

# Batteries 2

# Types of battery technology

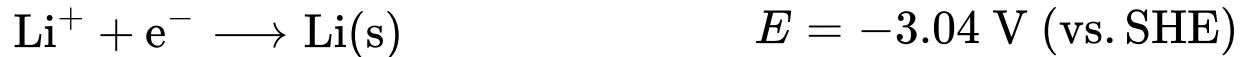
- Cationic battery
  - Li-ion
  - Metal-air
- Anionic battery
  - Hydroxide battery
  - Fluoride ion
- Flow battery



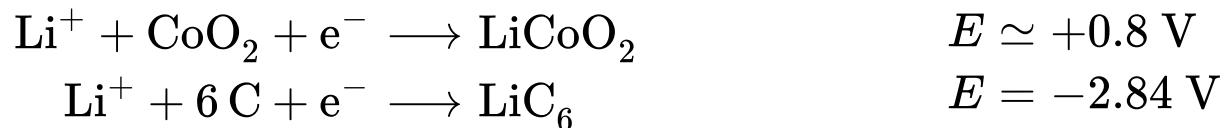
# Cationic Batteries

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

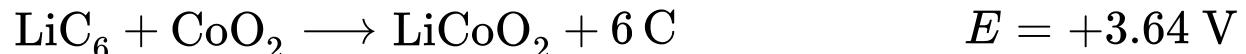
- Li/Li<sup>+</sup> has one of the most negative reduction potentials of any element:



This gives rise to a higher voltage (and therefore energy capacity), e.g.:



overall (on discharge):



$$\begin{aligned} \Delta G &= -nFE \\ &= -351.2 \text{ kJ mol}^{-1} \\ &= -97.5 \text{ Wh mol}^{-1} \end{aligned}$$

Note: 1 W = 1 J s<sup>-1</sup>, so 1 Wh = 3600 J = 3.6 kJ

# Cathode materials

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

**2D conductor**

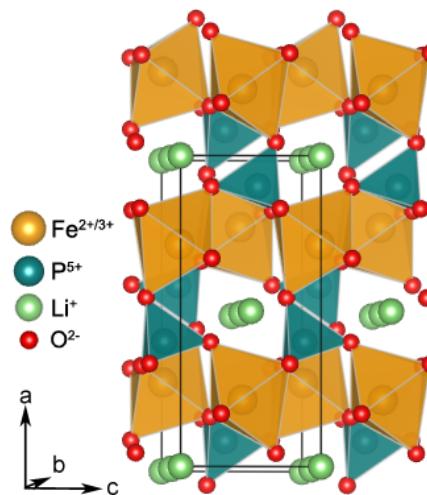
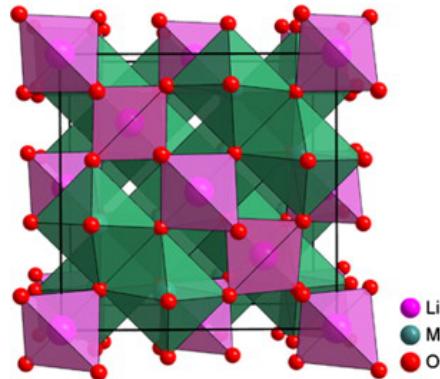
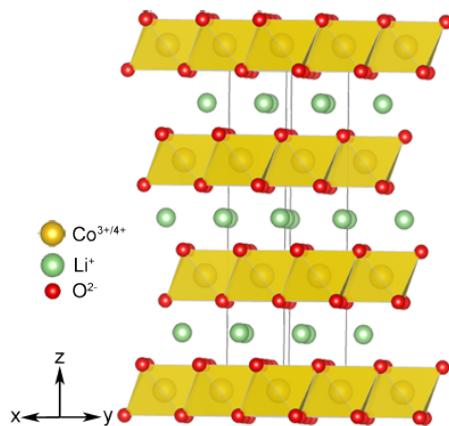
(e.g. layered  $\alpha\text{-NaFeO}_2$ )

**3D conductor**

(e.g. spinel)

**1D conductor**

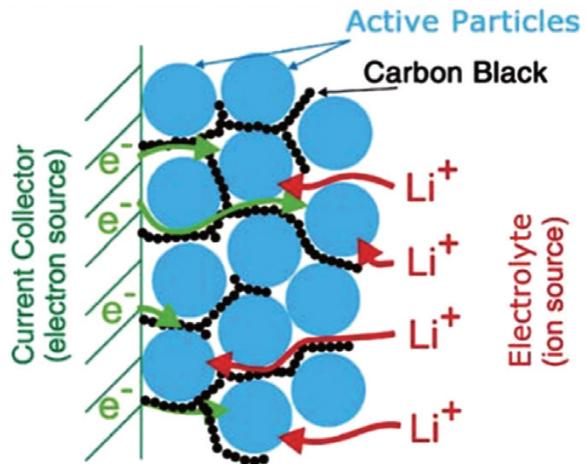
(e.g. olivine)



← 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  $Q_{\text{theo}}$ 
  - Chemical stability (e.g. in  $\text{Li}_x\text{CoO}_2$ ,  $0.5 \leq x \leq 1$ )
  - 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

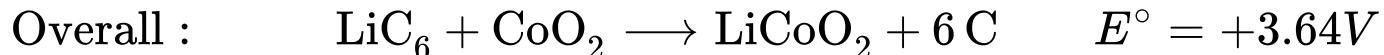
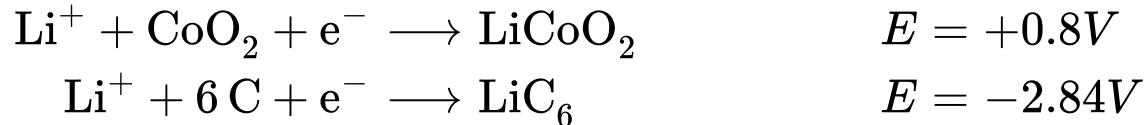
As  $\text{Li}^+$  is removed from the anode,  $E_{\text{meas}}$  changes:

This can be understood using the Nernst Equation:

$$E_{\text{meas}} = E^\circ - \frac{RT}{nF} \ln Q_r$$

where  $Q_r$  is the reaction quotient (how far it has proceeded).

e.g.:



$$E = 3.64 - \frac{RT}{F} \ln \frac{\text{moles}(\text{LiCoO}_2)}{\text{moles}(\text{CoO}_2)}$$

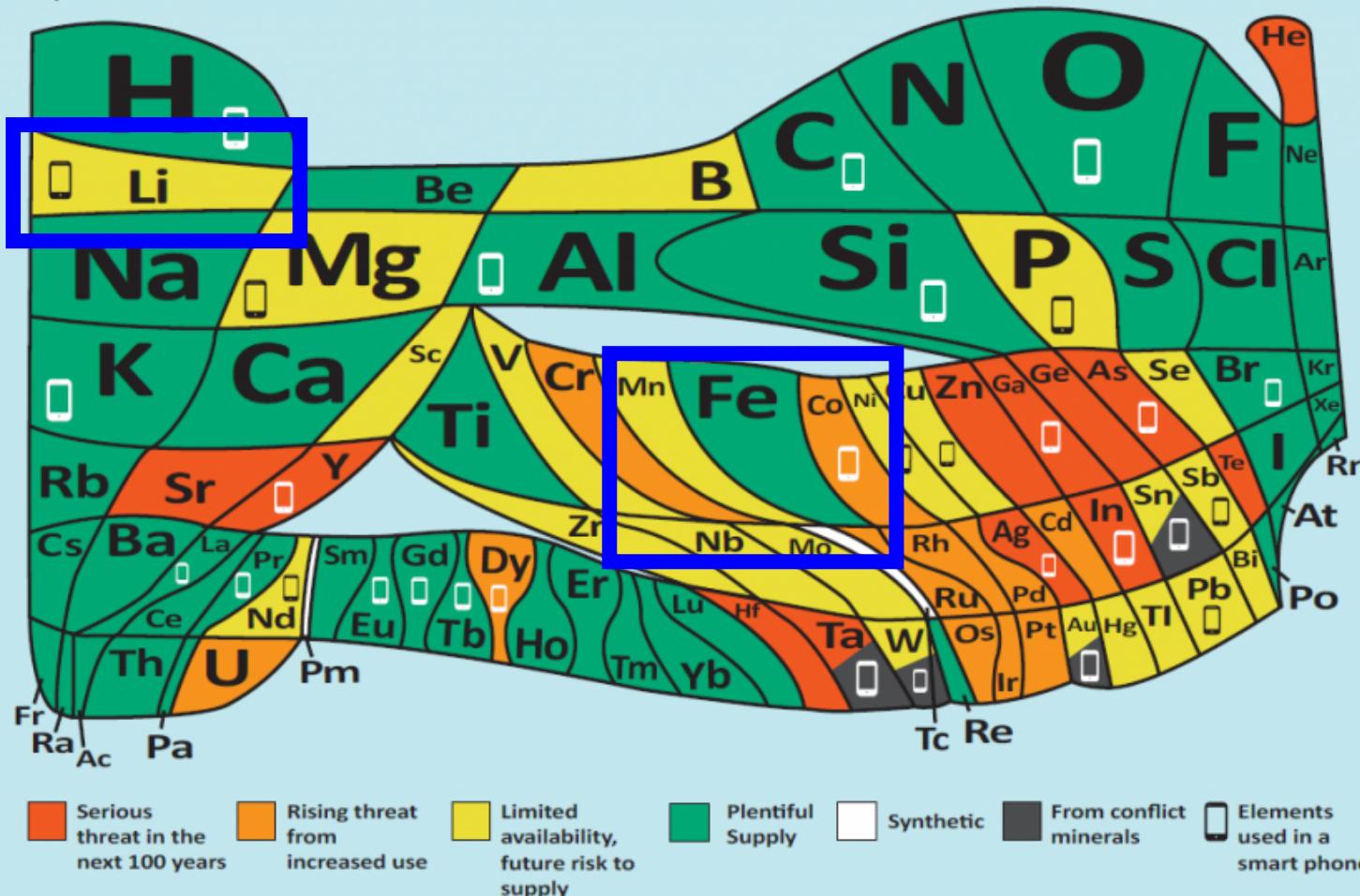


United Nations  
Educational, Scientific and  
Cultural Organization

International Year  
of the Periodic Table  
of Chemical Elements

# The 90 natural elements that make up everything

## How much is there? Is that enough?



Read more and play the video game <http://bit.ly/euchems-pt>

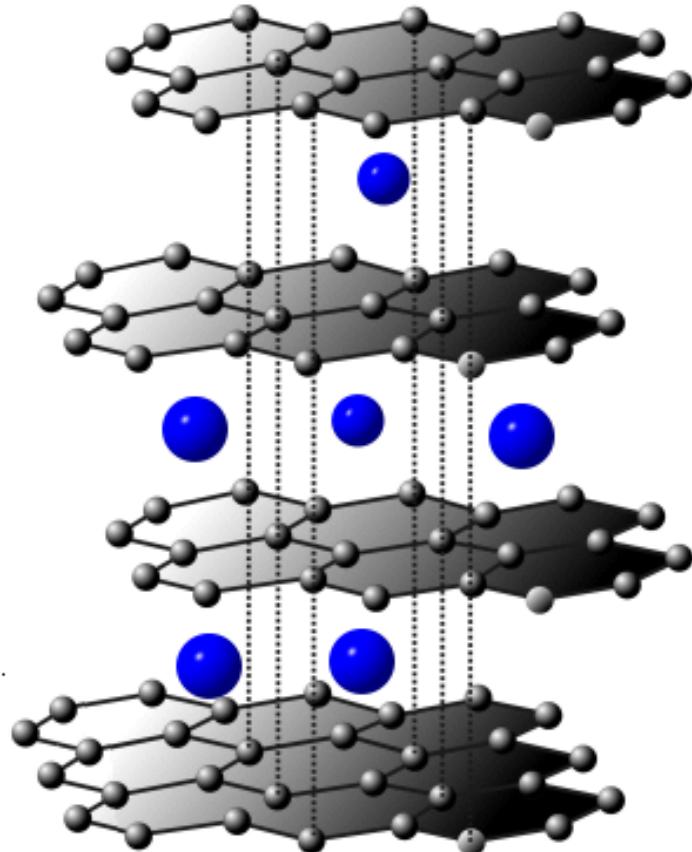


This work is licensed under the Creative Commons Attribution-NoDerivs CC-BY-ND

# 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  $339 \text{ mAh g}^{-1}$



# Anode Materials

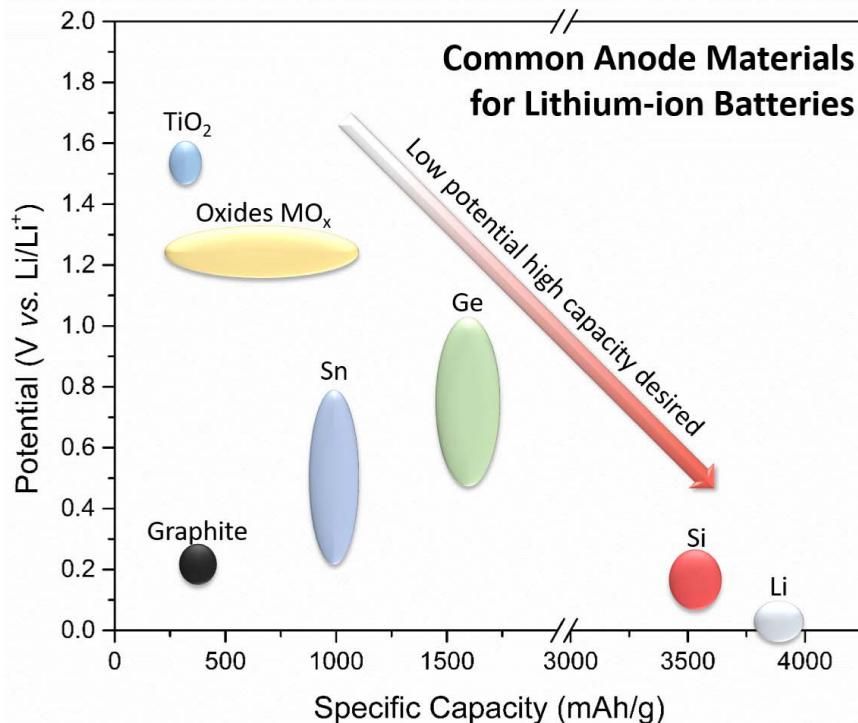
As cathode capacities improve, graphite will become the limiting cell capacity

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  $\text{Li(m)} \rightarrow \text{Li}^+$ .

- Safety of Li metal is also a concern



# 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**
  - $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$
  - Ethylene carbonate, dimethyl carbonate, diethyl carbonate

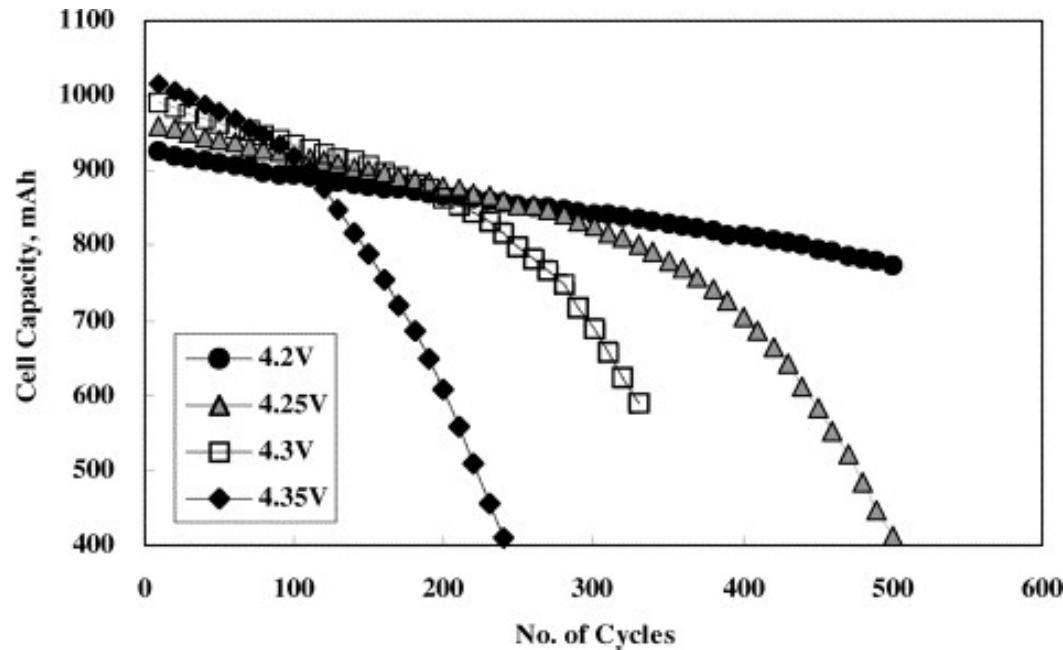


Solid electrolyte:

- Would avoid the problems of solvent leakage/flammability
- Typically use a Li-conducting ceramic (e.g. LISICON,  $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$ )
- Problems:
  - Conductivity is lower than liquid
  - Matching expansion/contraction at the electrode-electrolyte boundary

# 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

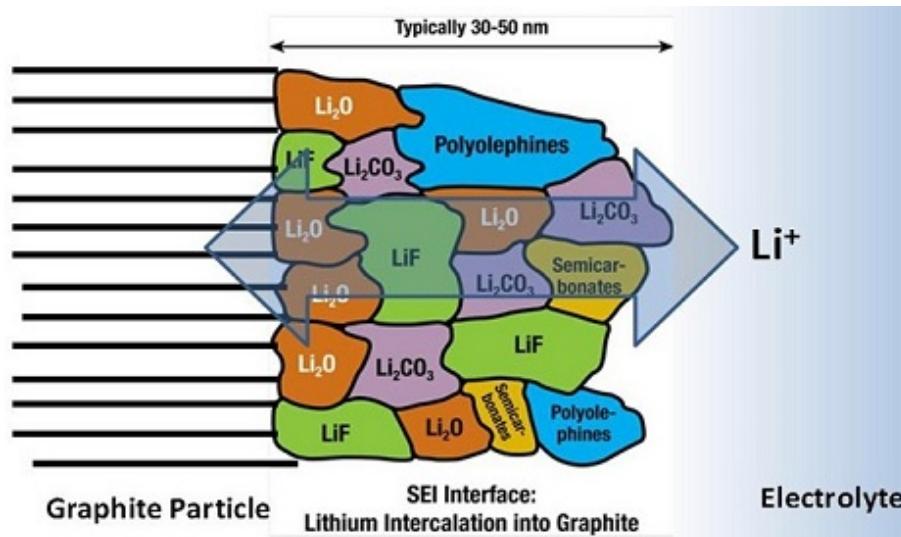
# Solid-Electrolyte Interphase (SEI)

Liquid electrolyte is thermodynamically *unstable* in presence of Li-rich graphite ( $\text{LiC}_6$ ) or Li-metal, decomposing to form SEI.

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

On charge/discharge, cracks in SEI allow further decomposition

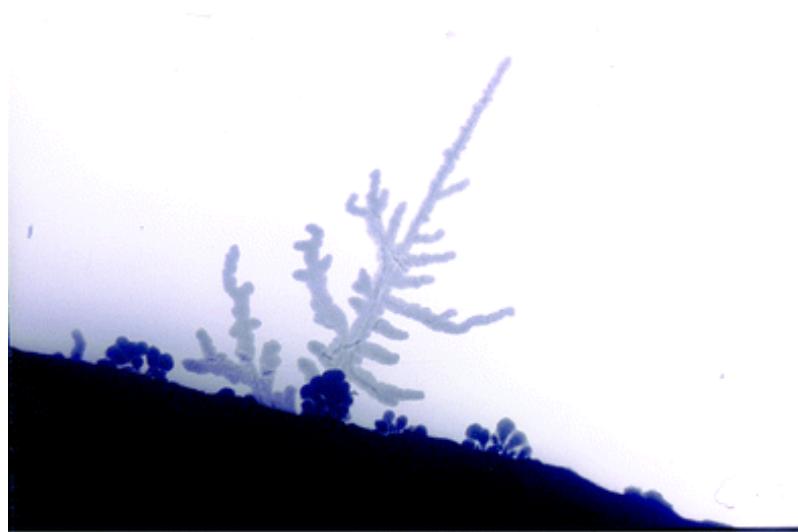
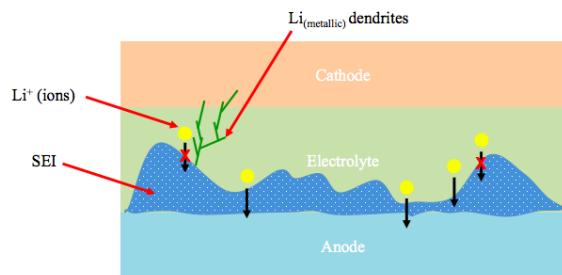
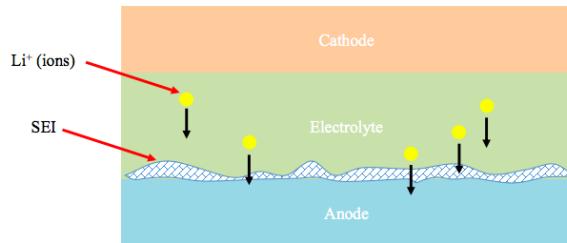
- SEI gets thicker
- Eventually, capacity/conductivity are reduced



# Dendrites

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

Currently this is prevented using separators and careful charging electronics, but this reduces capacity and/or increases cost. Solid-state electrolytes are a partial solution.

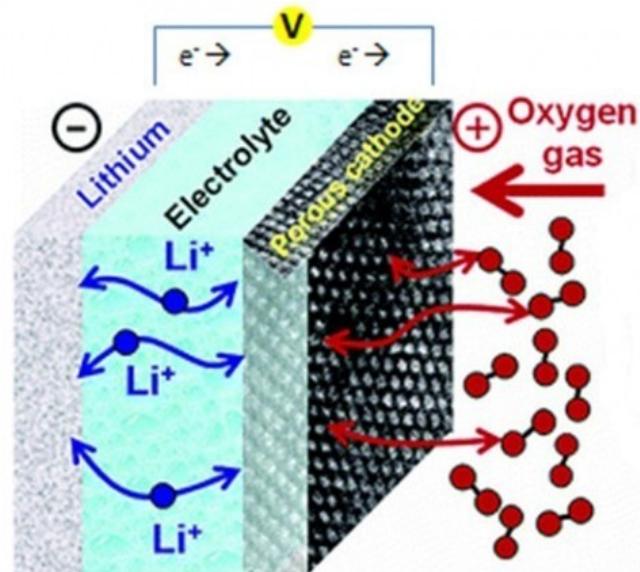


Optical image of Li dendrite

# The future of Li-ion?

Use lighter materials: the **lithium-air** battery:

- Form  $\text{Li}_2\text{O}_2$  as needed when discharging
- Removes much of the mass (and cost) of the cathode
  - replaced with porous carbon
- Has specific capacity 5-times that of current Li-ion



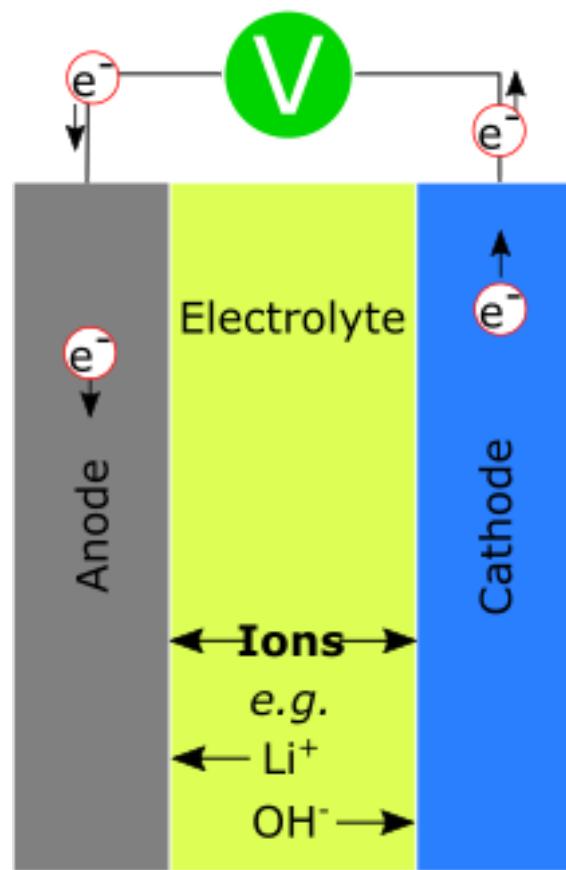
But:

- $\text{Li}_2\text{O}_2$  is highly insulating
- Stability of other components (particularly in the presence of  $\text{O}_2$ ) limits long-term use
- Relatively inefficient due to side-reactions
- Dendrites and SEI are highly problematic

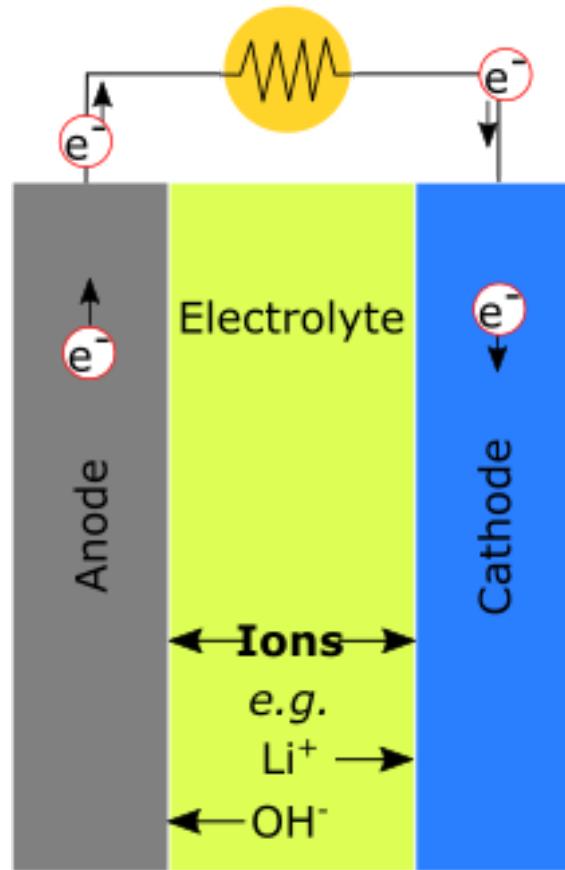
# Anionic Batteries

Charge can be carried by either cations or anions

## Charge



## Discharge



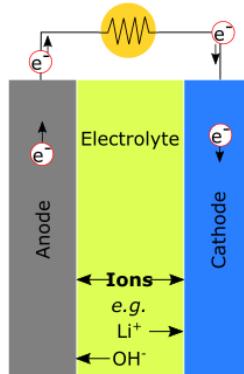
# e.g. Nickel-metal hydride (NiMH)

Anode	Electrolyte	Cathode
$\text{MH} + \text{OH}^- \rightarrow \text{M} + \text{H}_2\text{O} + \text{e}^-$ $E_{(\text{red})} \approx -0.83\text{V}$	Simple $\text{OH}^-$ source, e.g. KOH	$\text{NiO(OH)} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^-$ $E = +0.49\text{V}$

where M is a mixed-metal alloy, e.g.  $\text{LaNi}_5$

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

## Discharge



# NiMH Batteries

## Advantages

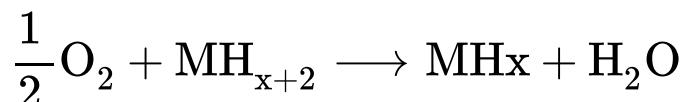
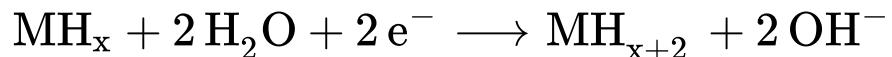
- Can be completely discharged without harm
  - Means cheaper control systems
- Capacity insensitive to charge rate (within reason)
- 'Safe' materials
- Quite robust to overcharging

## Disadvantages

- Relatively low cell voltage (1.2 V)
- Limited to low C-rates
- Voltage very sensitive to temperature
- Very high self-discharge



But luckily,  $\text{O}_2$  can diffuse to the anode:



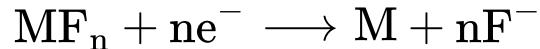
# Fluoride ion batteries

So far we have considered 1-electron redox processes  
(e.g.  $\text{Li}^+ + \text{CoO}_2 + \text{e}^- \rightarrow \text{LiCoO}_2$ )

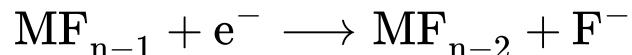
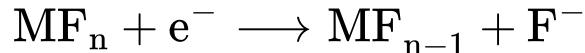
- why not use multiple electrons?

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

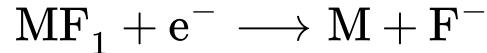
An alternative is multi-electron redox, incorporating more than one charge-carrier per mole, e.g.:



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



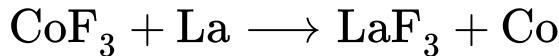
⋮



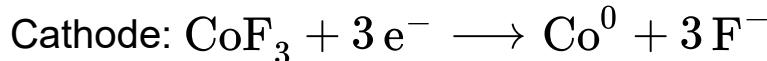
**Note:** Total potential for sequence of 1 electron reactions is  $E_{tot} = \frac{E_1+E_2+\dots+E_n}{n}$

# Fluoride ion batteries

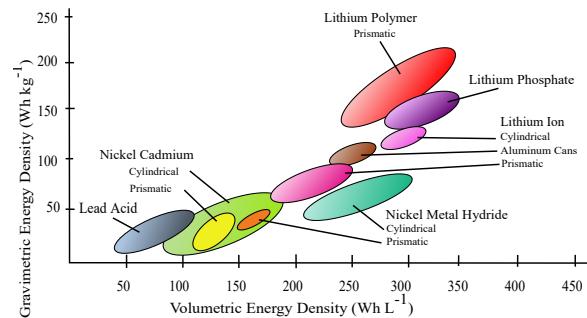
Fluoride ion batteries have theoretical *volumetric* energy density of > 8 times Li-ion batteries!



$$E = 3.31V$$



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



By combined mass:

$$M_w = 254.83 \text{ g mol}^{-1}$$

$$Q_{\text{grav.}} = 315 \text{ mAh g}^{-1}, \text{ so}$$

$$\begin{aligned} \text{Gravimetric energy density} &= \\ 1.04 \text{ Wh kg}^{-1} & \end{aligned}$$

By combined volume:

$$\text{LaF}_3 \text{ density} = 5.9 \text{ g cm}^{-3}$$

$$\text{Co density} = 1.14 \text{ g cm}^{-3}$$

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

$$\text{Volumetric energy density} = 7340 \text{ Wh L}^{-1}$$

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!

# Fluoride ion battery problems

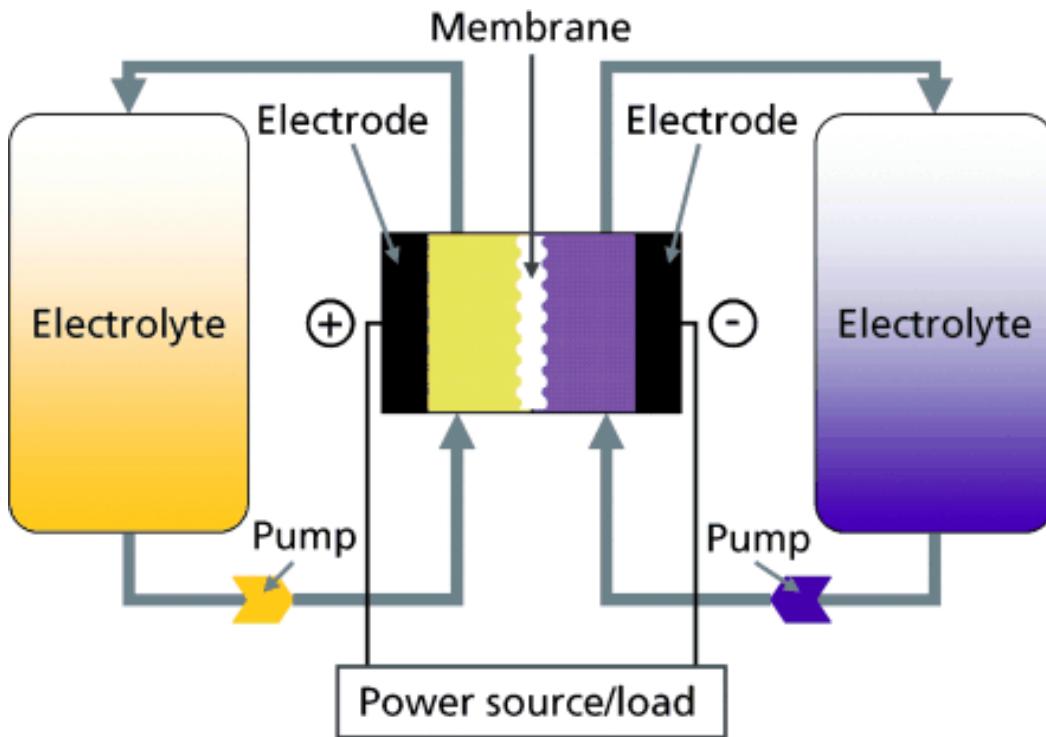
- Most fluoride ion conductors are solids, requiring high temperature ( $\geq 150^\circ$ ) operation
  - Recently,  $R_4N^+$  salts have provided low-temperature  $F^-$  conduction
- Potential safety risks if HF is generated (particulary likely at high temperatures)

Light Bulb in Hydrofluoric Acid (HF)



# Redox flow batteries

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



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

# Flow Battery chemistry

The all-vanadium flow battery is most developed:



## 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

