# 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$^+$ has one of the most negative reduction potentials of any element:

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

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

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

$$\begin{aligned} \mathrm{Li^+ + CoO_2 + e^-} &\longrightarrow \mathrm{LiCoO_2} && E \simeq +0.8\ \mathrm{V} \\ \mathrm{Li^+ + 6\,C + e^-} &\longrightarrow \mathrm{LiC_6} && E = -2.84\ \mathrm{V} \end{aligned}$$

overall (on discharge):

$$\mathrm{LiC_6 + CoO_2 \longrightarrow LiCoO_2 + 6\,C} \qquad E = +3.64\ \mathrm{V}$$

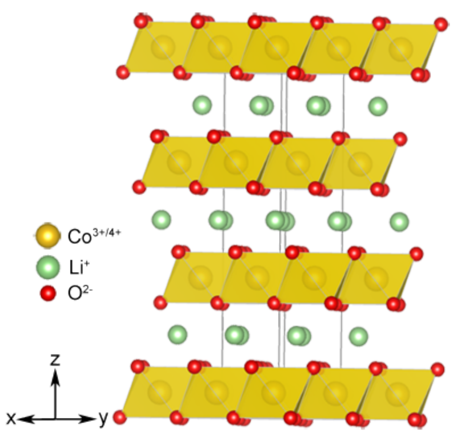
$$\begin{aligned} \Delta G &= -nFE \\ &= -351.2\ \mathrm{kJ\ mol^{-1}} \\ &= -97.5\ \mathrm{Wh\ mol^{-1}} \end{aligned}$$

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

# Cathode materials

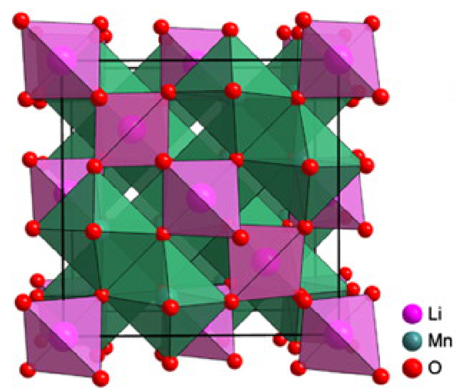
Materials for Li-ion cathodes fall into three main families:

**2D** conductor
(*e.g.* layered α-$NaFeO_2$)



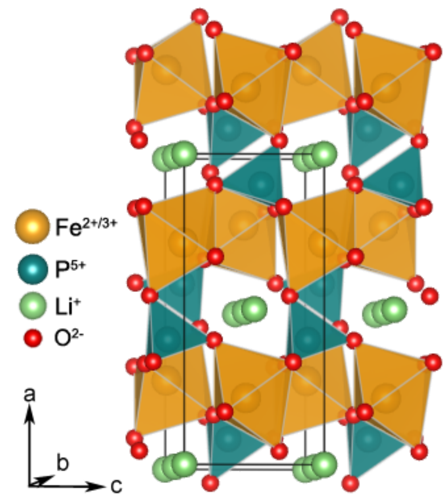

$LiCoO_2$
($Q_{theo}$ = 274 mAh $g^{-1}$)

**3D** conductor
(*e.g.* spinel)




$LiMn_2O_4$
(148 mAh $g^{-1}$)

**1D** conductor
(*e.g.* olivine)

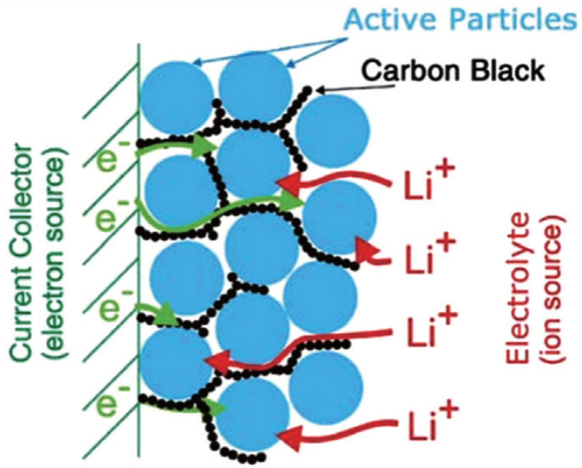



$LiFePO_4$
(170 mAh $g^{-1}$)

← 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



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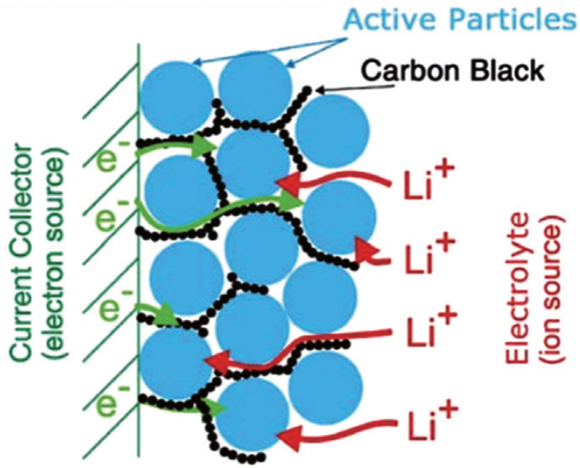
  - Chemical stability (*e.g.* in $Li_xCoO_2$, $0.5 \leq x \leq 1$)
  - Useable capacity is reduced even at low C-rates



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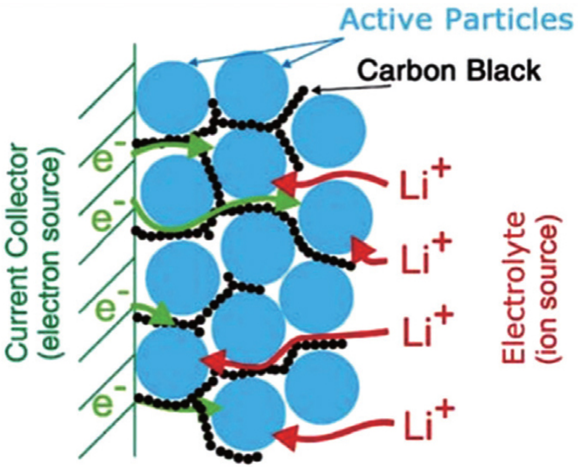


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  - Useable capacity is reduced even at low C-rates
- Practical energy capacity E is often < 30% of the ideal
  - Discharge voltages are lower than expected
    - Ohmic Losses: additional electronic and ionic resistance
    - Drop in voltage with change in Li concentration (concentration polarization)

# Concentration polarization

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

This can be understood using the Nernst Equation:

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

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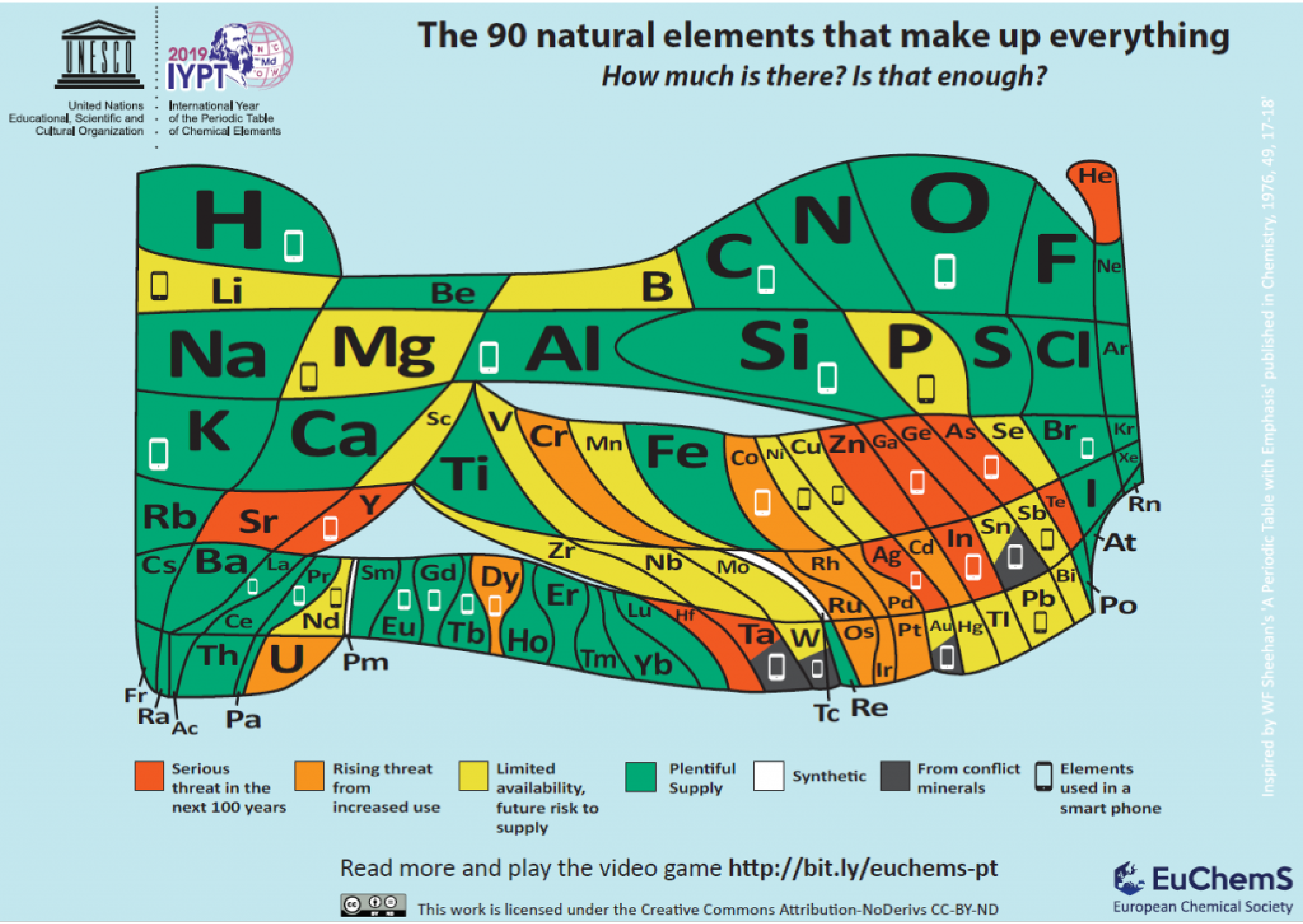
$$E = 3.64 - \frac{RT}{F} \ln \frac{\mathrm{moles(LiCoO_2)}}{\mathrm{moles(CoO_2)}}$$


The 90 natural elements that make up everything
How much is there? Is that enough?
UNESCO
United Nations Educational, Scientific and Cultural Organization
2019 IYPT
International Year of the Periodic Table of Chemical Elements
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Th Pa U
Serious threat in the next 100 years
Rising threat from increased use
Limited availability, future risk to supply
Plentiful Supply
Synthetic
From conflict minerals
Elements used in a smart phone
Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18'
Read more and play the video game http://bit.ly/euchems-pt
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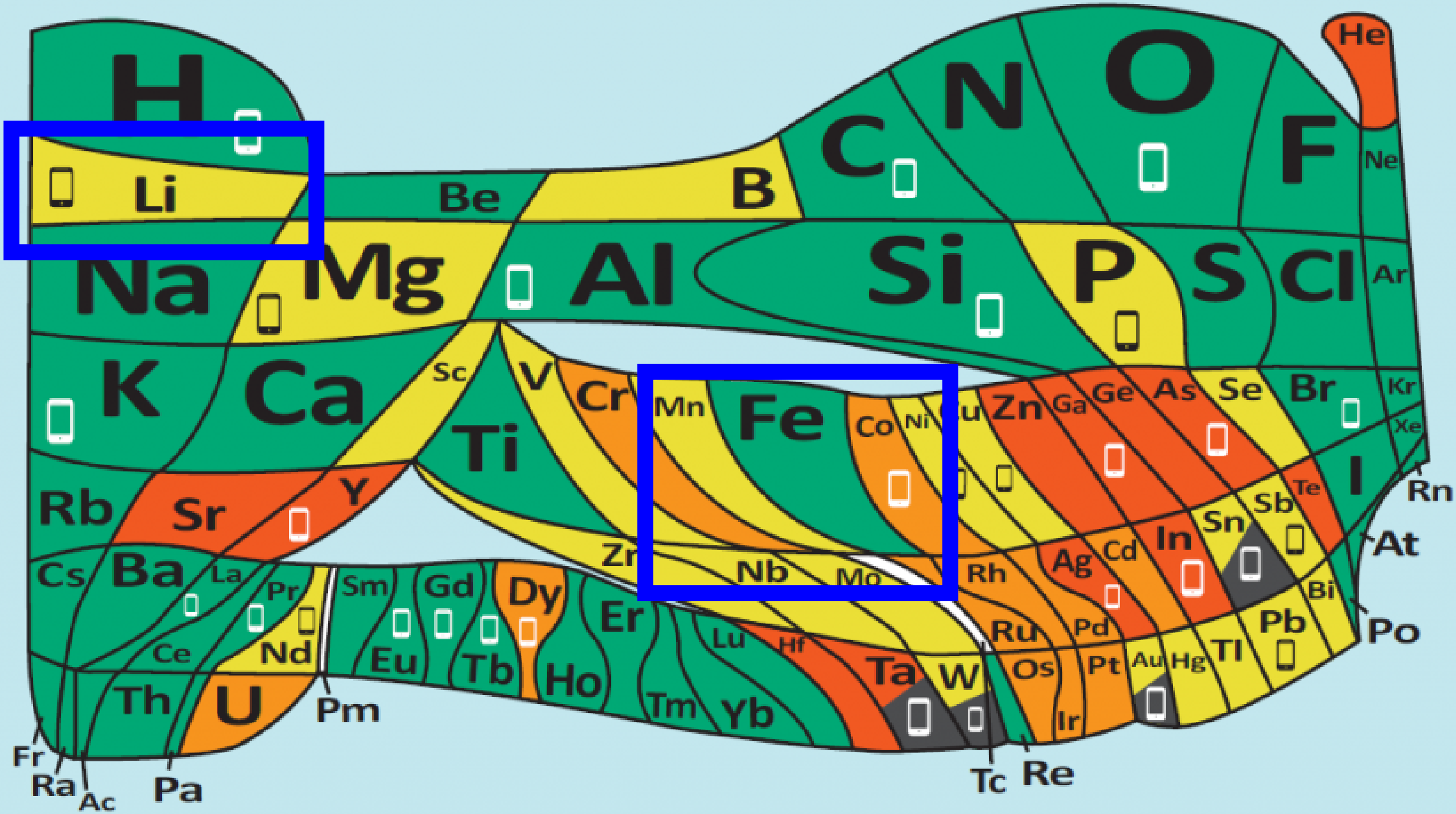
EuChemS
European Chemical Society

United Nations Educational, Scientific and Cultural Organization

2019 IYPT 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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Read more and play the video game **http://bit.ly/euchems-pt**

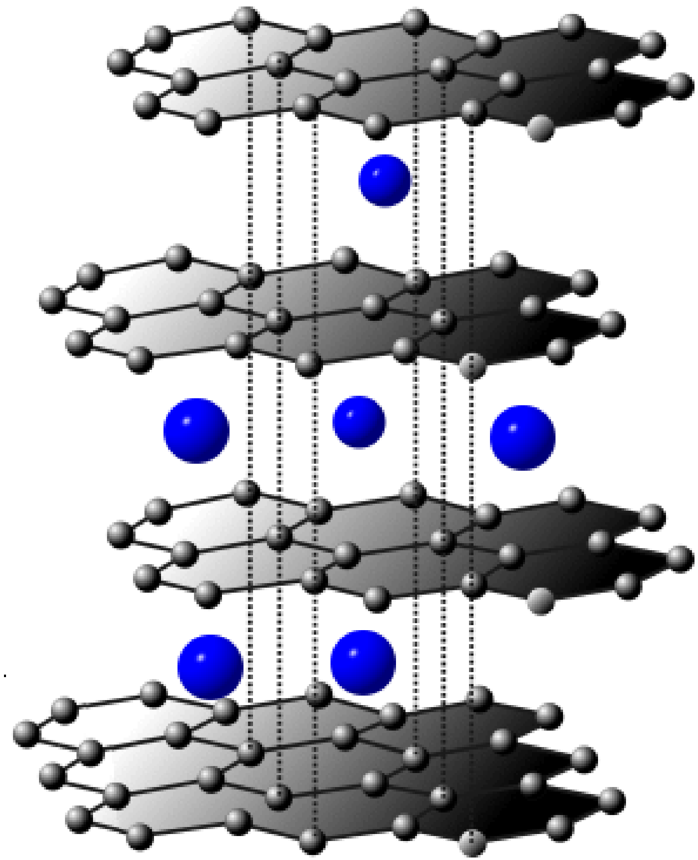


EuChemS European Chemical Society

# 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

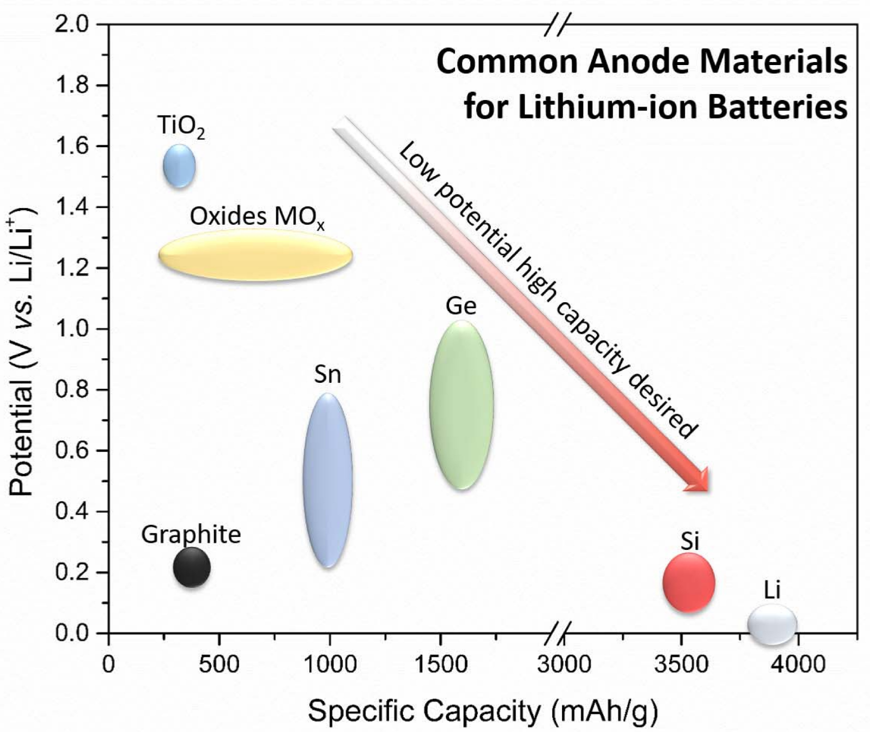
As cathode capacities improve, graphite will become the limiting cell capacity

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 Li(m) -> $Li^+$.

- Safety of Li metal is also a concern

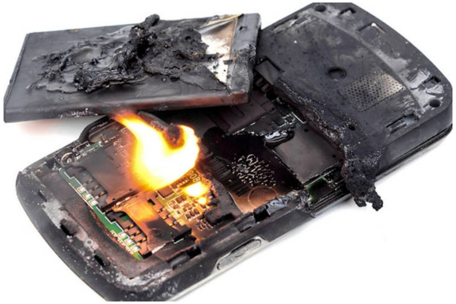



Y. Chen, *J. Carbon Res.* **2018**, 18.
*e.g.* https://www.sigmaaldrich.com/technical-documents/articles/materials-science/recent-developments-in-silicon-anode-materials.html for Si anodes

# 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



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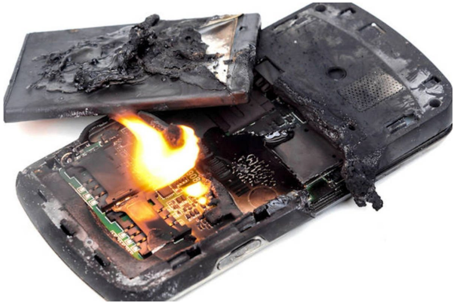
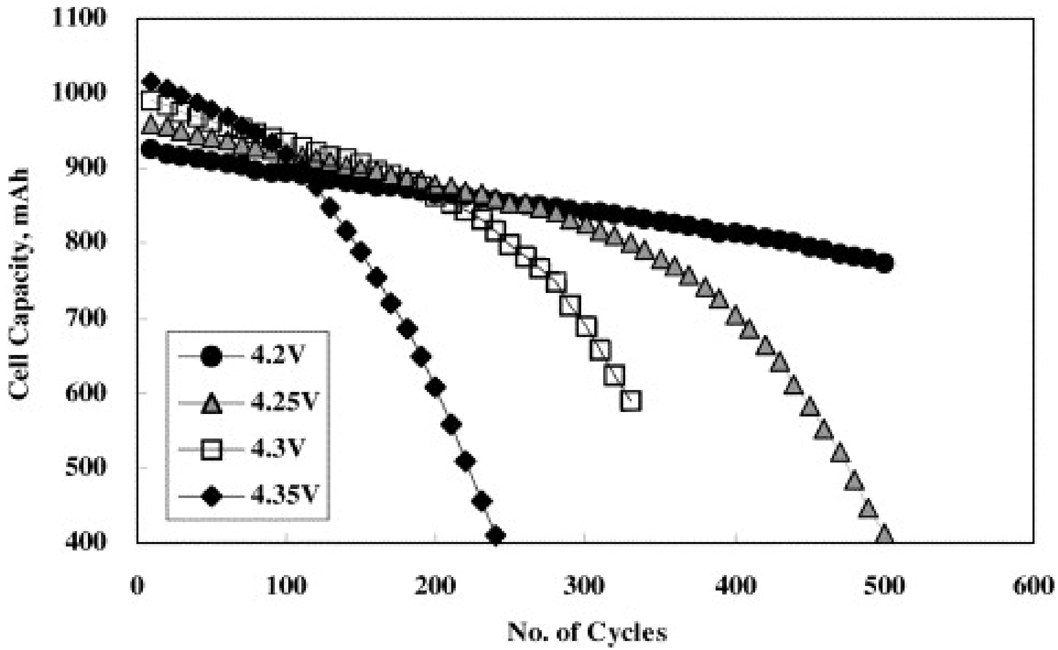


Solid electrolyte:

- Would avoid the problems of solvent leakage/flammability
- Typically use a Li-conducting ceramic (*e.g.* LISICON, $Li_{2+2x}Zn_{1-x}GeO_4$)
- 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:

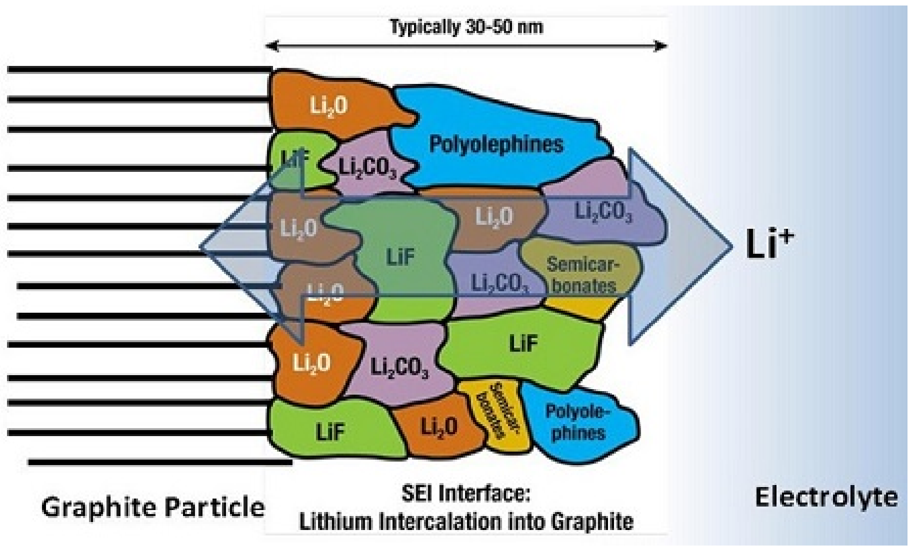
- Solid-Electrolyte Interphase (SEI)
- Dendrites

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



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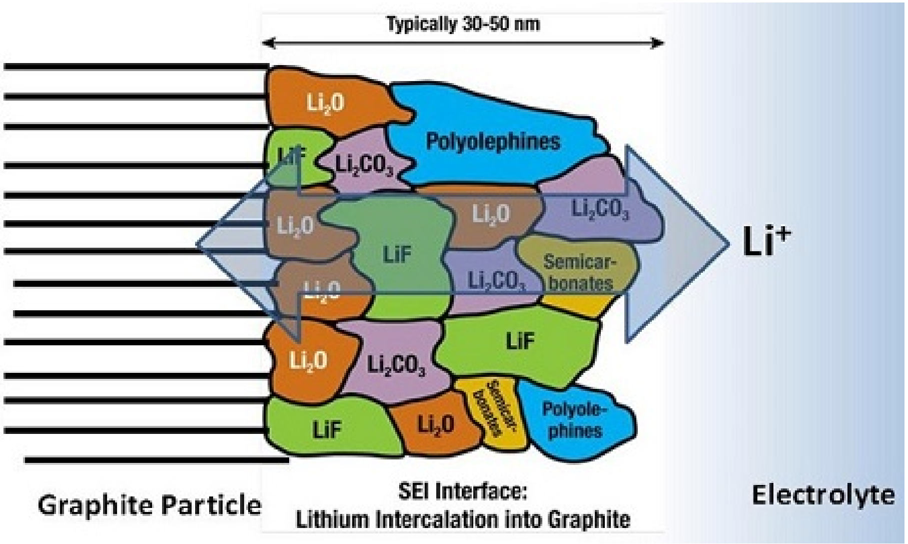
On charge/discharge, cracks in SEI allow further decomposition

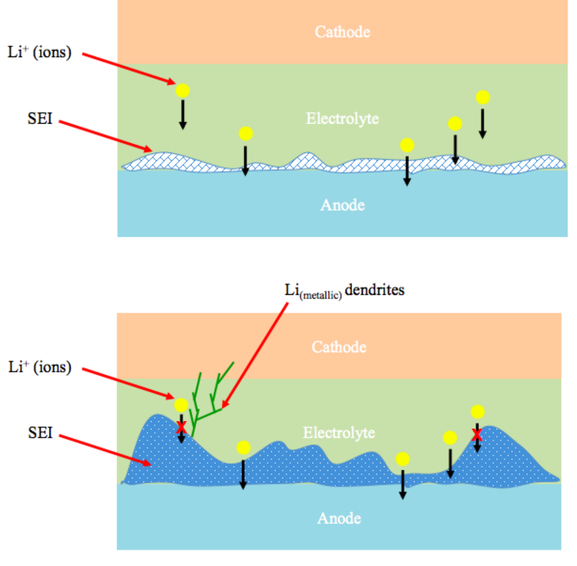
- SEI gets thicker
- Eventually, capacity/conductivity are reduced



# 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.

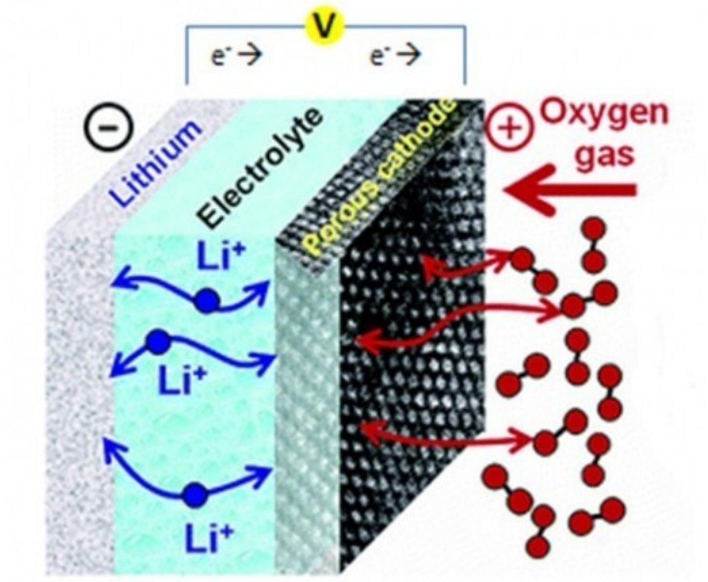



Optical image of Li dendrite

# The future of Li-ion?

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

- Form $Li_2O_2$ 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



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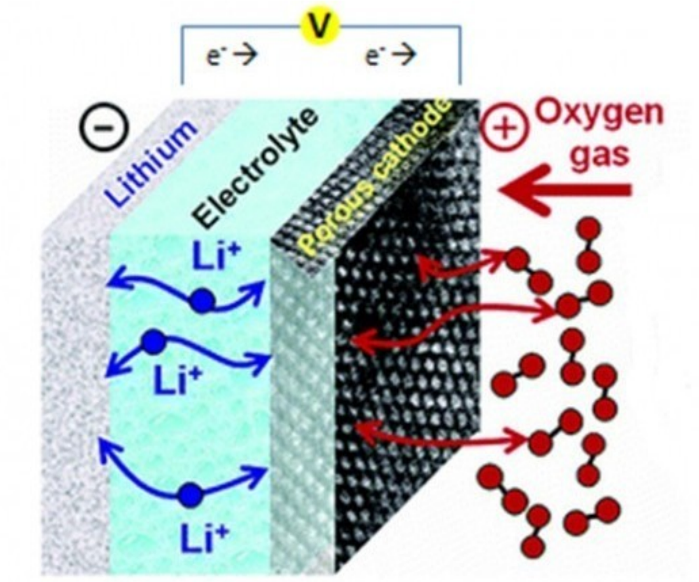
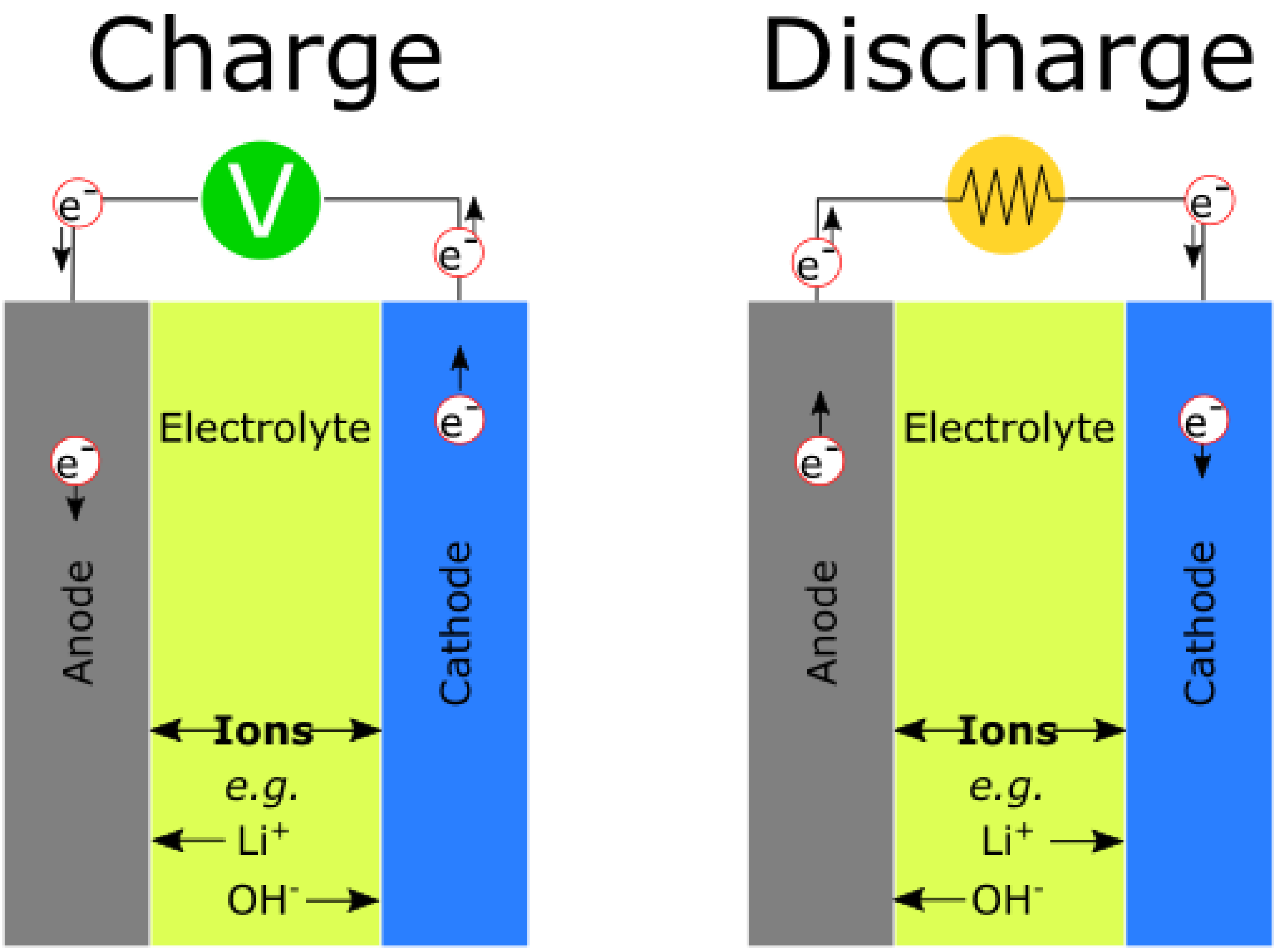



**But:**

- $Li_2O_2$ 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

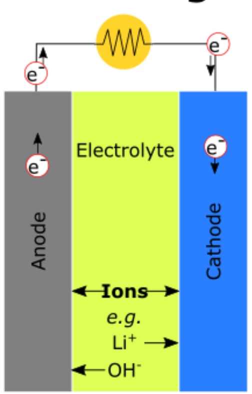


# *e.g.* Nickel-metal hydride (NiMH)

| **Anode** | **Electrolyte** | **Cathode** |
| --- | --- | --- |
| $\mathrm{MH} + \mathrm{OH}^- \longrightarrow \mathrm{M} + \mathrm{H_2O} + \mathrm{e}^-$ <br> $E_{(\mathrm{red})} \approx -0.83\mathrm{V}$ | Simple $OH^-$ source, *e.g.* KOH | $\mathrm{NiO(OH)} + \mathrm{H_2O} + \mathrm{e}^- \longrightarrow \mathrm{Ni(OH)_2} + \mathrm{OH}^-$ <br> $E = +0.49\mathrm{V}$ |

where M is a mixed-metal alloy, *e.g.* $LaNi_5$

Discharge




$$
\begin{aligned}
E_{\mathrm{cell}} &= 0.49\mathrm{V} - (-0.83\mathrm{V}) \\
&= 1.32\ \mathrm{V}
\end{aligned}
$$

# 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

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Problematic electrolyte reaction: $2\,\mathrm{OH^-} \longrightarrow \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2(g)} + 2\,\mathrm{e^-}$

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

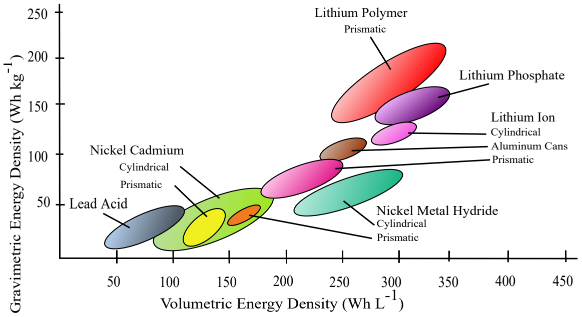
Fluoride ion batteries have theoretical *volumetric* energy density of > 8 times Li-ion batteries!

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

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

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

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



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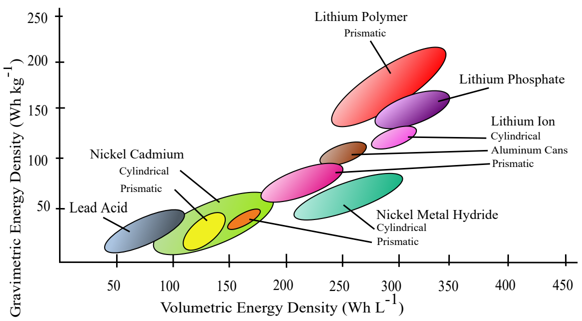


By combined mass:

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

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

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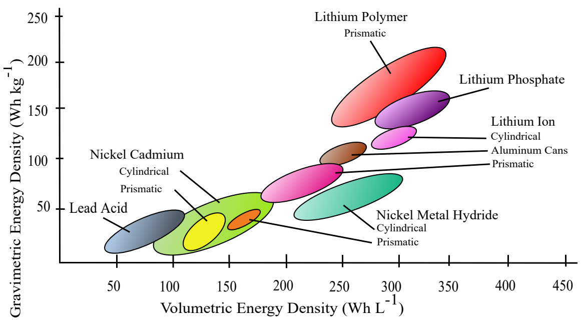


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By combined volume:

$LaF_3$ 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!

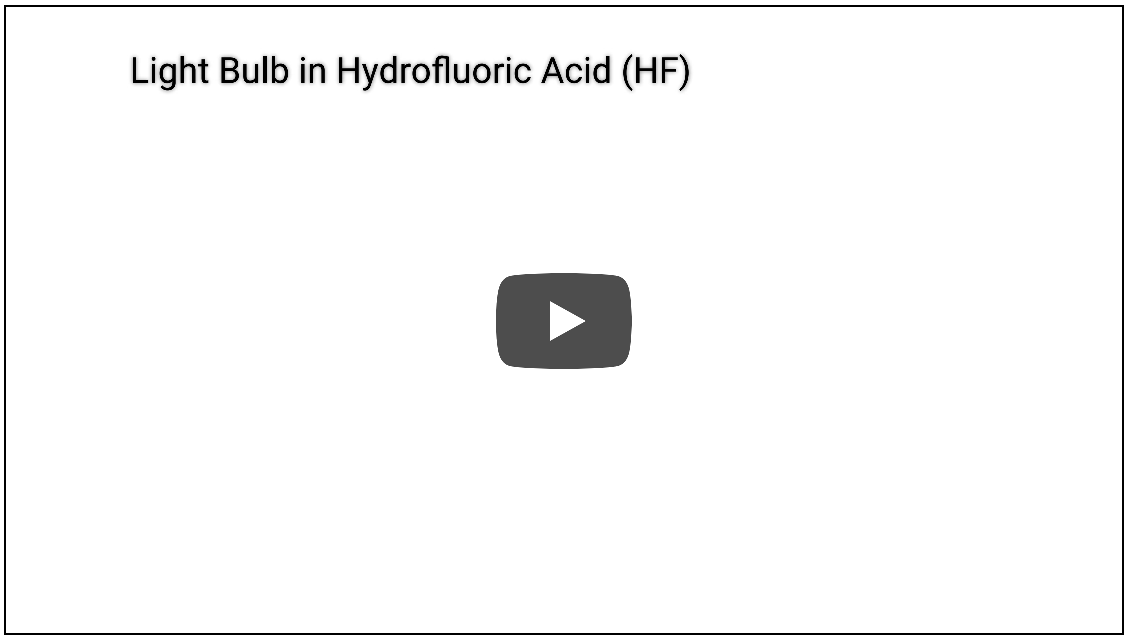
# Fluoride ion battery problems

- Most fluoride ion conductors are solids, requiring high temperature (≥ 150 °) operation
  - Recently, $R_4N^+$ salts have provided low-temperature $F^-$ conduction

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

# Fluoride ion battery problems

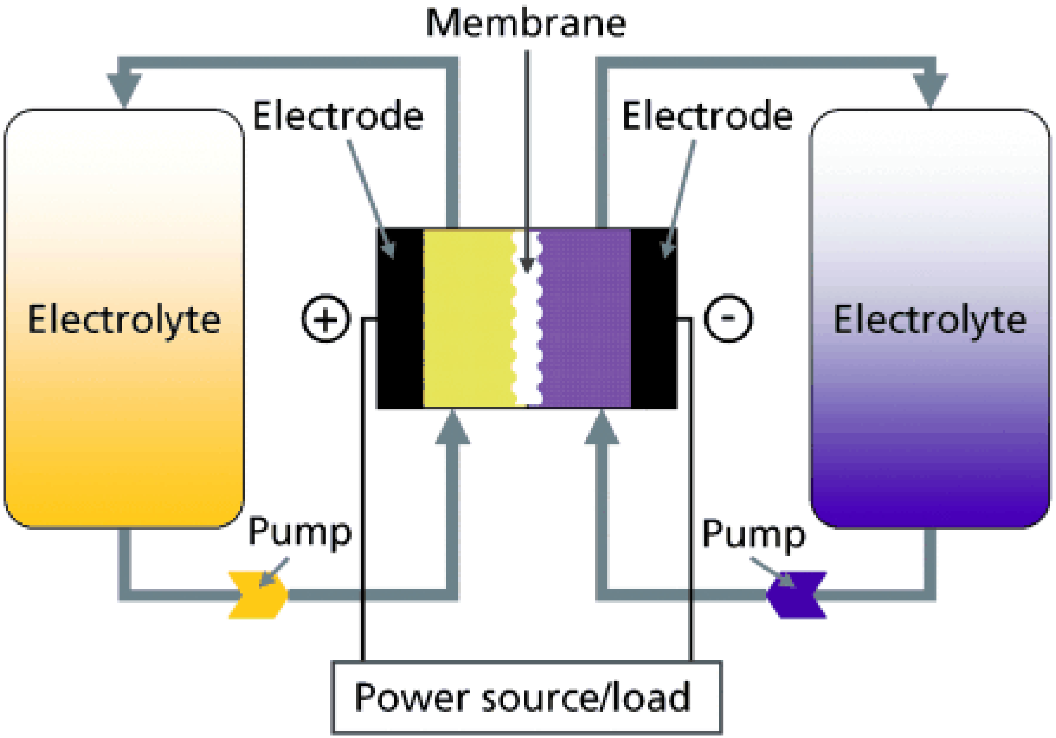
- Most fluoride ion conductors are solids, requiring high temperature (≥ 150 °) operation
    - Recently, $R_4N^+$ salts have provided low-temperature $F^-$ conduction
- Potential safety risks if HF is generated (particulary likely at high temperatures)




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 liquid 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}\\
&\text{Overall :} && VO_2^+ + 2\,H^+ + V^{2\,+} \longrightarrow VO^{2\,+} + V^{3\,+} + H_2O && E_{tot} = 1.246\ \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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The all-vanadium flow battery is most developed:

$$\begin{array}{lll}
\text{Cathode :} & VO_2^{+} + 2\,H^{+} + e^{-} \longrightarrow VO^{2\,+} + H_2O & E = +0.991\ \text{V} \\
\text{Anode :} & V^{3\,+} + e^{-} \longrightarrow V^{2\,+} & E = -0.255\ \text{V} \\
\text{Overall :} & VO_2^{+} + 2\,H^{+} + V^{2\,+} \longrightarrow VO^{2\,+} + V^{3\,+} + H_2O & E_{tot} = 1.246\ \text{V}
\end{array}$$

## 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

Rongke and Puneng flow cell installations

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