Lecture 4 - Batteries

Lecture summary

- Electrochemistry fundamentals
- Battery history and overview
- Battery definitions
- Improving capacity
- Essential materials properties

  ○ types of electrode behaviour

- Effect of charging rate on capacity
- Galvanostatic measurements

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
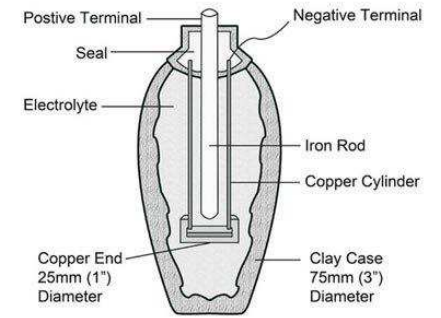- Grid-storage (e.g. from renewables)
- ...

Future batteries require more charge stored in a smaller volume and/or mass.
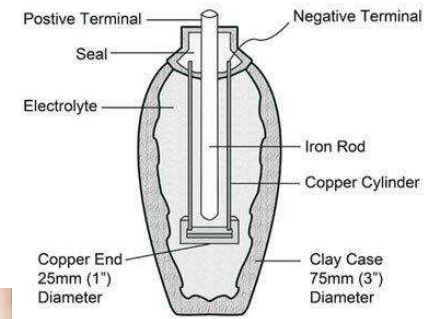
This requires *new materials* from chemistry.

(Brief) Battery History

- *ca.* **190 AD**: Baghdad (or Parthian) battery
    - Iron and copper electrodes, filled with vinegar
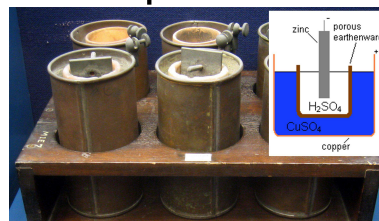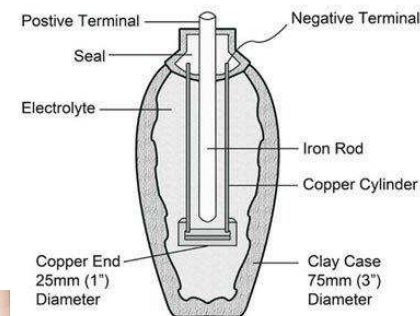
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- **1836**: Daniell cell:
  $Zn|Zn^{2+}, SO_4^{2-}||SO_4^{2-}|Cu^{2+}|Cu$
    - First practical electricity source (used to power telegraphs)
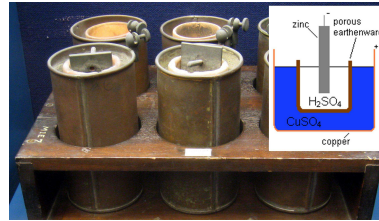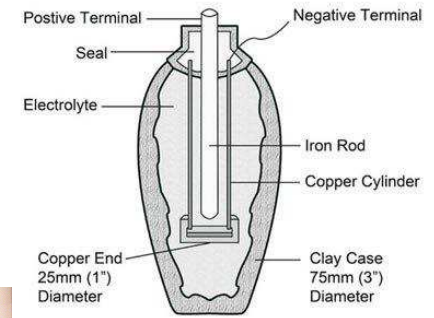- **1859** Lead-acid battery (first rechargeable)

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- **1886** The first dry cell:
  $Zn|NH_4Cl|MnO_2$
  - NH_4Cl immobilised with plaster of Paris $(CaSO_4 \cdot 0.5H_2O)$
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- **1991** Li-ion battery commercialised by Sony
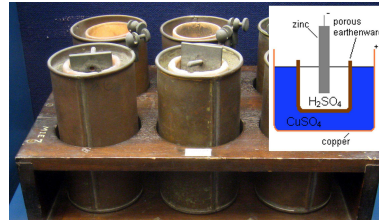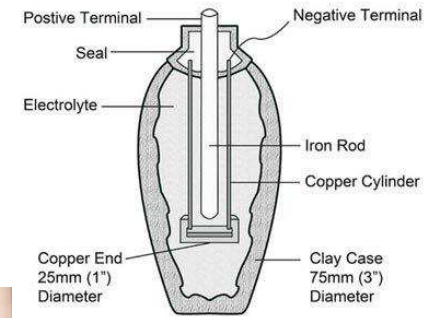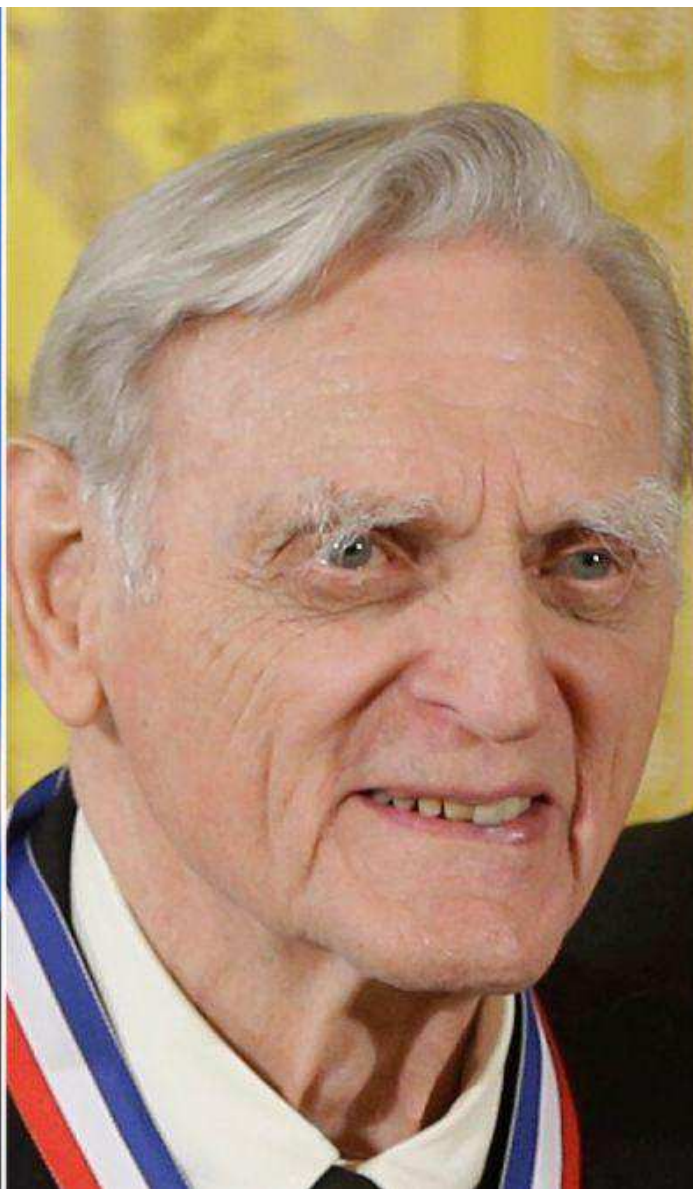
Chemistry Nobel prize 2019

Awarded for contributions to the development of the Li-ion battery
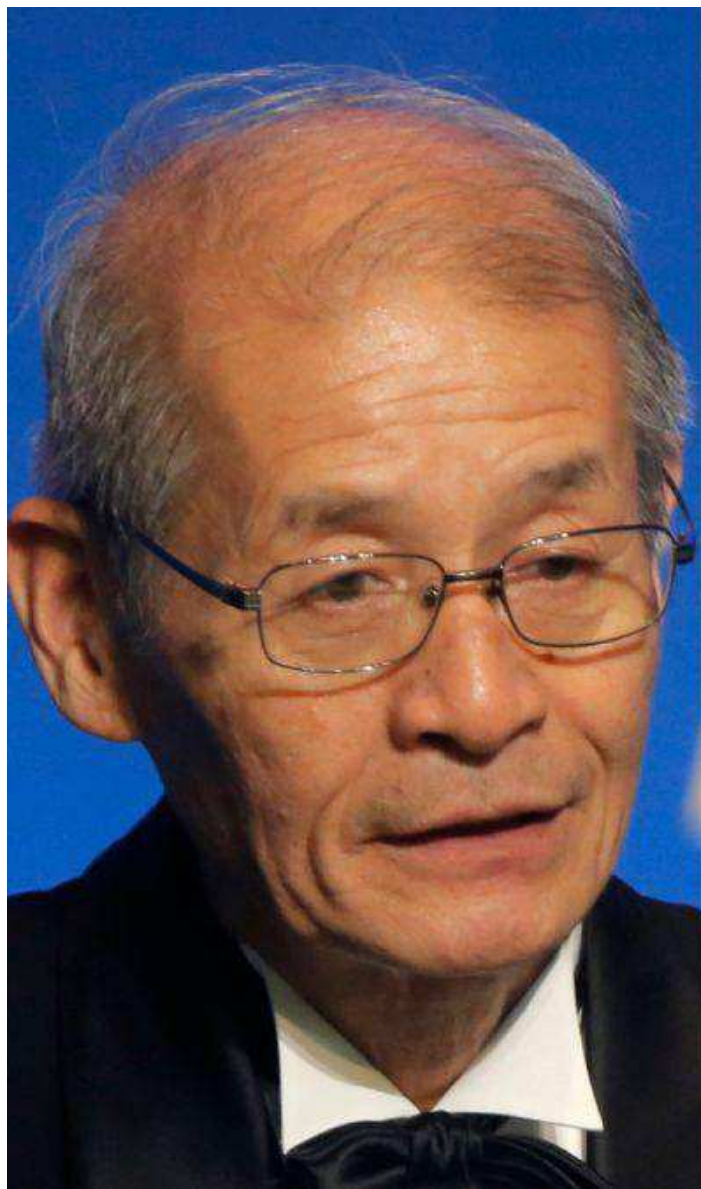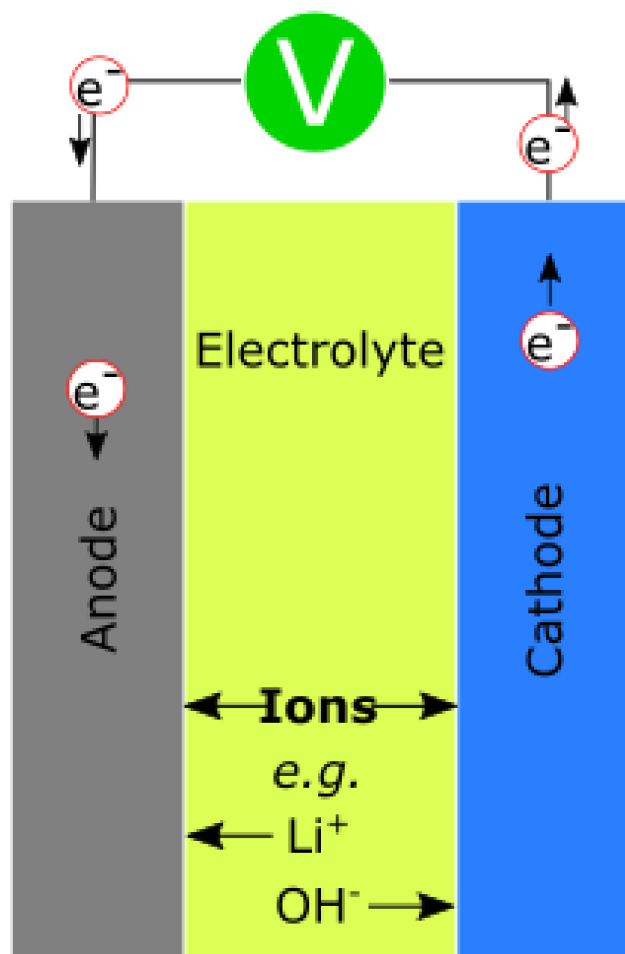

Akira Yoshino   John B. Goodenough   M. Stanley Whittingham
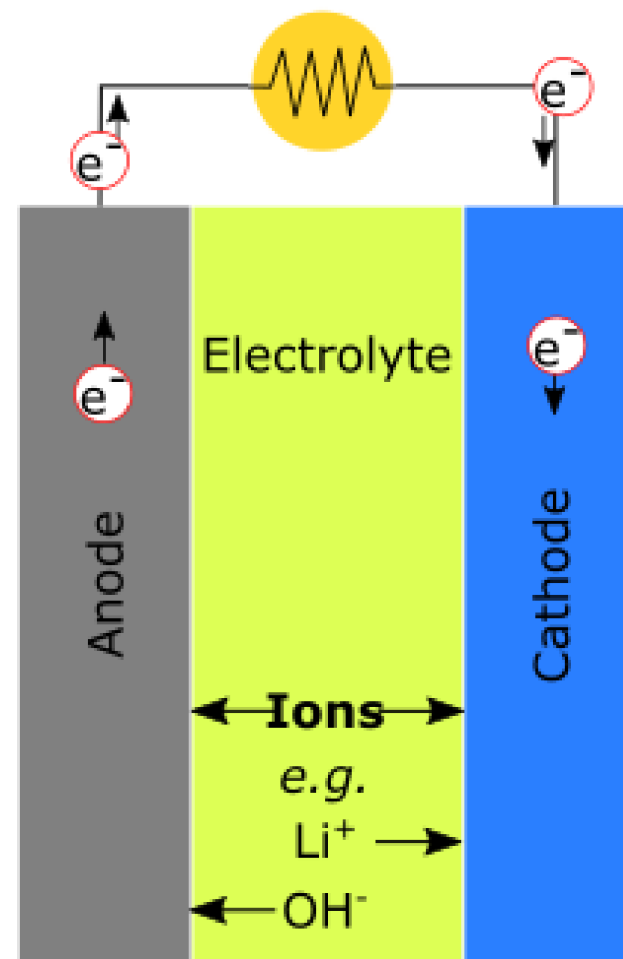
Definitions

Naming of *anode* and *cathode* is often unclear. Here we define:

- Cathode is **positive** electrode under **discharge** (being reduced)
- Anode is **negative** electrode under **discharge** (oxidised)

Main approaches

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*, $\mathrm{E_{bat}}$

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

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

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- E_{bat} is dependent on the amount of battery material. More useful are:

  - Specific (gravimetric) energy (Wh g^{-1}).
    Q per unit mass (Ah g^{-1})
  - (Volumetric) energy density (Wh L^{-1}).
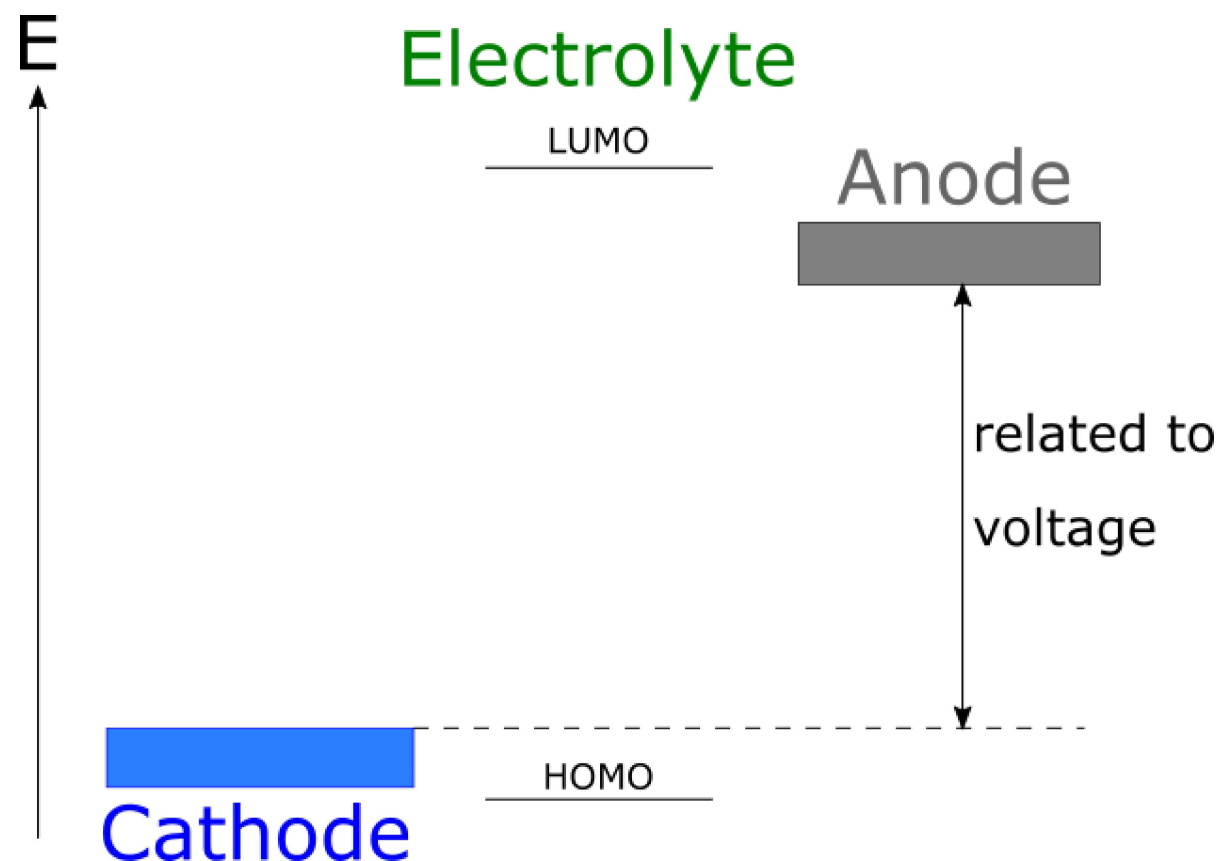   Q per unit volume (Ah L^{-1})

Improving batteries

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

11
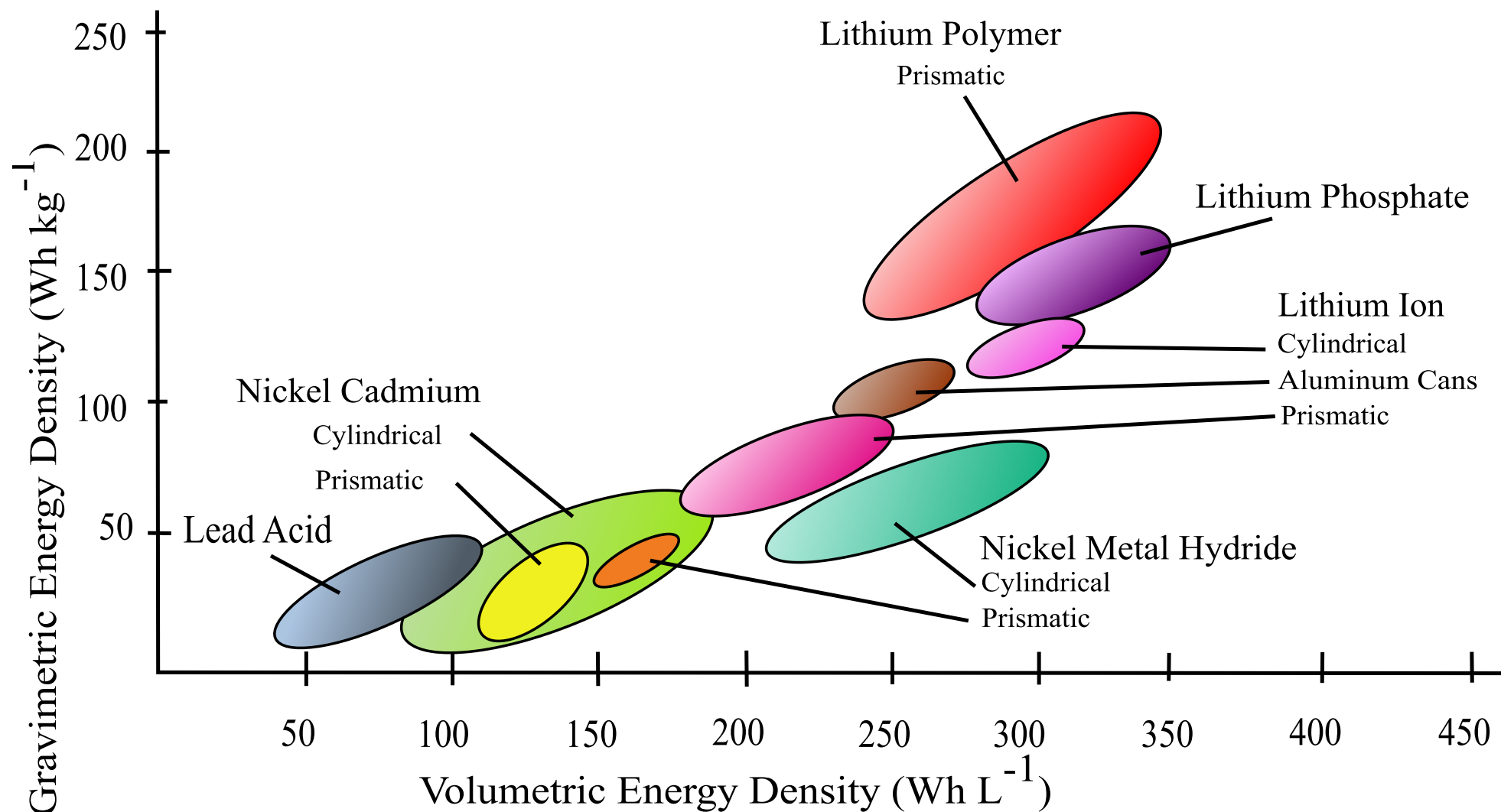
Approches to increase E_{bat}

1. Increase *operating voltage*, *V*

Need large (+ve or -ve) electrode potentials:
large electronegativity differences (e.g. Li^+, F^-)

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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In reality, the charge stored is less than the theoretical maximum

- CoO_2 is unstable: $2\,\text{Co}^{\text{IV}}\text{O}_2 \longrightarrow \text{Co}_2^{\text{III}}\text{O}_3 + \frac{1}{2}\text{O}_2$

    - We can only safely reach $\text{Li}_{0.5}\text{CoO}_2$, so the useful capacity is 137 mAh g^{-1}

Which will give the highest energy capacity

Which of the following cathode combinations will give the highest E_{bat}?

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

Calculate per mole of reactants as written

Vote

Mentimeter

Which will give the largest energy capacity?

- ◯ LiCoPO4 (4.7V)

- ◯ Ag + LiF (4.1V)

- ◯ LiTiS2 (2.0V)

Submit

Powered by Mentimeter   Terms

Results

Which will give the largest energy capacity?

0	0	0
LiCoPO4 (4.7V)	Ag + LiF (4.1V)	LiTiS2 (2.0V)

Ideal materials properties

Anode/Cathode	Electrolyte
High capacity for charge-carrying ion	High ionic conductivity
Large potential difference (cell voltage)	Low electronic conductivity
Good ionic and electronic conductor (ideally)	Stable in contact with electrodes

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Electrode materials fall into two categories:

- Conversion
- Intercalation

Conversion electrodes

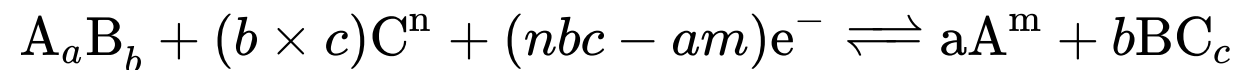Electrochemical reaction proceeds during charge/discharge.
As a general equation,

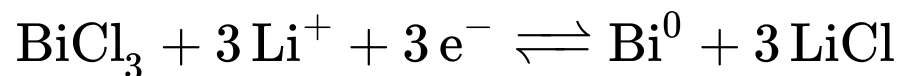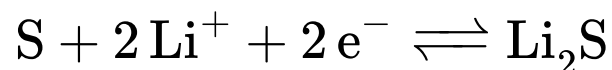$$\mathrm{A}_a\mathrm{B}_b + (b \times c)\mathrm{C}^{\mathrm{n}} + (nbc - am)\mathrm{e}^- \rightleftharpoons a\mathrm{A}^{\mathrm{m}} + b\mathrm{BC}_c$$

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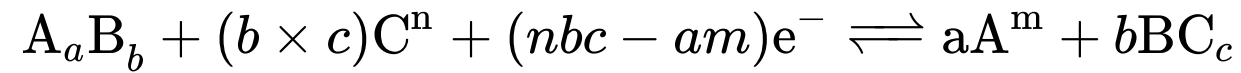
Examples:

Chloride-ion battery cathodes:

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

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

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

Metal hydride anode (used in NiMH):
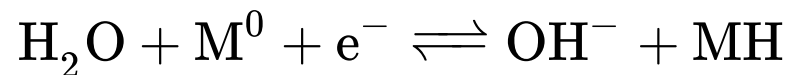
$$H_2O + M^0 + e^- \rightleftharpoons OH^- + MH$$

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
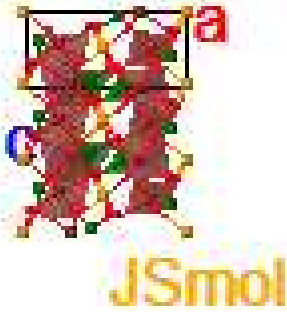
Intercalation electrodes

No chemical 'reaction'; mobile species is 'inserted' into a material able to accommodate its charge/size.

Example: Li_xCoO_2

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

Intercalation cathode families

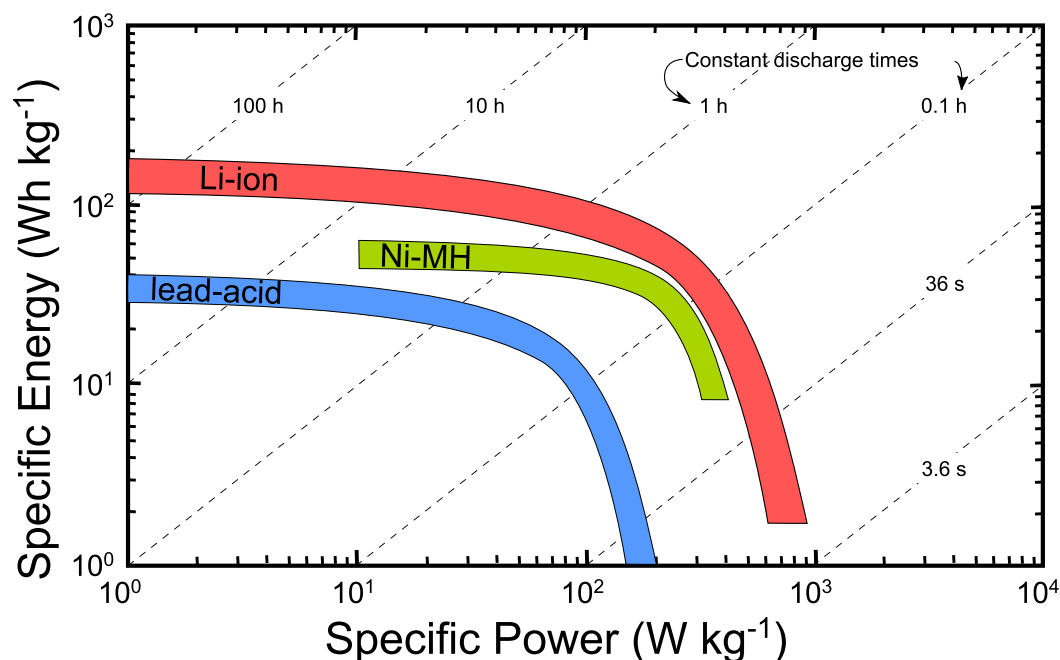|	2D conductor	3D conductor	1D conductor
Type	$\alpha-NaFeO_2$	spinel	olivine
Structure			
Formula	$LiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
$Q_{\mathrm{theo.}}$ / mAh g^{-1}	274	148	170

◄------------------◄ Better Li conduction ◄------------------◄

►------------------------► Safer ►------------------------►

◄----------------------◄ (Higher cost) ◄------------------------◄

Charging rates

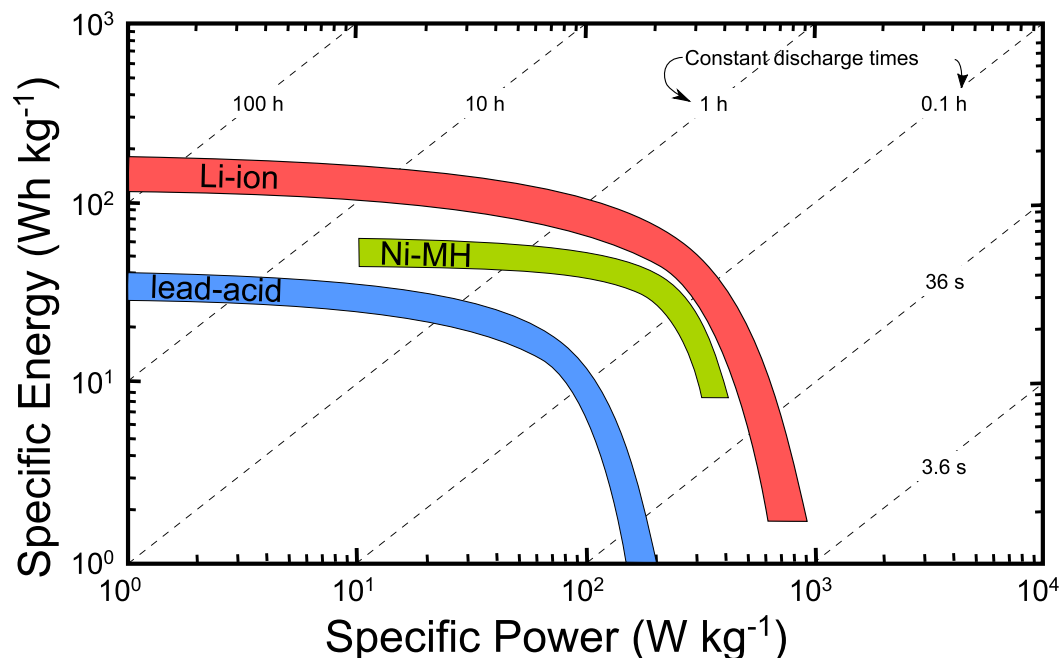A high E_{bat} is good, but we want to (dis)charge batteries quickly!

- Tradeoff between *Power* ($P = IV$) and $E_{bat} (= ItV)$
- Seen on a Ragone plot:

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- Seen on a Ragone plot:

E_{bat} depends on the (dis)charge rate, so to compare different materials we use the $C-\text{rate} = \frac{I}{Q}$

- e.g. for a 1000 mAh battery: $1C$ would sustain 1 A for 1 hour, $2C$ gives 2A for 30 mins, $\frac{C}{6}$ gives 0.167 A for 6 hours, etc.
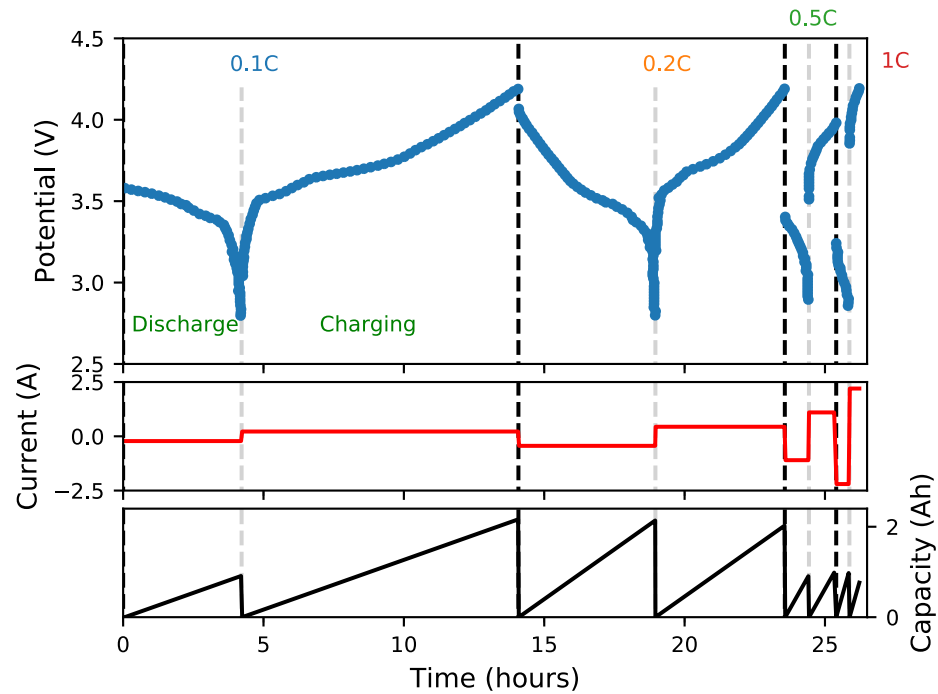
Electrochemical measurements

To avoid variations in rate, battery analysis uses *Galvanostatic* (constant current) electrochemistry

- measure the resulting potential.
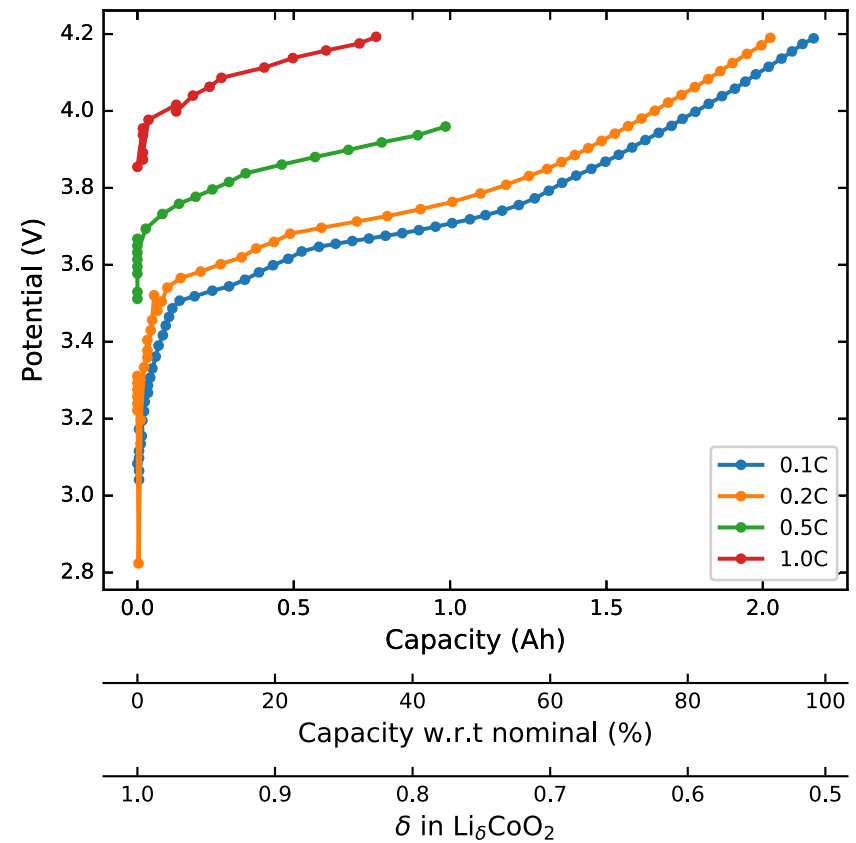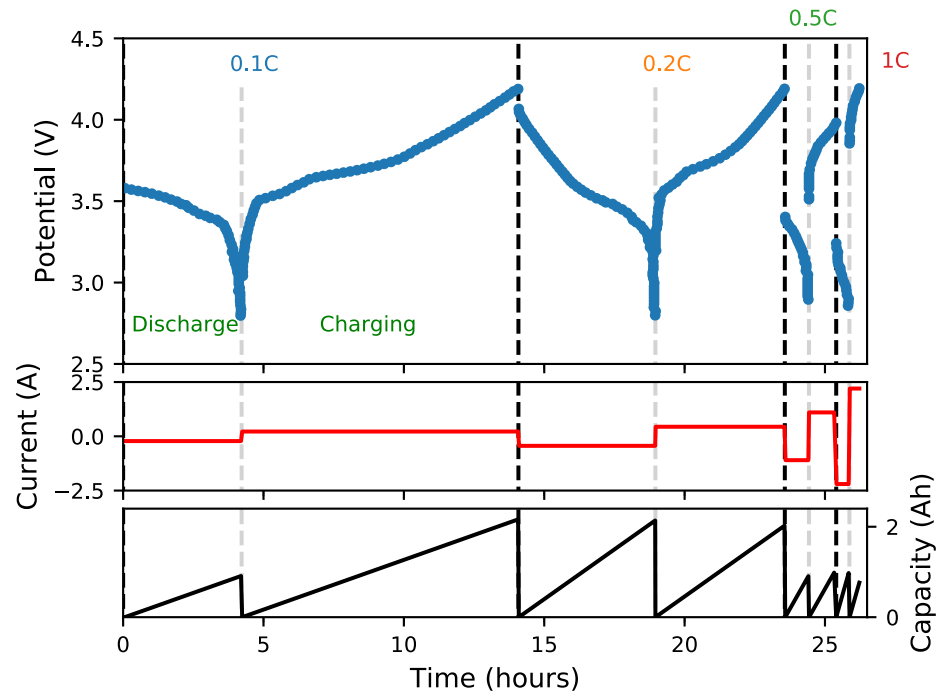- easier to separate chemistry effects from rate effects
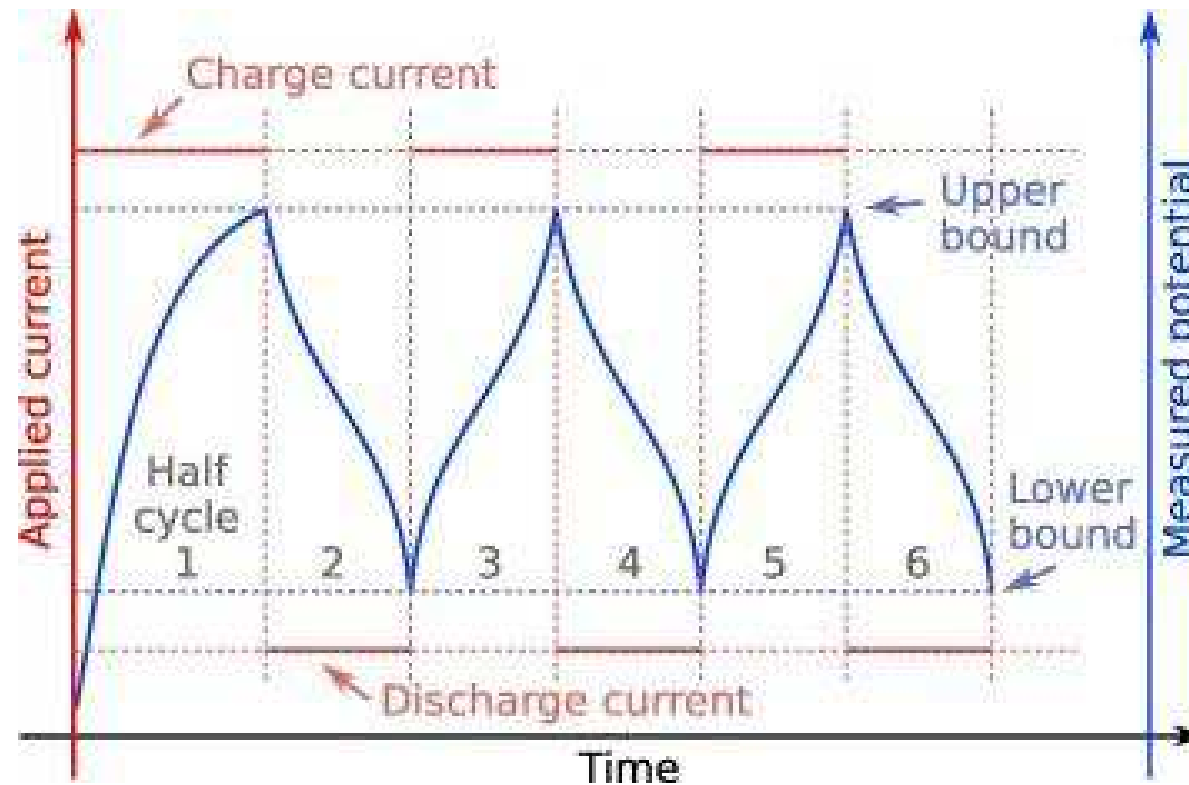
Electrochemical measurements (2)
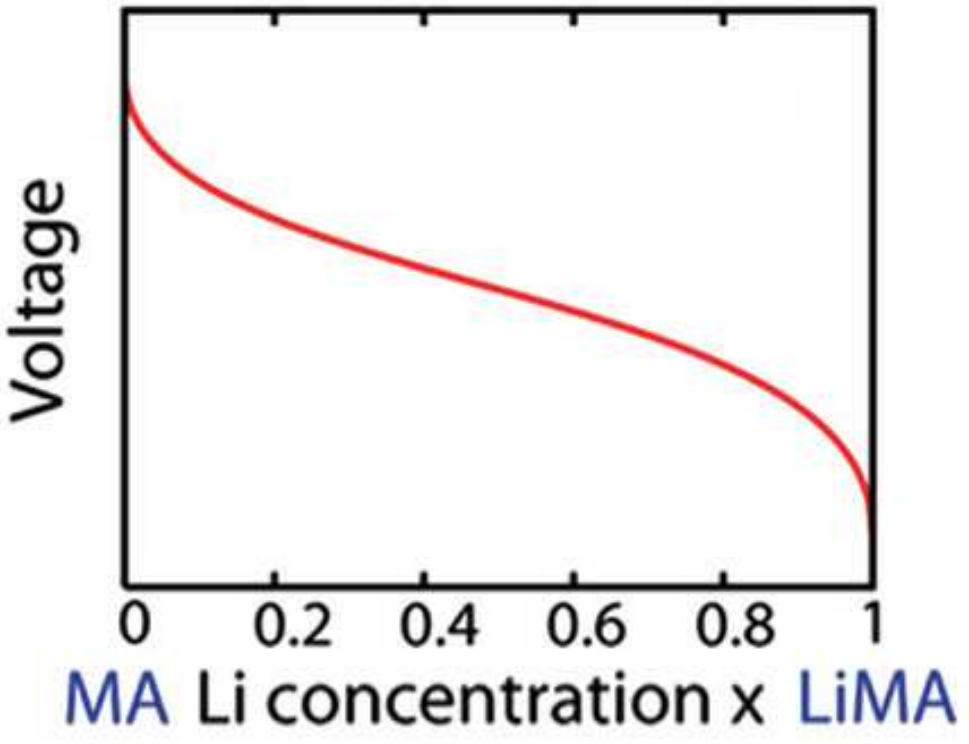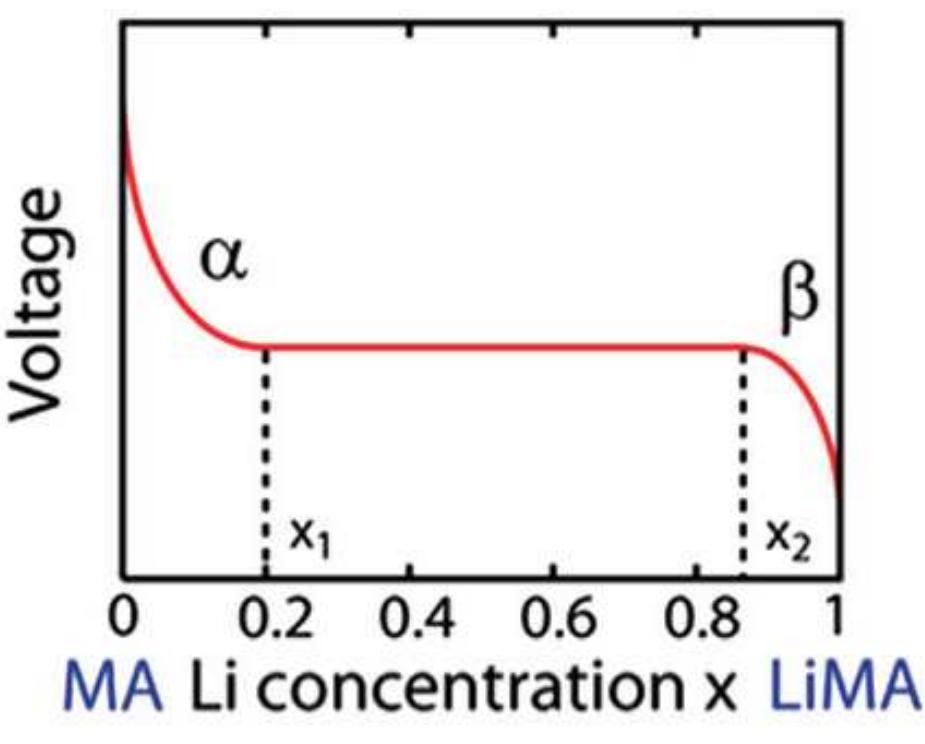
e.g. for a 2.2 Ah battery:

Electrochemical measurements (2)

e.g. for a 2.2 Ah battery:

Capacity is often expressed in a number of formats

Material insights from galvanostats

Solid Solution	Two-phase region
Ions can be continously added/removed from the material without a structural transition	Two distinct compositions exist together, and the relative proportions change with x

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

- we can use galvanostatic measurements to learn a lot