Lecture 4 - Batteries

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Lecture summary

- Electrochemistry fundamentals
- Battery history and overview
- Battery definitions
- Improving capacity
- Essential materials properties
    - types of electrode behaviour
- average vs local structure picture

Essential electrochemistry

Quantities

Throughout this course, we will see a number of electronics/electrochemistry terms, summarised here:

Term	Symbol	Description	Units
Potential (or voltage)	E or V	the 'push' moving the electrons	Volts (V)
Current	I	the rate at which electrons move	Amperes (A)
Charge	Q	amount of electrons	Coloumbs (C) or Amp-hours (Ah, 1 mAh = 3.6 C)
Resistance	R	effects reducing the current	Ohms (Ω)
Capacitance	C	ability to store charge	Farads (F)
Power	P	how much current, and with what force	Watts (W)

Important relationships

Ohm's law - current and potential are linked:

$$V = IR$$

(Ohm's law) A current flowing for a period of time gives an overall charge:

$$Q = It$$

Power is a combination of current and voltage:

$$P = IV$$

Resistivity (ρ) and conductivity (σ) are inversely related. Note that resistance (R) is related to resistivity (ρ) by accounting for the geometry of the object.

$$\rho = \frac{1}{\sigma}$$

Why batteries?

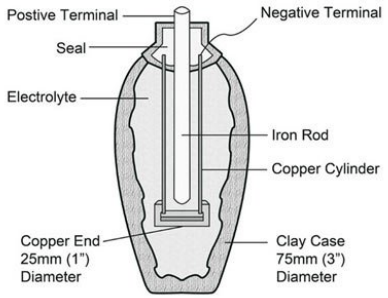
- Portable electronics
- Electric vehicles
- Grid-storage (e.g. from renewables)
- ...

Future batteries require more charge stored in a smaller volume and/or mass.

This requires *new materials* from chemistry.

(Brief) Battery History

- ***ca.* 190 AD**: Baghdad (or Parthian) battery



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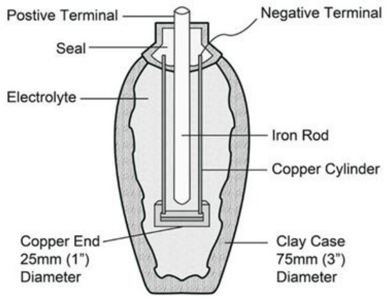
- ***ca.* 190 AD**: Baghdad (or Parthian) battery
- **1800**: Volta created the voltaic pile
  - Alternating Ag and Zn discs, NaCl electrolyte
  - Enabled *chemistry* e.g. $2\,H_2O \longrightarrow 2\,H_2 + O_2$



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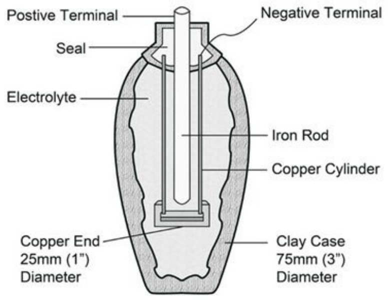

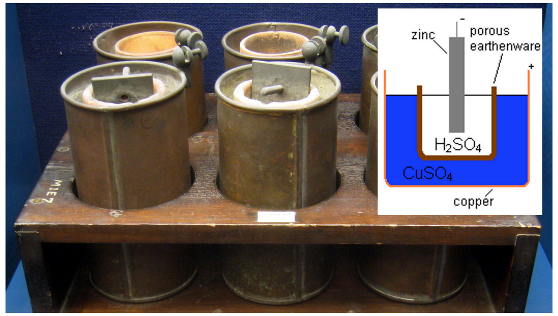

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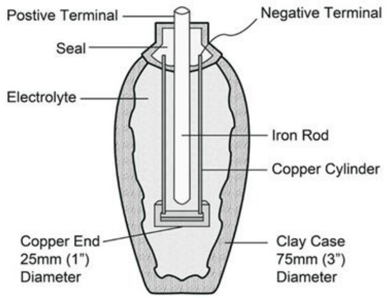
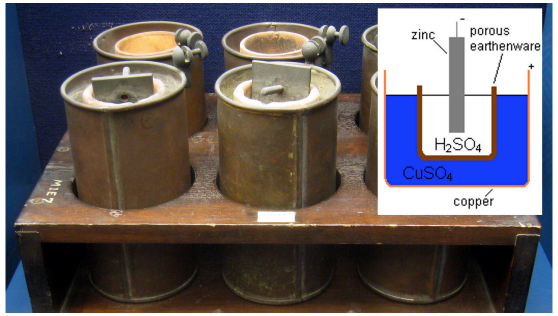
- **1886** The first dry cell: $Zn|NH_4Cl|MnO_2$
  - NH_4Cl immobilised with plaster of Paris $(CaSO_4 \cdot 0.5H_2O)$
- **1899** The first alkaline battery: $NiO(OH)|KOH|Cd$
- **1991** Li-ion battery commercialised by Sony





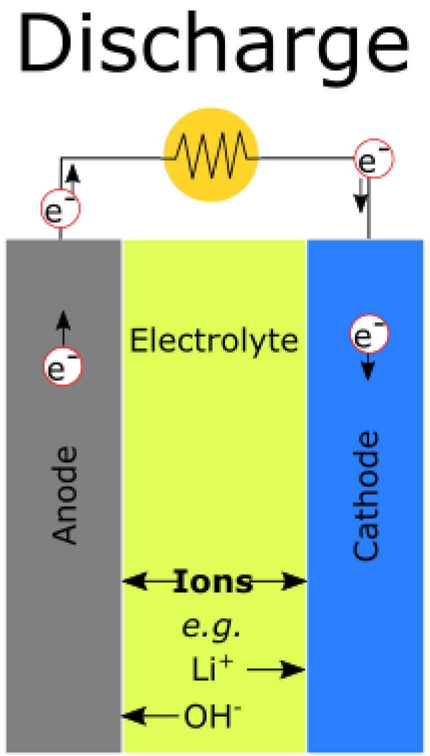
Definitions

A battery consists of two electrodes (cathode and anode) and an electrolyte.

Defining the *anode* and *cathode* depends whether we are charging or discharging.

In this course, we will use **discharge** definitions:

- Cathode is the **positive** electrode (gets reduced)
- Anode is the **negative** electrode (gets oxidised)



Charge carriers

Cationic battery

Charge carried across electrolyte by cations

- Li^{+}, Na^{+} ...
- Mg^{2+}, Ca^{2+}, ...
- Even Zn^{2+}, Al^{3+}

Anionic battery

Anion charge carrier in electrolyte

- OH^{-} (NiCd or NiMH)
- F^{-}, Cl^{-}
- HSO_4^{-} (in Pb-acid)

What makes a 'good' battery?

Perhaps the most important parameter in batteries is the total *energy capacity*, $\mathrm{E}_{\mathrm{bat}}$

- Combination of cell voltage (*V*) and amount of charge (*Q*) stored in the material:

$$\mathrm{E}_{\mathrm{bat}} = QV$$

Q is expressed in units of Ah, so E_{bat} is in Wh (Watt-hours).
A 3 Wh battery can supply 3 W of power for 1 hour

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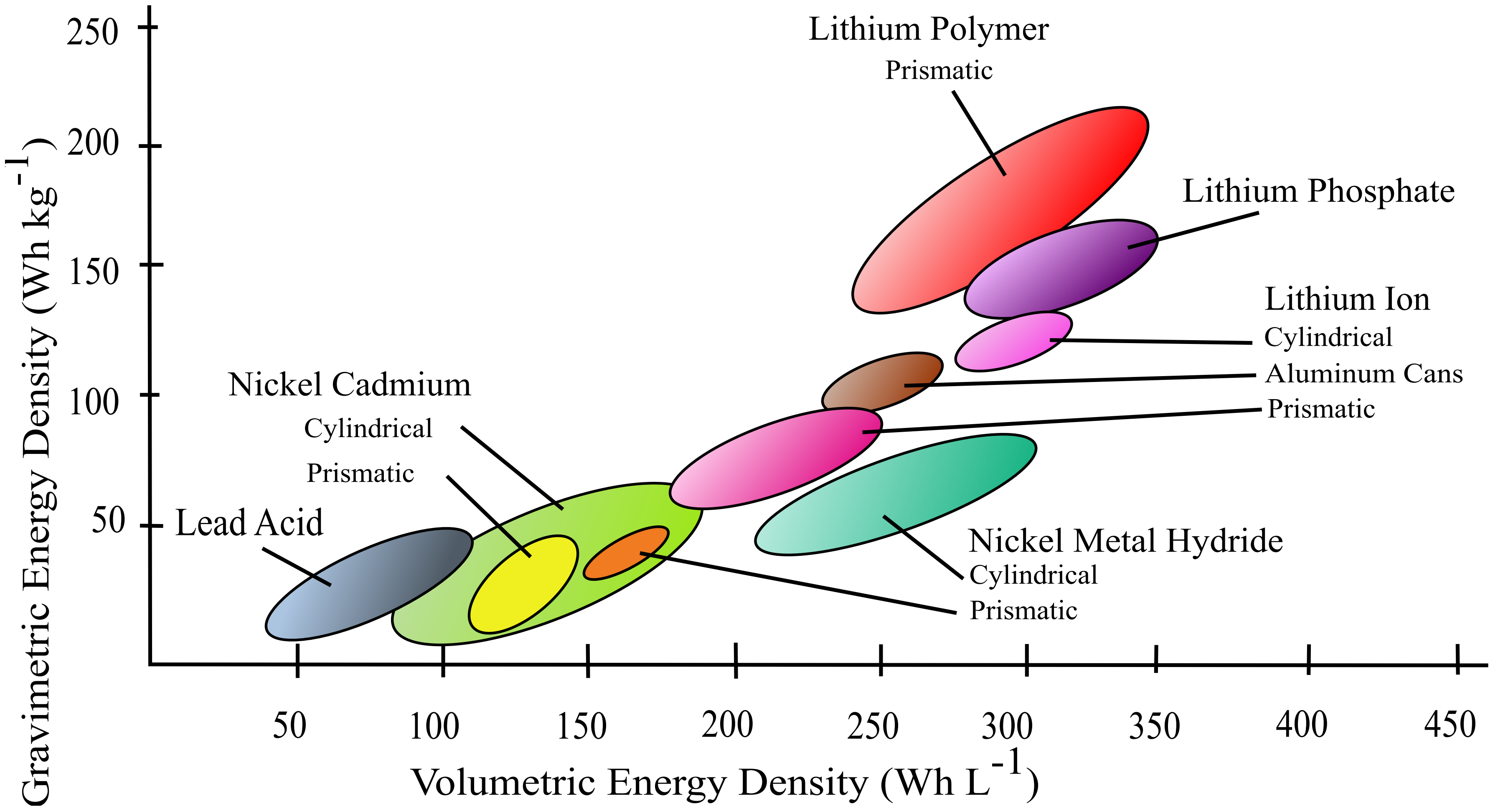
- E_{bat} is dependent on the amount of battery material. More useful are:
  - Specific (gravimetric) energy (Wh g^{-1}).
  - (Volumetric) energy density (Wh L^{-1}).

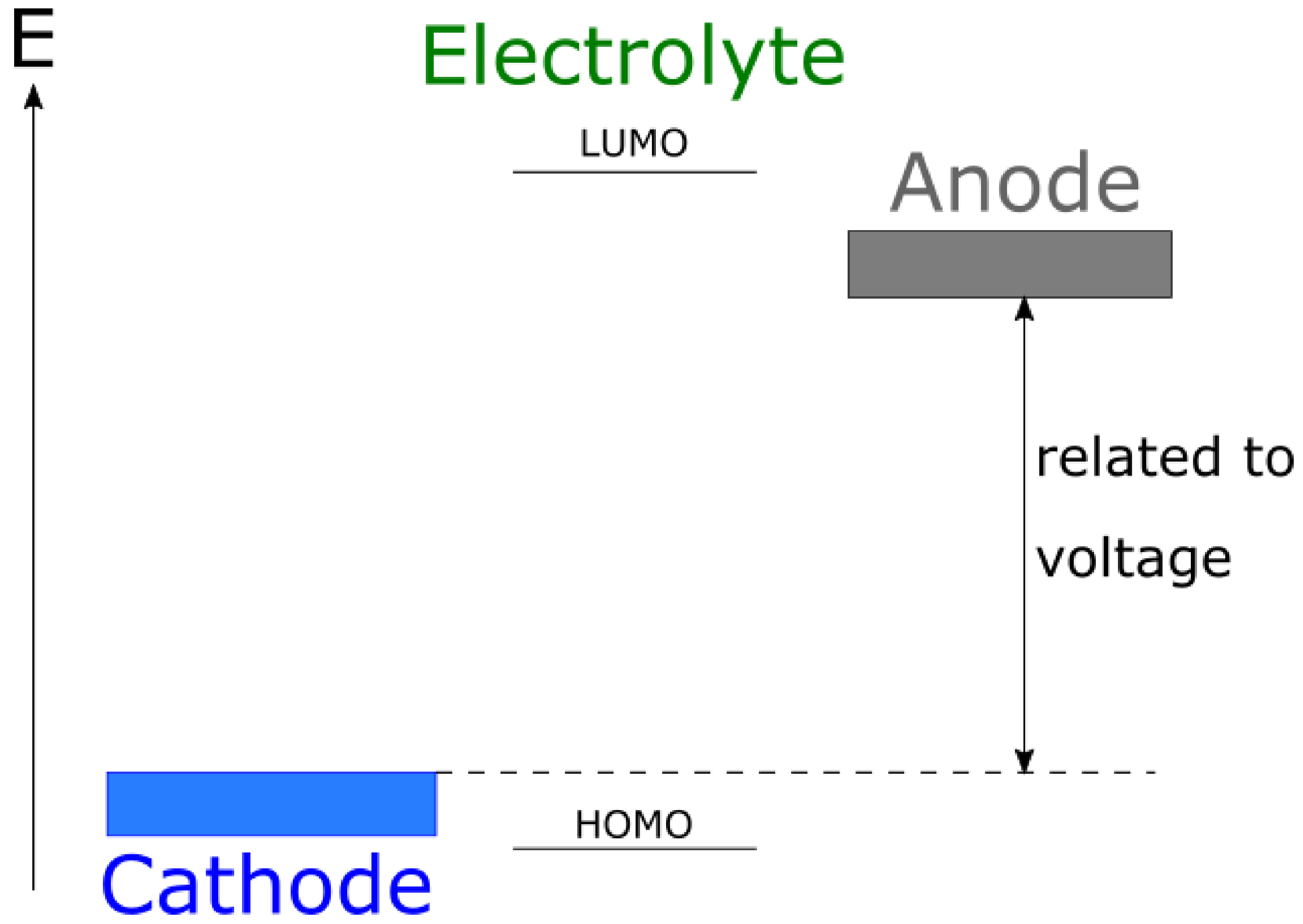
Improving batteries

Ideally, we want to maximise *both* volumetric and gravimetric energy densities



Approaches to increase E_{bat}

1. Increase *operating voltage, V*



Need large (+ve or -ve) electrode potentials:

2. Increase *charge stored, Q*

The charge stored in a material can be calculated using Faraday's Law:

$$Q_{\text{theoretical}} = \frac{nF}{3.6M_w} \qquad (\text{in mAh g}^{-1})$$

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$$n = 1, F = 96485.3\ \mathrm{As\,mol^{-1}}, M_w = 97.873\ \mathrm{g\,mol^{-1}}$$
$$\therefore Q = 274\,\mathrm{mAh\,g^{-1}}$$

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In reality, the charge stored is less than the theoretical value.

- In this case, CoO_2 is unstable: $\mathrm{2\,Co^{IV}O_2 \longrightarrow Co_2^{III}O_3 + \frac{1}{2}O_2}$
  - We can only safely reach $Li_{0.5}CoO_2$, so the useful capacity is 137 mAh g^{-1} or less

Quiz: Energy capacity

The following table shows the charging half reactions for three potential cathodes.

Which will give the highest gravimetric energy storage?

Reaction	Potential vs. Li/Li^{+} (V)
$\mathrm{LiCoPO_4 \longrightarrow Li^+ + CoPO_4 + e^-}$	4.7
$\mathrm{LiF + Ag^0 \longrightarrow AgF + Li^+ + e^-}$	4.1
$\mathrm{LiTiS_2 \longrightarrow Li^+ + TiS_2 + e^-}$	2.0

Vote

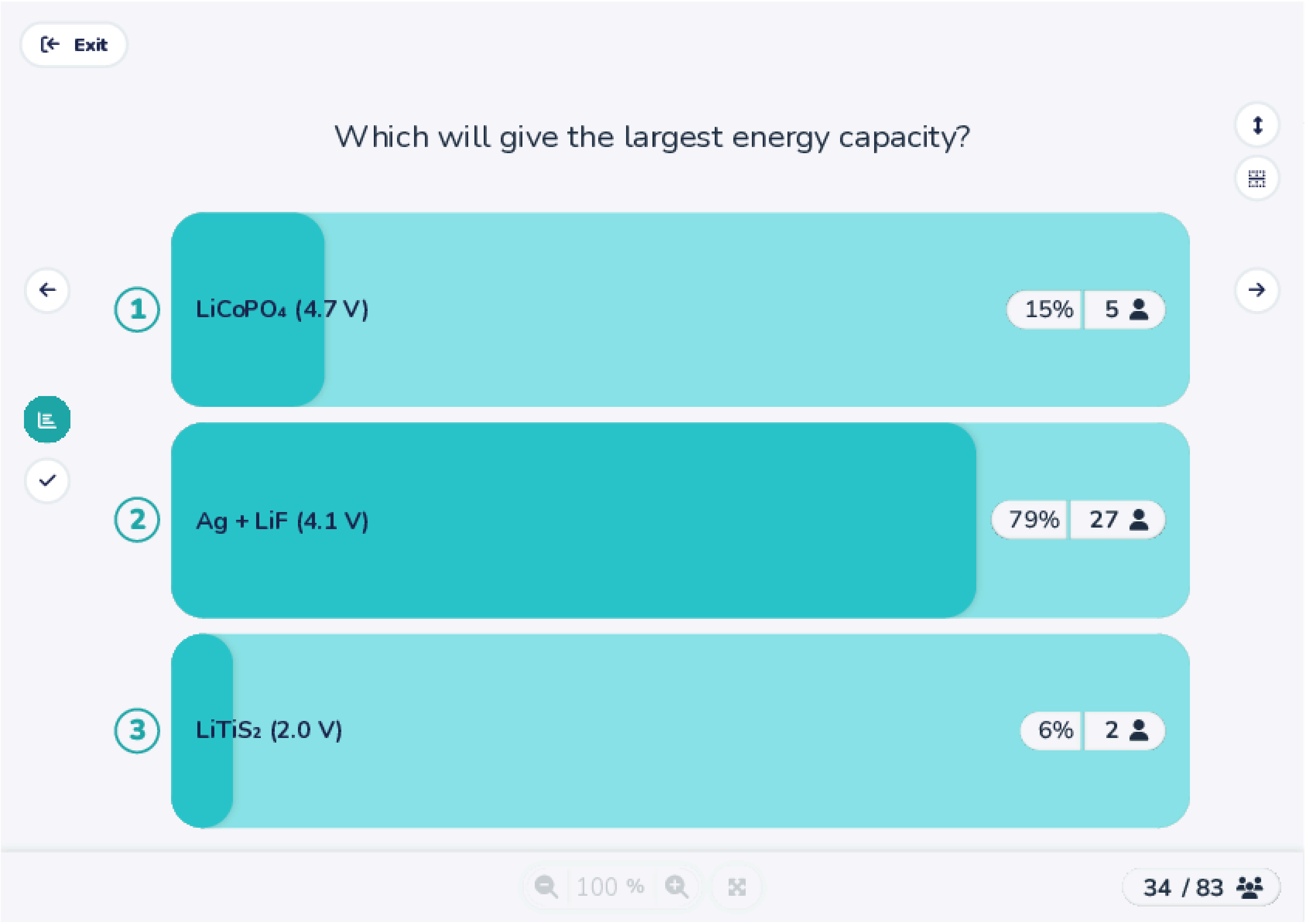
Which will give the largest energy capacity?

$LiCoPO_4$ (4.7 V)

Ag + LiF (4.1 V)

Submit

Results


Exit
Which will give the largest energy capacity?
1
LiCoPO₄ (4.7 V)
15%
5
2
Ag + LiF (4.1 V)
79%
27
3
LiTiS₂ (2.0 V)
6%
2
100 %
34 / 83

"Design rules" for battery materials

- Electrodes need to store lots of charge
  - High proportion of carrier ion *and/or* highly charged ions
- Anode and cathode should have large potential difference
  - Large electronegativity difference helps (hence Li and F)
- Electrodes should (ideally) conduct ions and electrons
- Electrolyte should conduct ions, but not electrons

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Electrode materials are grouped into two categories:

- Conversion
  - Redox reactions result in a significant structural change
- Intercalation
  - Ions are inserted into the structure, but the structure remains largely unchanged

Conversion electrodes

This category covers a wide range of chemistries.
As a general equation:

$$\mathrm{A}_a\mathrm{B}_b + (b \times c)\mathrm{C}^{\mathrm{n}} + (nbc - am)\mathrm{e}^- \rightleftharpoons \mathrm{aA}^{\mathrm{m}} + b\mathrm{BC}_c$$

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Examples:

Chloride-ion battery cathodes:

$$\mathrm{BiCl_3} + 3\,\mathrm{Li}^+ + 3\,\mathrm{e}^- \rightleftharpoons \mathrm{Bi}^0 + 3\,\mathrm{LiCl}$$

Lithium-sulfur cathode (here, $a = 0$):

$$\mathrm{S} + 2\,\mathrm{Li}^+ + 2\,\mathrm{e}^- \rightleftharpoons \mathrm{Li_2S}$$

Metal hydride anode (used in NiMH):

$$\mathrm{OH}^- + \mathrm{MH} \rightleftharpoons \mathrm{H_2O} + \mathrm{M}^0 + \mathrm{e}^-$$

Conversion electrodes (2)

Advantages

- Wide range of reactions possible
  - could avoid scarce/expensive elements by using e.g. Fe, Cu, O...
- Large theoretical capacities
  - More than one charge carrier per heavy metal (see $BiCl_3$ example)

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Disadvantages

- Often low conductivity (ionic and/or electronic)
- Substantial volume changes during cycling
- Side reactions/dissolution of intermediate species

Wu & Yushin, Energy Environ. Sci., 2017, 435.

Intercalation electrodes

Material acts like an electrochemical "sponge", reversibly incorporating carrier ions.

Example: $CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$

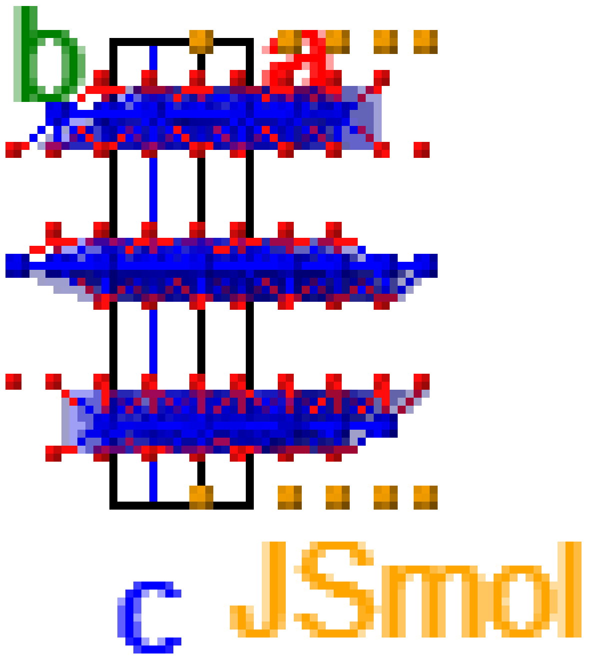
- Close-packed FCC oxygen array
- Co occupies alternate layers of octahedral holes
- Li^+ can insert between Co layers, reducing $\mathrm{Co}^{\mathrm{IV}} \rightleftharpoons \mathrm{Co}^{\mathrm{III}}$
  - Layer spacing varies with x
  - High Li^+ conductivity due to 2D vacancy-hopping mechanism

Local vs Average structure

Different measurement techniques probe different length scales

Local picture (e.g. NMR)

Single Li atoms are removed at random



Long-range picture (Crystallography)

Li position shows a *fractional occupancy*

Lecture recap

- we define cathode and anode under discharge conditions!
- two main categories of battery (based on mobile ion):
  - cationic or anionic
- we want to maximise
  - Charge stored Q in materials, and
  - operating voltage V
- Two types of electrode operation:
  - Conversion
    - wide range of chemistry, but problems with volume change and side reactions
  - intercalation
    - limited number of suitable materials
- the picture from crystallography is an average, while other techniques (e.g. NMR) give a more local picture

Feedback

What did you like or dislike about lecture 4?

Write your answer...

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