

# Lecture 4 - Batteries

# 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 ( $\Omega$ )                             |
| 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 ( $\rho$ ) and conductivity ( $\sigma$ ) are inversely related. Note that resistance ( $R$ ) is related to resistivity ( $\rho$ ) by accounting for the geometry of the object.

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

# Why batteries?

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

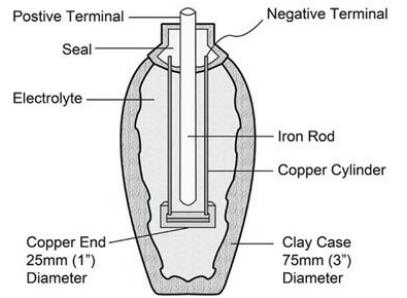
Future batteries require more charge stored in a smaller volume and/or mass.

This requires *new materials* from chemistry.



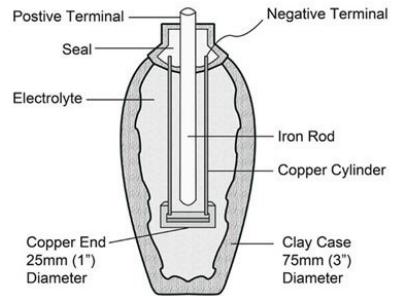
# (Brief) Battery History

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



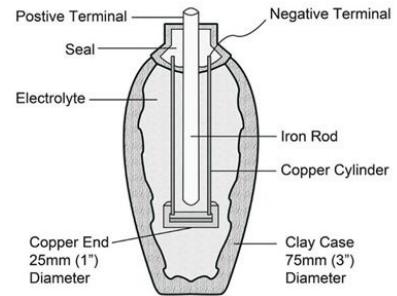
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- **1800:** Volta created the voltaic pile
  - Alternating Ag and Zn discs, NaCl electrolyte
  - Enabled *chemistry* e.g.  $2 \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{O}_2$



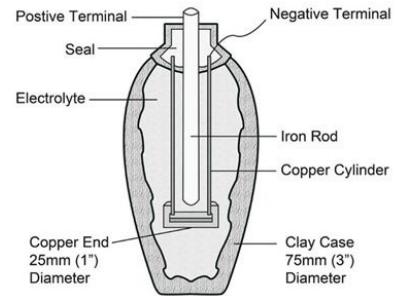
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- **1836:** Daniell cell:  
 $\text{Zn}|\text{Zn}^{2+}, \text{SO}_4^{2-}||\text{SO}_4^{2-}|\text{Cu}^{2+}|\text{Cu}$ 
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- **1859** Lead-acid battery (first rechargeable)
- **1886** The first dry cell:  $\text{Zn}|\text{NH}_4\text{Cl}|\text{MnO}_2$ 
  - $\text{NH}_4\text{Cl}$  immobilised with plaster of Paris ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ )
- **1899** The first alkaline battery:  $\text{NiO(OH)}|\text{KOH}|\text{Cd}$
- **1991** Li-ion battery commercialised by Sony



# Definitions

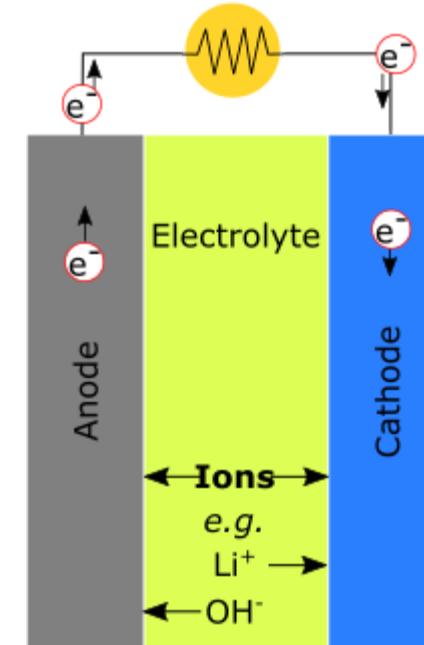
A battery consists of two electrodes (cathode and anode) and an electrolyte.

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)

## Discharge



# Charge carriers

## Cationic battery

Charge carried across electrolyte by cations

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



## Anionic battery

Anion charge carrier in electrolyte

- $\text{OH}^-$  (NiCd or NiMH)
- $\text{F}^-$ ,  $\text{Cl}^-$
- $\text{HSO}_4^-$  (in Pb-acid)

# What makes a 'good' battery?

Perhaps the most important parameter in batteries is the total *energy capacity*,  $E_{\text{bat}}$

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

$$E_{\text{bat}} = QV$$

$Q$  is expressed in units of Ah, so  $E_{\text{bat}}$  is in Wh (Watt-hours).

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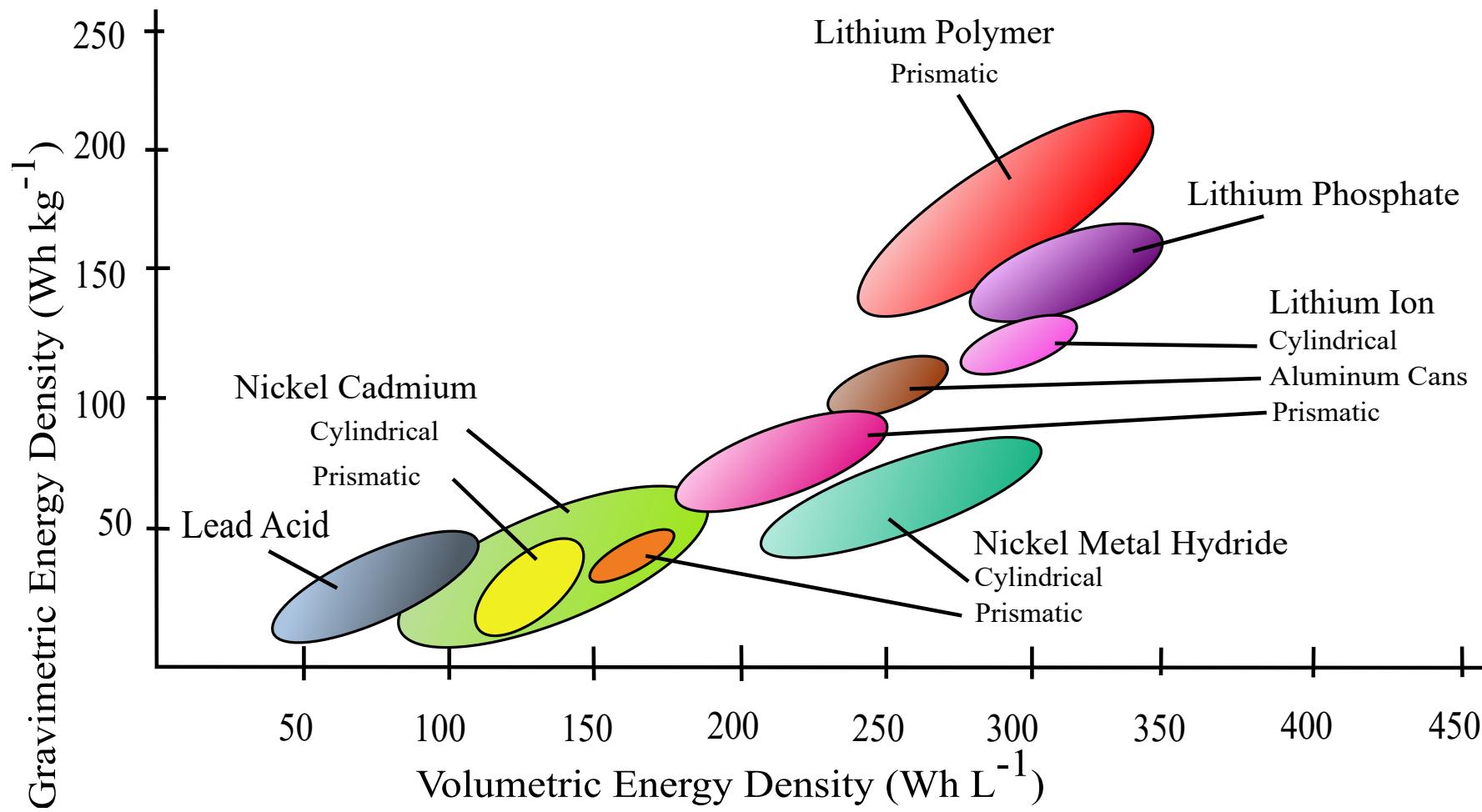
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- $E_{\text{bat}}$  is dependent on the amount of battery material. More useful are:
  - Specific (gravimetric) energy (Wh g<sup>-1</sup>).
  - (Volumetric) energy density (Wh L<sup>-1</sup>).

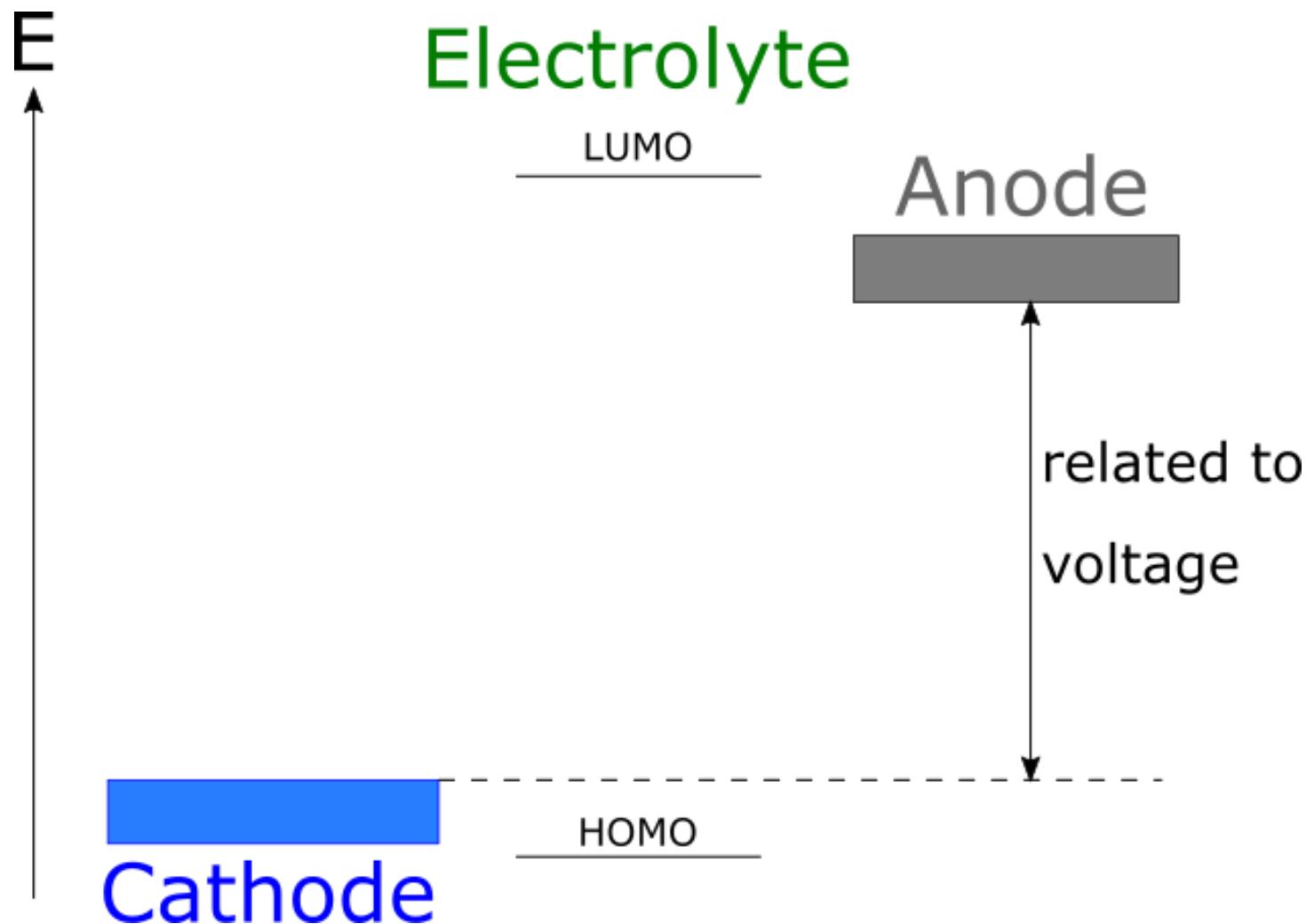
# Improving batteries

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



# Approaches to increase $E_{\text{bat}}$

## 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:

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

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

- In this case,  $\text{CoO}_2$  is unstable:  $2 \text{Co}^{\text{IV}}\text{O}_2 \rightarrow \text{Co}_2^{\text{III}}\text{O}_3 + \frac{1}{2}\text{O}_2$ 
  - We can only safely reach  $\text{Li}_{0.5}\text{CoO}_2$ , so the useful capacity is  $137 \text{ mAh g}^{-1}$  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 <sup>+</sup> (V) |
|--|--------------------------------------|
| $\text{LiCoPO}_4 \rightarrow \text{Li}^+ + \text{CoPO}_4 + \text{e}^-$       | 4.7                                  |
| $\text{LiF} + \text{Ag}^0 \rightarrow \text{AgF} + \text{Li}^+ + \text{e}^-$ | 4.1                                  |
| $\text{LiTiS}_2 \rightarrow \text{Li}^+ + \text{TiS}_2 + \text{e}^-$         | 2.0                                  |

# Vote



**Which will give the largest energy capacity?**

LiCoPO<sub>4</sub> (4.7 V)

Ag + LiF (4.1 V)



Submit



# Results

**wooclap**

Quiz results will be available here  
after the lecture

# "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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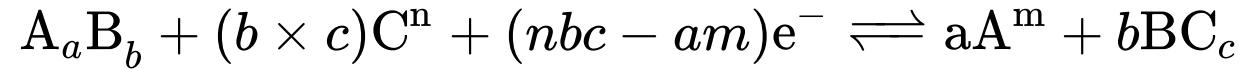
Electrode materials are grouped into two categories:

- 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.

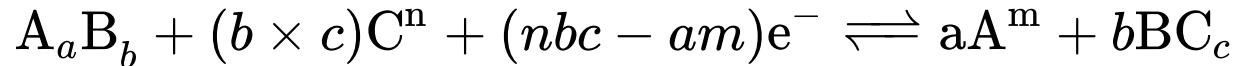
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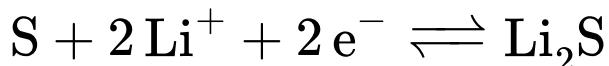


Examples:

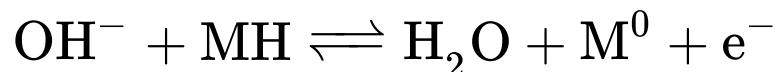
Chloride-ion battery cathodes:



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



Metal hydride anode (used in NiMH):



# 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  $\text{BiCl}_3$  example)

# Conversion electrodes (2)

## Advantages

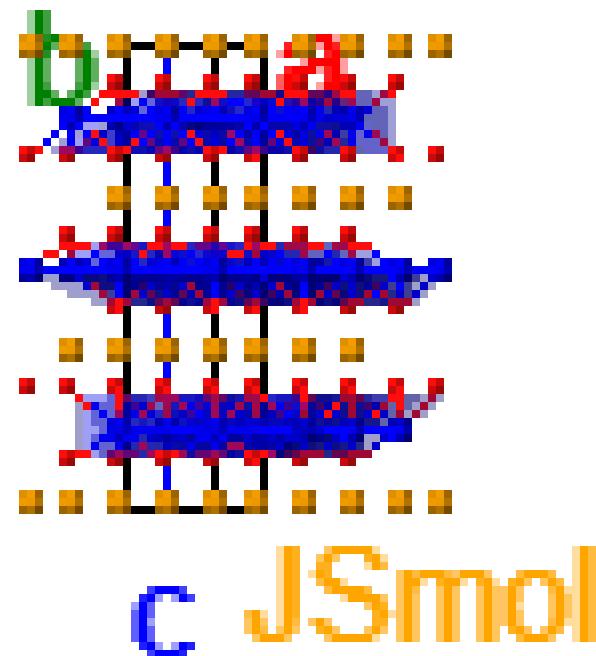
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- Large theoretical capacities
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## Disadvantages

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

# Intercalation electrodes

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



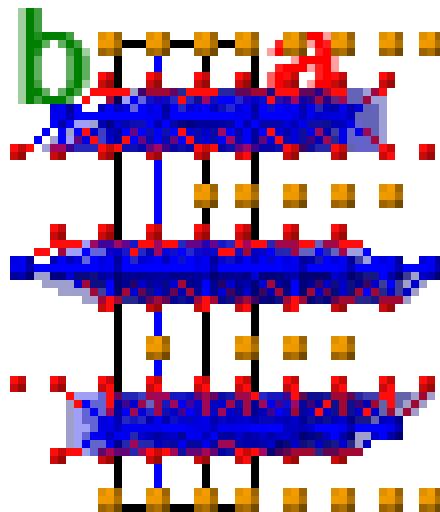
- Close-packed hcp **oxygen** array
- **Co** occupies alternate layers of octahedral holes
- **Li<sup>+</sup>** can insert between Co layers, reducing  $\text{Co}^{\text{IV}} \rightleftharpoons \text{Co}^{\text{III}}$ 
  - Layer spacing varies with  $x$
  - High  $\text{Li}^+$  conductivity due to 2D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

# Local vs Average structure

Different measurement techniques probe different length scales

## Local picture (e.g. NMR)

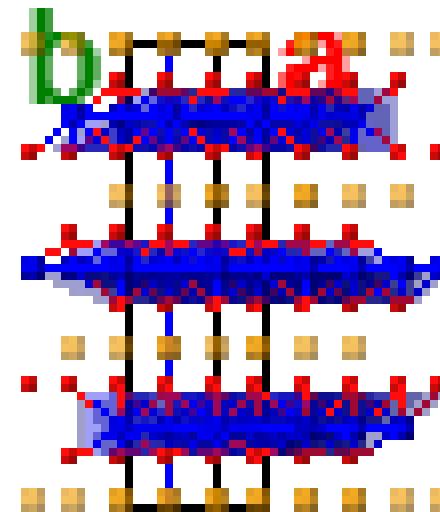
Single Li atoms are removed at random



c JSmol

## Long-range picture (Crystallography)

Li position shows a *fractional occupancy*



c JSmol

# 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...



Submit



