Batteries 2

Types of battery technology

- Cationic battery
  - Li-ion
  - Metal-air
- Anionic battery
  - Hydroxide battery
  - Fluoride ion
- Flow battery

Cationic Batteries

Li-ion batteries have come to dominate the commericial market. Why?

- Li/Li^+ has one of the most negative reduction potentials of any element:

$$\mathrm{Li^+ + e^- \longrightarrow Li(s)} \qquad\qquad E = -3.04\mathrm{V} \quad (\mathrm{vs.\,SHE})$$

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e.g.:

$$\mathrm{Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2} \qquad E = +0.6V$$

$$\mathrm{Li^+ + 6\,C + e^- \longrightarrow LiC_6} \qquad E = -2.84V$$

overall (discharge):

$$\mathrm{LiC_6 + CoO_2 \longrightarrow LiCoO_2 + 6\,C} \qquad E = +2.90V$$

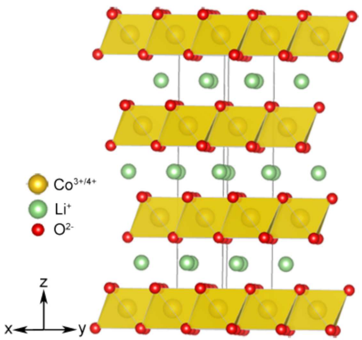
$$\begin{aligned}\Delta G &= -nFE \\ &= -279.8\ \mathrm{kJ\ mol^{-1}} \\ &= -77.7\ \mathrm{Wh\ mol^{-1}}\end{aligned}$$

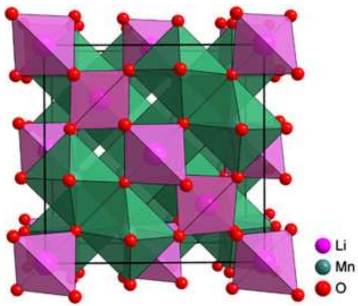
Note: 1 W = 1 J s^{-1}, so 1 Wh = 3600 J = 3.6 kJ

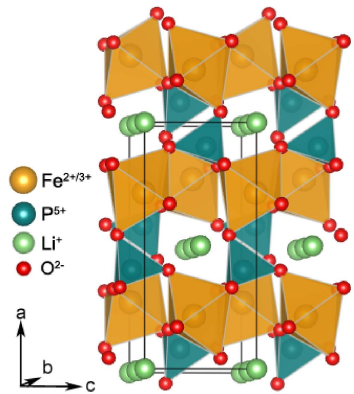
Cathode materials

Materials for Li-ion cathodes fall into three main families:

2D conductor (e.g. layered α-$NaFeO_2$)	3D conductor (e.g. spinel)	1D conductor (e.g. olivine)







$LiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
(Q_{theo} = 274 mAh g^{-1})	(148 mAh g^{-1})	(170 mAh g^{-1})

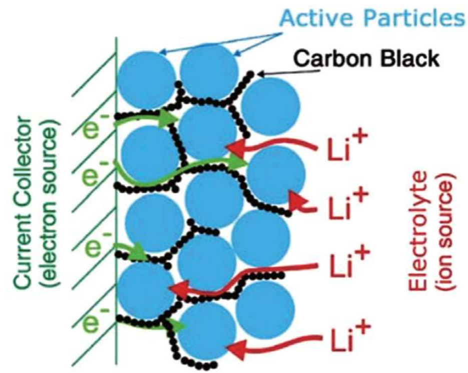
← Better Li conduction ←

→ Safer →

← (Higher cost) ←

Cathode disadvantages

- Many materials are electrically insulating
  - They must be mixed with a conductor (carbon) to allow charge transfer
- Realistic capacity Q is often much lower than Q_{theo}
  - Chemical stability (*e.g.* in Li_xCoO_2, $0.5 \leq x \leq 1$)
  - Useable capacity is reduced even at low C-rates
- Practical energy capacity E is often < 30% of the ideal
  - Discharge voltages are lower than expected
    - Ohmic Losses: additional electronic and ionic resistance
    - Drop in voltage with change in Li concentration (concentration polarization)



Concentration polarization

As Li^+ is removed from the anode, E_{meas} changes:

Nernst Equation:

$$E_{meas} = E^\circ - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]}$$

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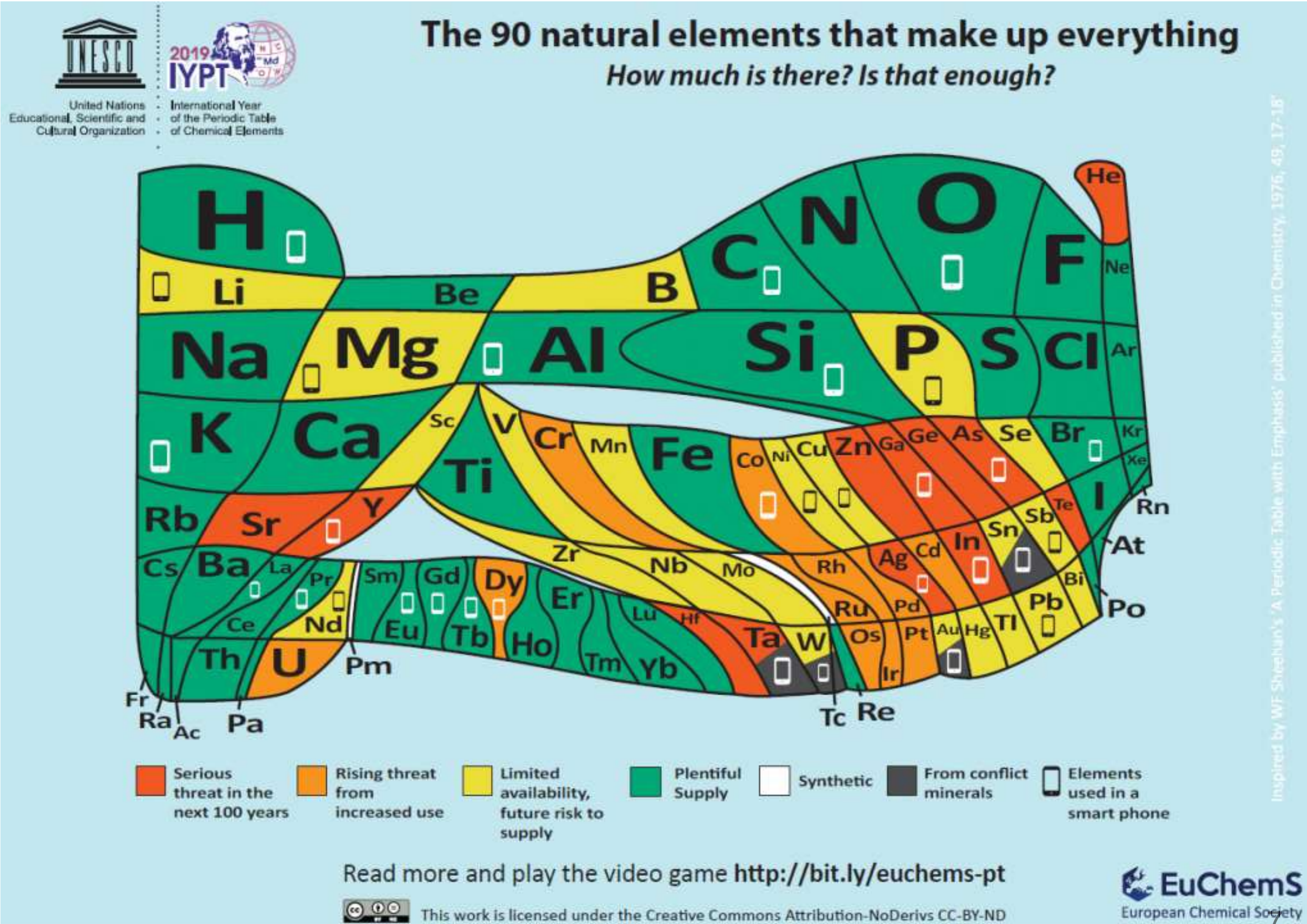
$$E = 2.90 - \frac{RT}{F}\ln\frac{[\mathrm{LiCoO_2}]}{[\mathrm{LiC_6}]}$$


United Nations Educational, Scientific and Cultural Organization
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International Year of the Periodic Table of Chemical Elements
The 90 natural elements that make up everything
How much is there? Is that enough?
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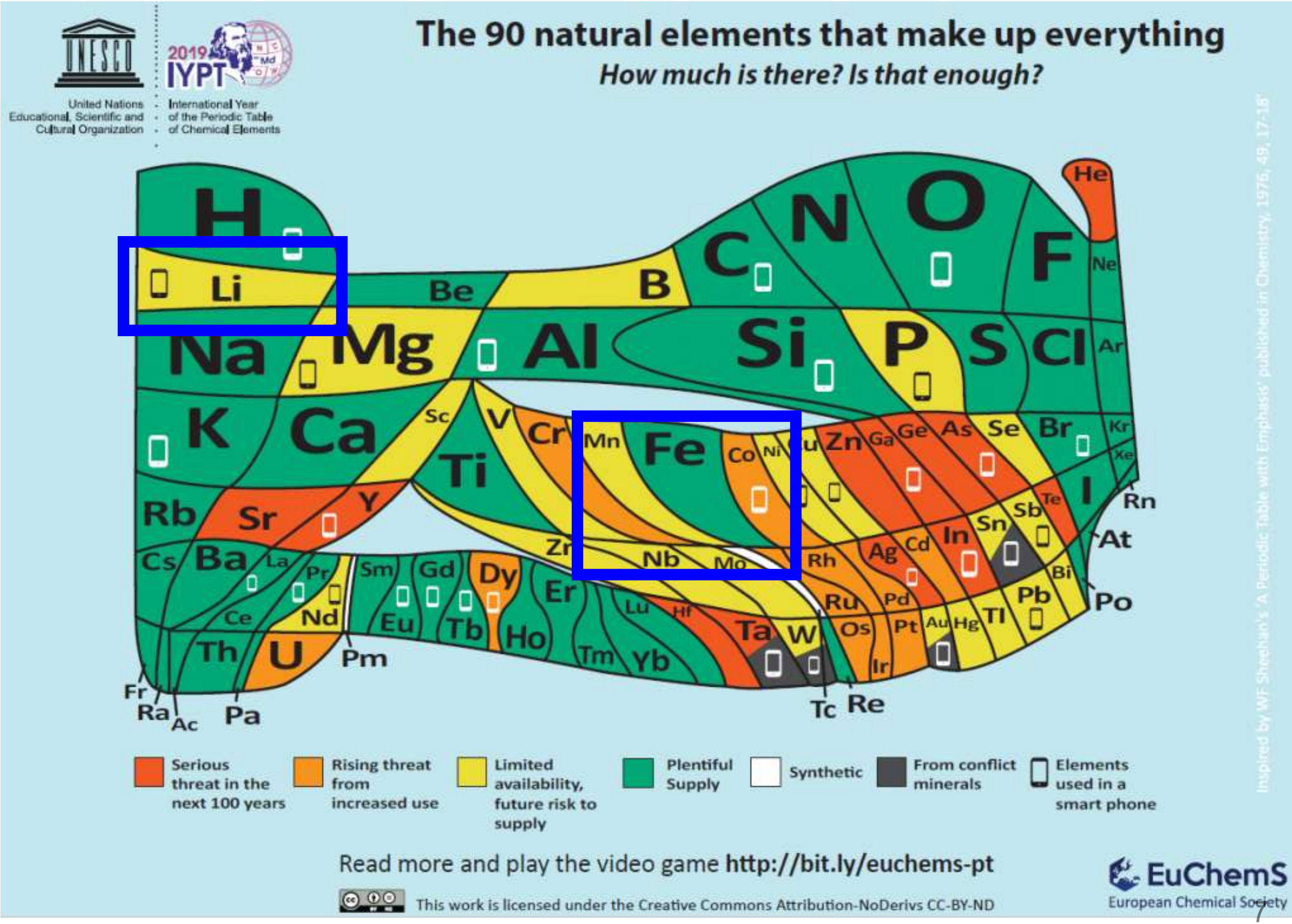
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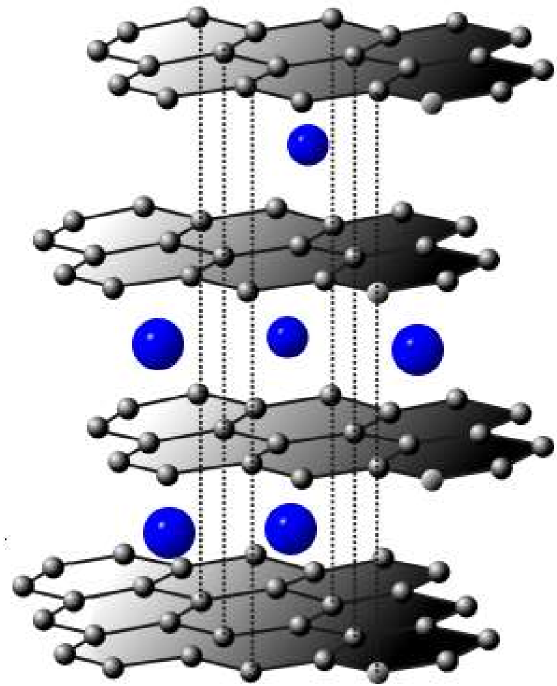
Anode Materials

Typically, graphite is used as the anode in Li-ion batteries:

- Cheap
- Low potential (*cf.* oxides)
    - Gives high cell voltage
- Electrically conducting
- Li intercalates between graphite sheets
    - High Li storage capacity of 339 mAh g^{-1}



Anode Materials

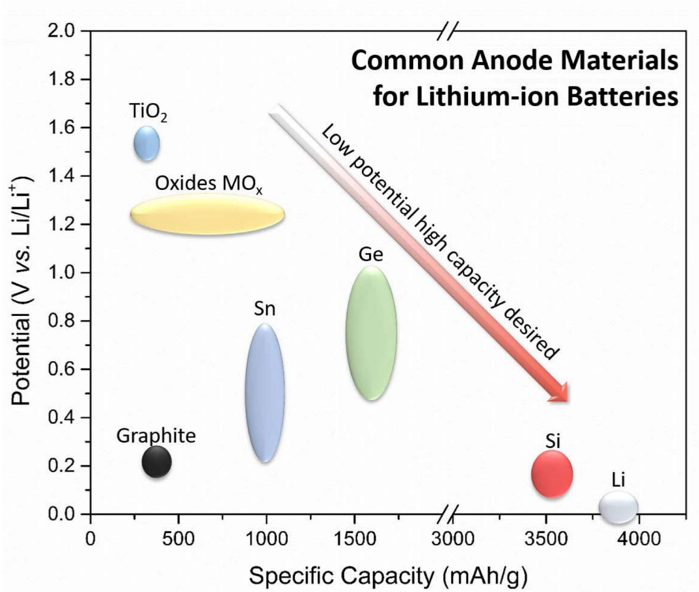
As cathode capacities improve, graphite will become the limiting cell cacpacity

Silicon has a clear advantage in capacity, but breaks down due to massive (320 %) volume changes.

Nano-structured Si (particles or wires) is one potential solution

NOTE: Li anodes have a very high capacity, but this assumes all Li(m) -> Li^+.

- Safety of Li metal is also a concern



Y. Chen, *J. Carbon Res.* **2018**, 18.
e.g. https://www.sigmaaldrich.com/technical-documents/articles/materials-science/recent-developments-in-silicon-anode-materials.html for Si anodes

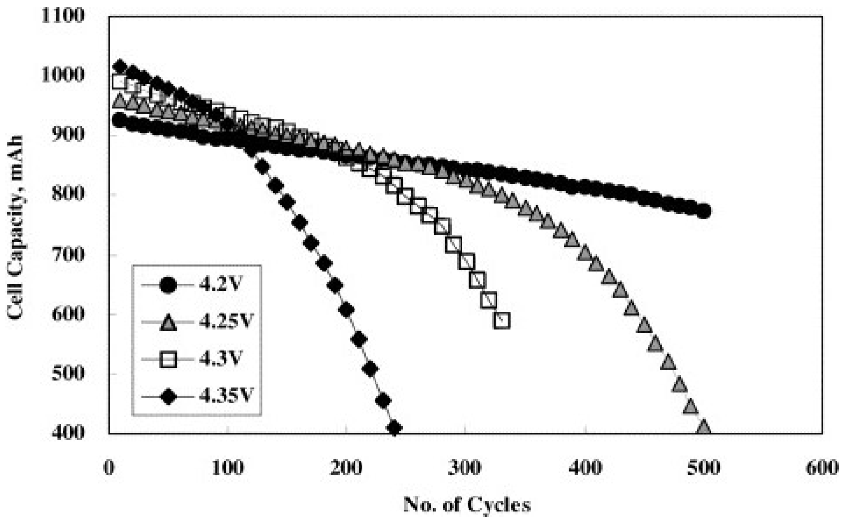
Electrolyte

Liquid electrolyte:

- Must be stable across the potential range of the cell
- **Must** be non-aqueous
- Typically consist of a lithium salt in organic solvent
    - $LiPF_6$, $LiBF_4$, $LiClO_4$
    - Ethylene carbonate, dimethyl carbonate, diethyl carbonate

Limitations of Li-ion batteries

We're all used to Li-ion batteries degrading over time:



Two factors contribute to the 'demise' of Li-ion batteries:

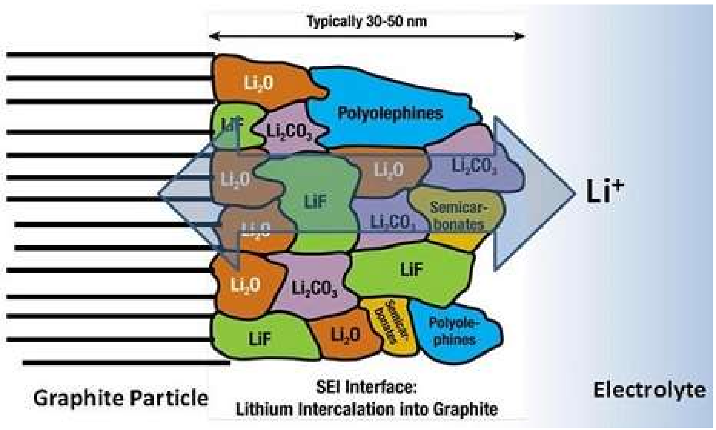
- Solid-Electrolyte Interphase (SEI)
- Dendrites

S.S. Choi, *J. Power Sources*, 2002, 130.

Solid-Electrolyte Interphase (SEI)

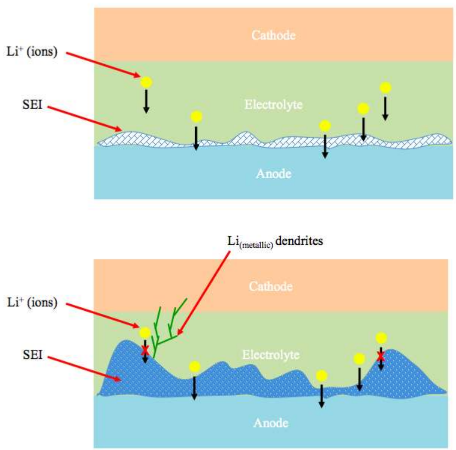
Liquid electrolyte is thermodynamically *unstable* in presence of Li-rich graphite (LiC_6) or Li-metal, decomposing to form SEI.

- ionically-conducting (but worse than electrolyte)
- electrically insulating



Dendrites

- Main cause of fire/explosion in Li batteries
- Short-circuit causes local heating
  - Solvent catches fire...

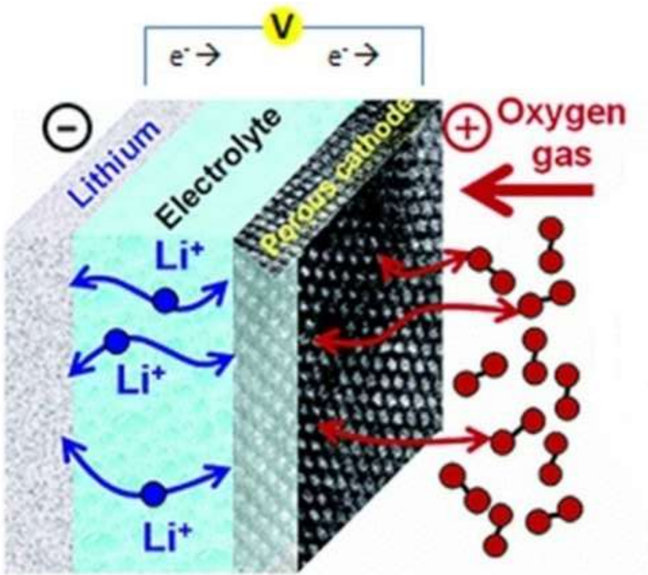


Optical image of Li dendrite

Beyond current Li-ion

One possible solution is the lithium-air battery:

- Removes much of the mass (and cost) of the cathode
  - replaced with porous carbon
- Has energy capacity 5-times that of current Li-ion



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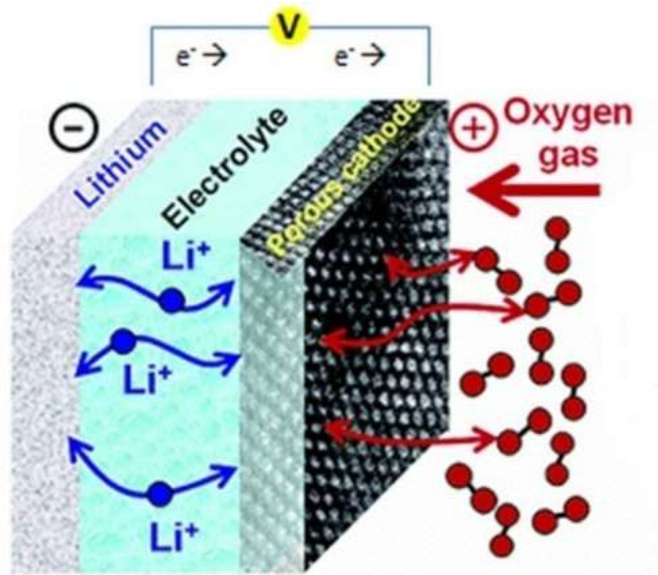
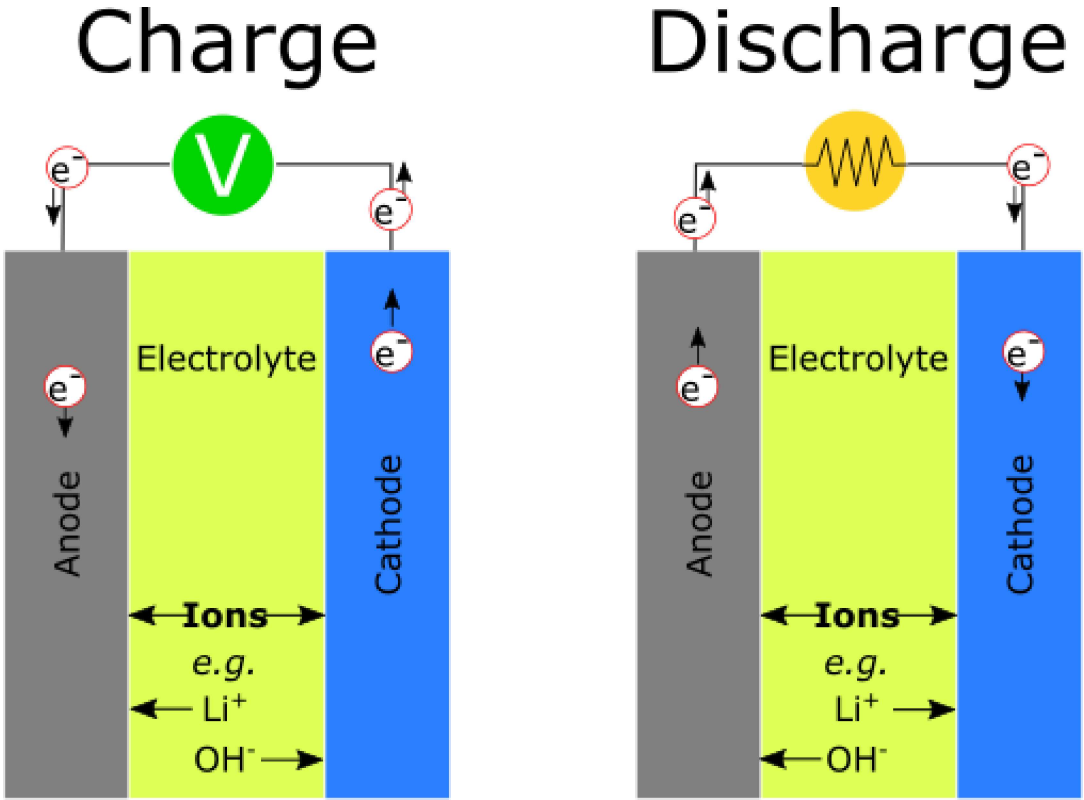


But:

- Li_2O_2 is highly insulating
- Stability of other components (particularly in the presence of O_2) limits long-term use
- Relatively inefficient due to side-reactions
- Dendrites and SEI are highly problematic

Anionic Batteries

Charge can be carried by either cations or anions

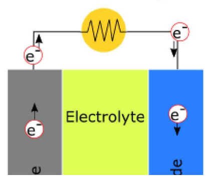


e.g. Nickel-metal hydride (NiMH)

Anode	Electrolyte	Cathode
$MH + OH^- \longrightarrow M + H_2O + e^-$ $E \approx -0.83V$ where M is a mixed-metal alloy, *e.g.* $LaNi_5$	Simple OH^- source, *e.g.* KOH	$NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$ $E = +0.49V$

$$E_{cell} = 0.49V - (-0.83V) = 1.32V$$

Discharge



NiMH Batteries

Advantages

- Can be completely discharged without harm
  - Means cheaper control systems
- Capacity insensitive to charge rate (within reason)
- 'Safe' materials
- Quite robust to overcharging

Disadvantages

- Relatively low cell voltage (1.2 V)
- Limited to low C-rates
- Voltage very sensitive to temperature
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But luckily, O_2 can diffuse to the anode:

$$\mathrm{MH_x} + 2\,\mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{MH_{x+2}} + 2\,\mathrm{OH^-}$$

$$\frac{1}{2}\mathrm{O_2} + \mathrm{MH_{x+2}} \longrightarrow \mathrm{MHx} + \mathrm{H_2O}$$

Fluoride ion batteries

So far we have considered 1-electron redox processes (*e.g.* $\mathrm{Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2}$) why not use multiple electrons?

One solution is di- or tri-valent charge carriers (*e.g.* Mg^{2+}) **but** ionic conduction becomes harder.

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An alternative is multi-electron redox, incorporating more than one charge-carrier per mole, *e.g.*:

$$\mathrm{MF_n + ne^- \longrightarrow M + nF^-}$$

which can occur either as a single reaction or multiple 1-electron processes:

$$\begin{aligned} \mathrm{MF_n + e^-} &\longrightarrow \mathrm{MF_{n-1} + F^-} \\ \mathrm{MF_{n-1} + e^-} &\longrightarrow \mathrm{MF_{n-2} + F^-} \\ &\vdots \\ \mathrm{MF_1 + e^-} &\longrightarrow \mathrm{M + F^-} \end{aligned}$$

NOTE: Total potential for sequence of 1 electron reactions is $E_{tot} = \frac{E_1 + E_2 + ... + E_n}{n}$

V.K. Davies et al., *Science*, 2018, 1144.

Fluoride ion batteries

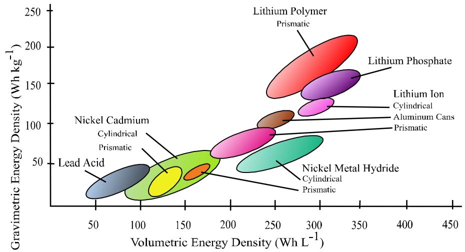
Fluoride ion batteries have theoretical *volumetric* energy density of > 8 times Li-ion batteries!

$$\mathrm{CoF_3} + \mathrm{La} \longrightarrow \mathrm{LaF_3} + \mathrm{Co} \qquad E = 3.31V$$

Cathode: $\mathrm{CoF_3} + 3\,\mathrm{e}^- \longrightarrow \mathrm{Co}^0 + 3\,\mathrm{F}^-$

Anode: $\mathrm{LaF_3} + 3\,\mathrm{e}^- \longleftarrow \mathrm{La} + 3\,\mathrm{F}^-$

$$Q_{\mathrm{theo}} = \frac{3F}{3.6} = 80404\ \mathrm{mAh\ mol^{-1}}$$



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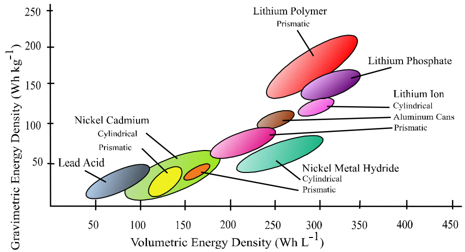

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By (combined) mass:

M_W = 254.83 g mol^{-1}

$Q_{grav.}$ = 315 mAh g^{-1}, so
Gravimetric energy density =
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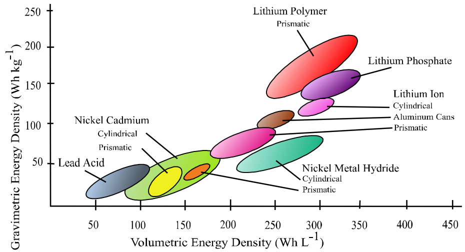

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By combined volume:

LaF_3 density = 5.9 g cm^{-3}

Co density = 1.14 g cm^{-3}

$Q_{vol.}$ = 315 × (5.9 + 1.14) = 2217.6 Ah dm^{-3}

Volumetric energy density = **7340 Wh L^{-1}**

NOTE: These calculations ignore electrolyte and electrode contributions. Including this, volumetric density is still ca. 5069 Wh L^{-1}, *cf.* 400 Wh L^{-1} for Li-ion!

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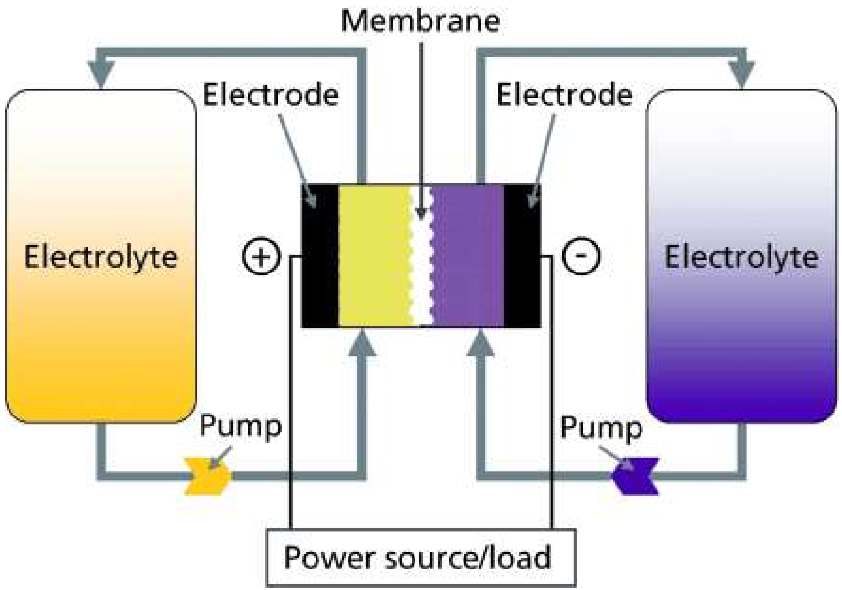
V.K. Davies et al., *Science*, 2018, 1144.

Redox flow batteries

Rather than storing a fixed amount of charge in an electrode, why not use a flowing redox reaction?



- Can be operated with 'rechargable' or replaceable fuel
- Best suited to stationary power applications (to maximise electrolyte storage)

Flow Battery chemistry

The all-vanadium flow battery is most developed:

$$\begin{aligned}
&\text{Cathode:} && VO_2^+ + 2\,H^+ + e^- \longrightarrow VO^{2+} + H_2O && E = +0.991\ \mathrm{V} \\
&\text{Anode:} && V^{3+} + e^- \longrightarrow V^{2+} && E = -0.255\ \mathrm{V} \\
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Advantages

- Simple electrodes (often porous carbon)
- Low maintenance
- Capacity increased by storing more electrolyte

Disadvantages

- Membranes are not perfect
- Cost of metals
- Solubility issues with cycling

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Rongke and Puneng flow cell installations

G. Soloveichik, *Chem. Rev.* 2015, 11533.