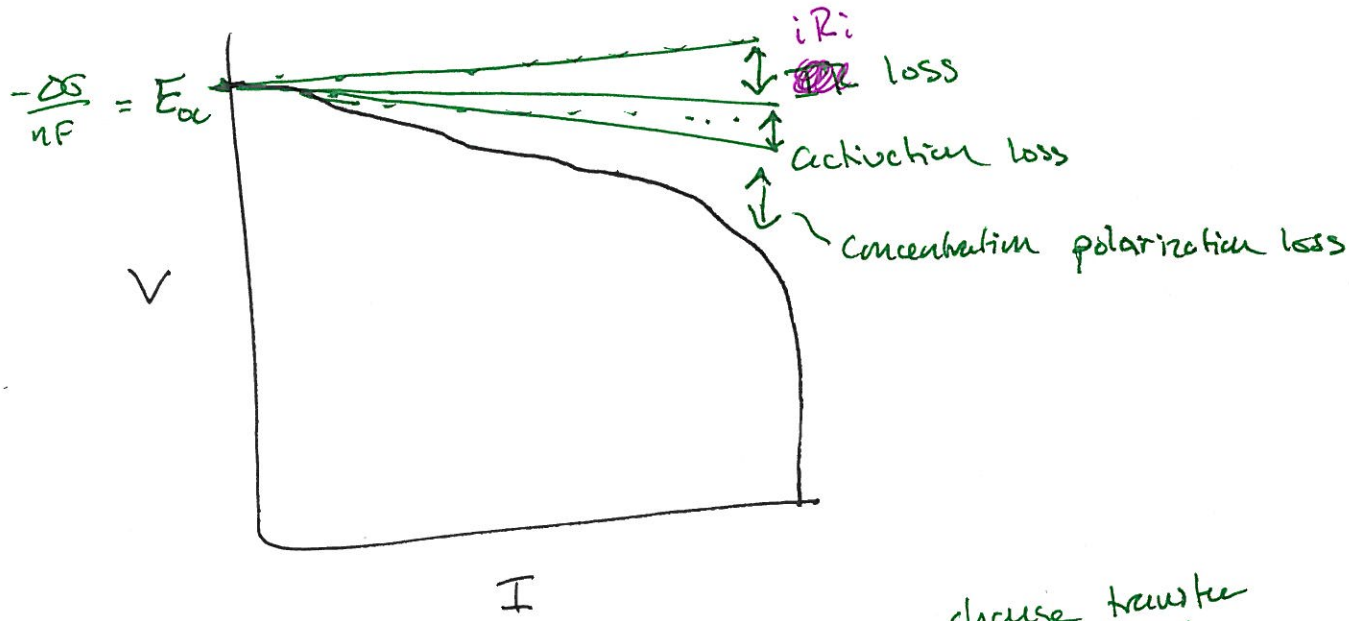
$$MTSE = \left(\frac{x E}{W_+}\right) F \qquad W_+ = W(xA) + W(R)$$

(so batteries w/ Pb are heavier per electron transferred than those with Li)

What voltage is generated by the battery?

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

Cell polarization as a function of current



$$E = E_o - \underbrace{[(\eta_{ct})_a + (\eta_{cn})_a]}_{\text{charge transfer overpotentials}} - [(\eta_{ct})_c + (\eta_c)_c] - iR_i$$

$$E = E_o - iR_{tot}$$

concentration overpotentials

internal resistance due to finite conductivity of the electrolyte.

Review: what are the charge transfer (activation) and ~~activation~~ concentration overpotentials due to?

A: kinetics + Mass transport (ie diffusion)

Tafel $\rightarrow \eta = a \pm b \log i$

Voltage needed to set up diffusion gradient in the solution.

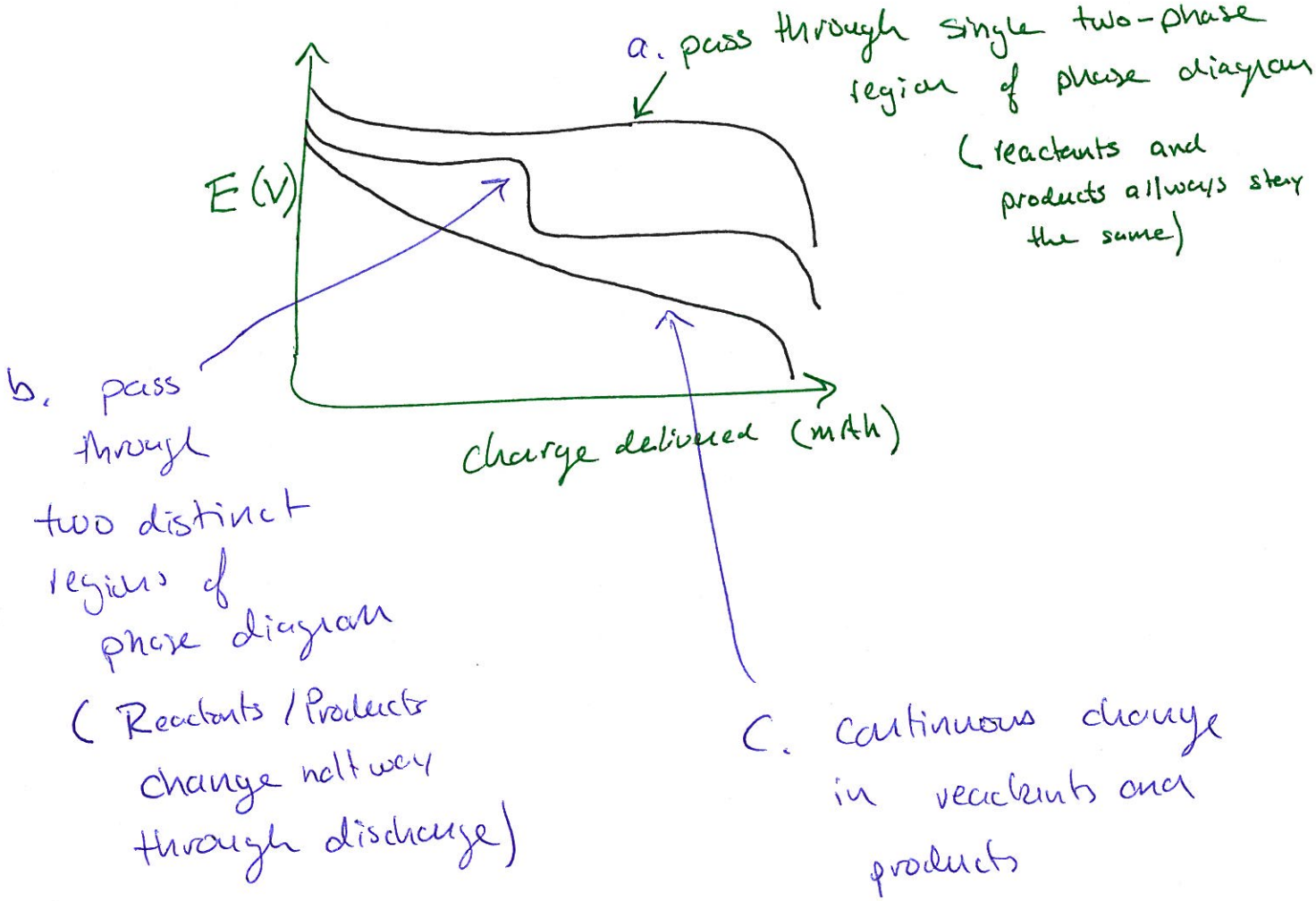
$$\eta_c = \frac{RT}{nF} \ln\left(\frac{i_\ell}{i_\ell - i}\right)$$

Practical implication: faster discharge, less voltage to do useful work, more wasted as heat!

$\rightarrow$ same is true for <u>charging</u>.

fast charging, more heat generated...

The cell voltage can also depend on the extent of reaction



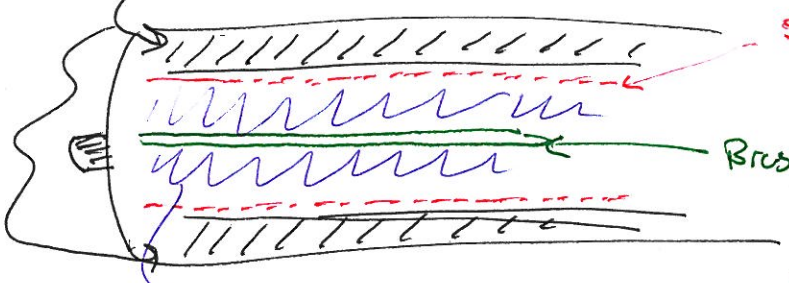
Overview of Battery Technologies

Primary (non-rechargeable)

→ "alkaline" batteries (ie typical AA etc)
1960's

Cathode (positive) electrode = manganese dioxide

$MnO_2 + H_2O + e \rightarrow MnOOH + OH^-$



→ Zn powder anode (negative electrode)

$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$

$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

$Zn(OH)_2 \rightarrow ZnO + 2H_2O$

$E_{max} \sim 1.65\ V$, $E_{avg} \sim 1.2\ V$

$2\ MnO_2 + Zn + 2H_2O \rightarrow 2\ MnOOH + ZnOH_2$

(why not rechargeable?)

Secondary Batteries

Lead-Acid Battery

Negative Electrode (anode)

$$Pb \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Pb^{2+} + 2e$$

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \quad \text{(in solution)}$$

Positive Electrode (cathode)

$$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$$

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$$

$$\boxed{E_{cell} = 2.1\ V}$$

Overall

$$\underset{Pb^0}{Pb} + \underset{Pb^{4+}}{PbO_2} + 2H_2SO_4 \rightleftharpoons \underset{Pb^{2+}}{2PbSO_4} + 2H_2O$$

But ... use aqueous electrolyte! decomposition?

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Overcharge and Self discharge

Cell voltage is larger than that need to split water

Negative $2H^+ + 2e \rightarrow H_2$

Positive $H_2O \rightarrow 1/2 O_2 + 2H^+ + 2e^-$

water splitting is a side reaction during charging ... that is also why older Pb-acid batteries were known to blow up!

Sitting Batteries also can self discharge:

$$PbO_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + 1/2 O_2$$

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$$

Ni-MH Battery (used in the first / second generation Prius es)

chemistry:

$$NiOOH + H_2O + e \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^- \qquad \cancel{E^\circ = 0.52V}$$

$$MH + OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M + H_2O + e \qquad \cancel{E^\circ = 0.83V}$$

Metal Hydride

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overall reaction $\quad MH + NiOOH \rightarrow M + Ni(OH)_2$

highly reducing

highly oxidizing

M = V-Ti-Zr-Ni alloy optimized for MH formation and kinet

Li - ion battery → current leader for power/energy density

→ in chevy Volta / Tesla Roadster etc.

→ Li is one of the lightest elements

→ best power/energy density

Chemistry

	Negative Electrodes	V vs Li/Li^+	Capacity (Ah/g)
not used due to dendrites →	Li metal	0	3.86
Currently used, very stable →	LiC_6 ← graphite	0.1 ~ 0.5	0.37
new tech. → large volume expansion/contraction problematic → now Si/C composites used.	$4.4LiSi$	0.5 ~ 1	2

$$LiC_6 \rightarrow Li^+ + e^- + C_6$$

Positive Electrodes (cathodes)

material	E vs Li/Li+	capacity Ah/g	
$LiCoO_2$	3.7	.135	← typical commercial material
$LiMn_2O_4$	4.0	.10	← high voltage causes electrolyte breakdown
$LiFePO_4$	3.3V	.150	↑ high rate capacity, used in power tools, etc.

* $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xe^- + xLi^+$

$x \sim 0.5$, reversibly (theoretical capacity 2x higher, but hard to get last Li species out!)

Cathodes for Li-ion batteries

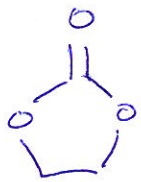
major road block for increasing the capacity.

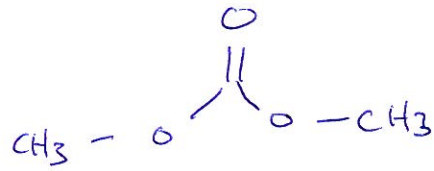
Electrolytes

→ need

1. good ionic conductivity
2. good Li salt solubility
3. wide electrochemical window (0-5V vs Li/Li^+)
4. Thermally stable

eg. ethylene carbonate, dimethyl carbonate etc





Salts → $LiClO_4$, $LiPF_6$, $LiBF_4$

Also need separator to keep + and − from internally shorting.

overall reaction

$$x\,LiC_6 + Li_{1-x}CoO_2 \rightarrow C_6 + LiCoO_2$$

↑ charged. ↑ discharge

total voltage ~ 3.5V

Why do. Li-ion (and other) batteries fail?

→ Li-ion can explode if internal short causes discharge

→ volume expansion/contraction causes pieces of anode/cathode to fall apart

→ electrolyte breaks down under highly oxidizing/reducing conditions and blocks access to material.