

Lecture 3 - 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)
- ...

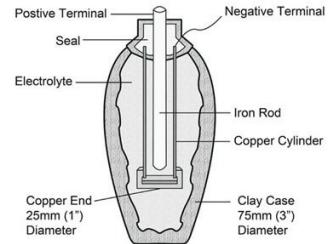
Future batteries require more charge stored in a smaller volume and/or mass.

This requires *new materials* from chemistry.



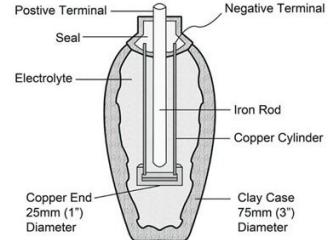
(Brief) Battery History

- **ca. 190 AD:** Baghdad (or Parthian) battery
 - Iron and copper electrodes, filled with vinegar



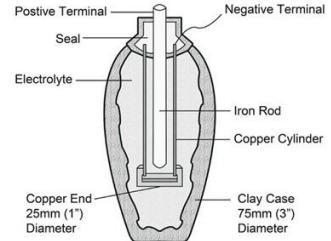
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 - Alternating Ag and Zn discs, NaCl electrolyte
 - Enabled *chemistry* e.g. $2 \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{O}_2$



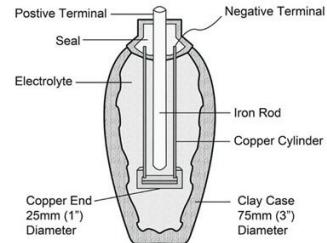
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- **1836:** Daniell cell:
 $\text{Zn}|\text{Zn}^{2+}, \text{SO}_4^{2-}||\text{SO}_4^{2-}|\text{Cu}^{2+}|\text{Cu}$
 - First practical electricity source (used to power telegraphs)
- **1859** Lead-acid battery (first rechargeable)



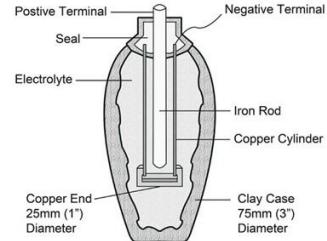
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- **1886** The first dry cell: $\text{Zn}|\text{NH}_4\text{Cl}|\text{MnO}_2$
 - NH_4Cl immobilised with plaster of Paris ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$)
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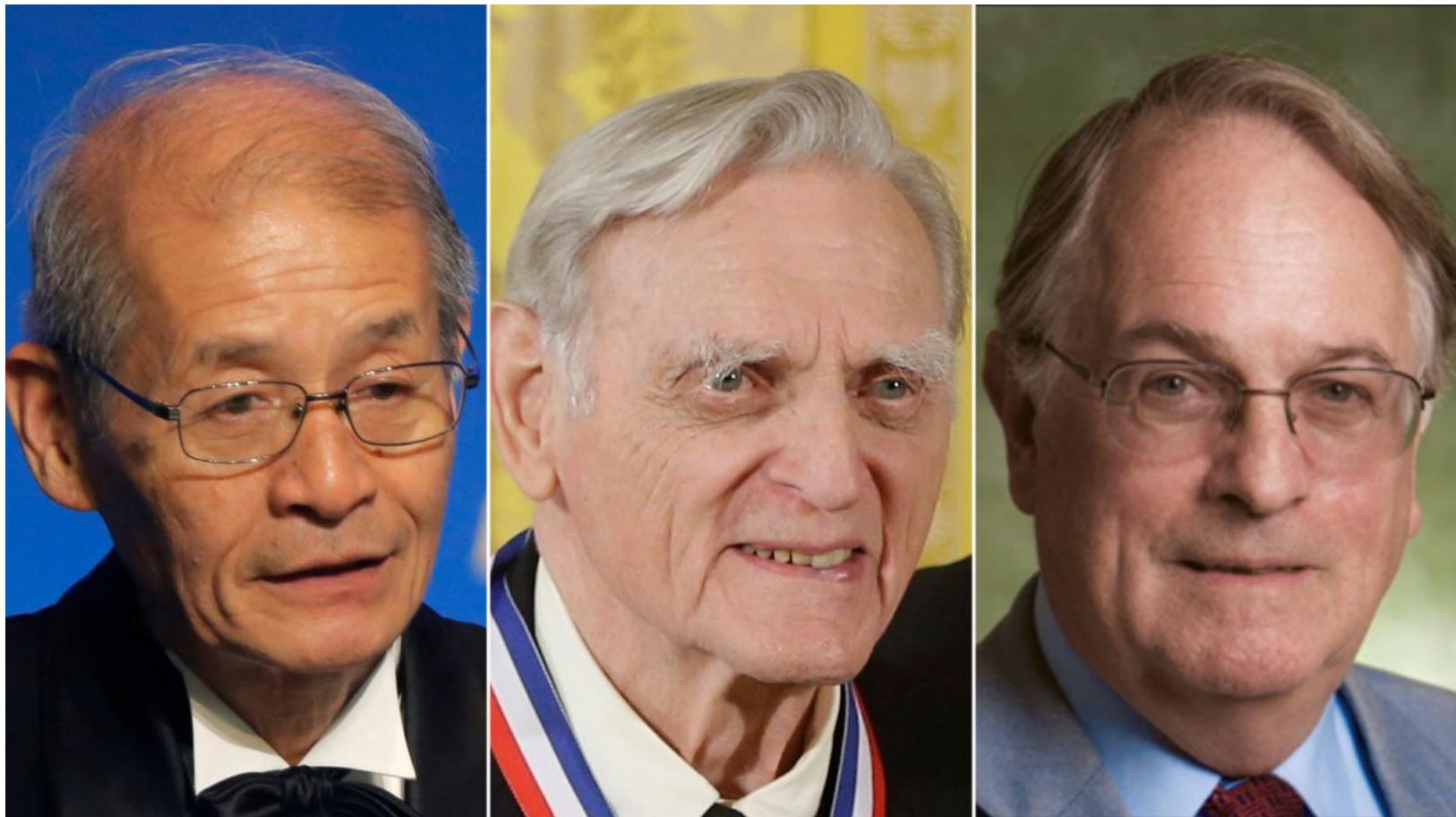
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- **1899** The first alkaline battery: $\text{NiO(OH)}|\text{KOH}|\text{Cd}$
- **1991** Li-ion battery commercialised by Sony



Chemistry Nobel prize 2019



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



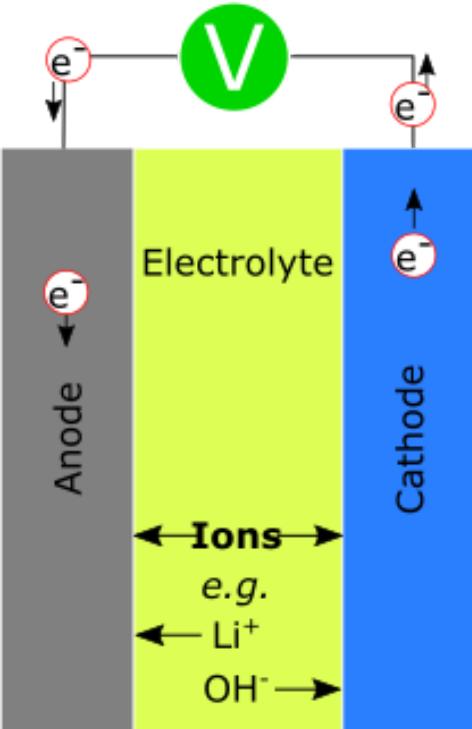
Akira Yoshino

John B. Goodenough

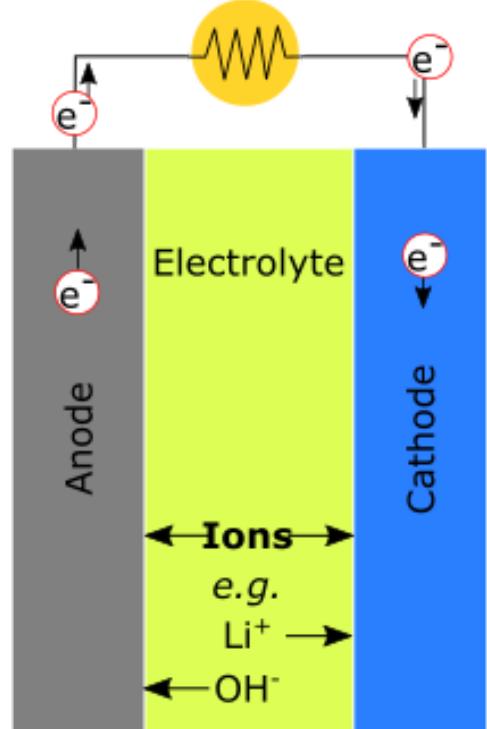
M. Stanley Whittingham

Definitions

Charge



Discharge



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, E_{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_{bat} is in Wh (Watt-hours)

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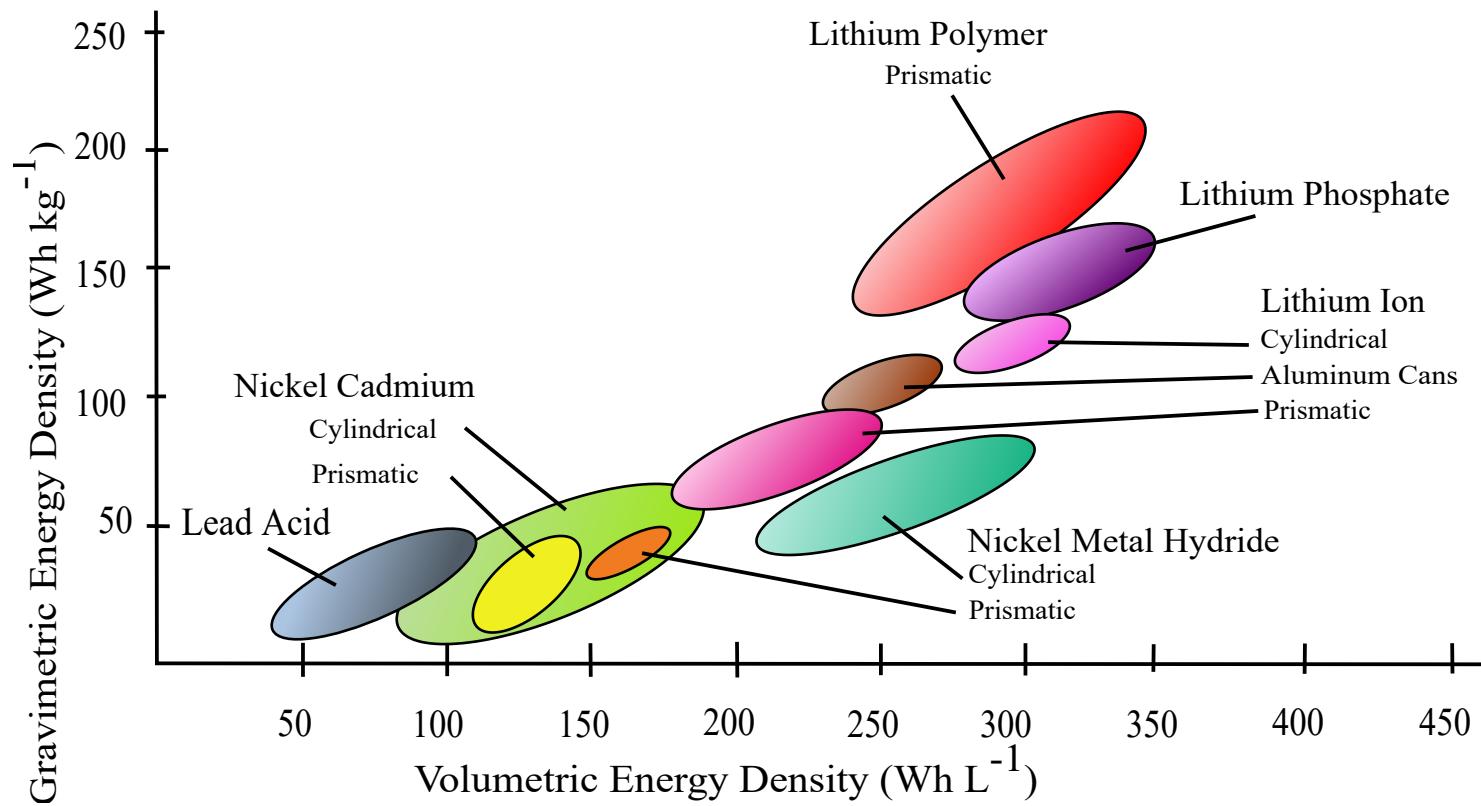
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- E_{bat} is dependent on the amount of battery material. More useful are:

- 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)

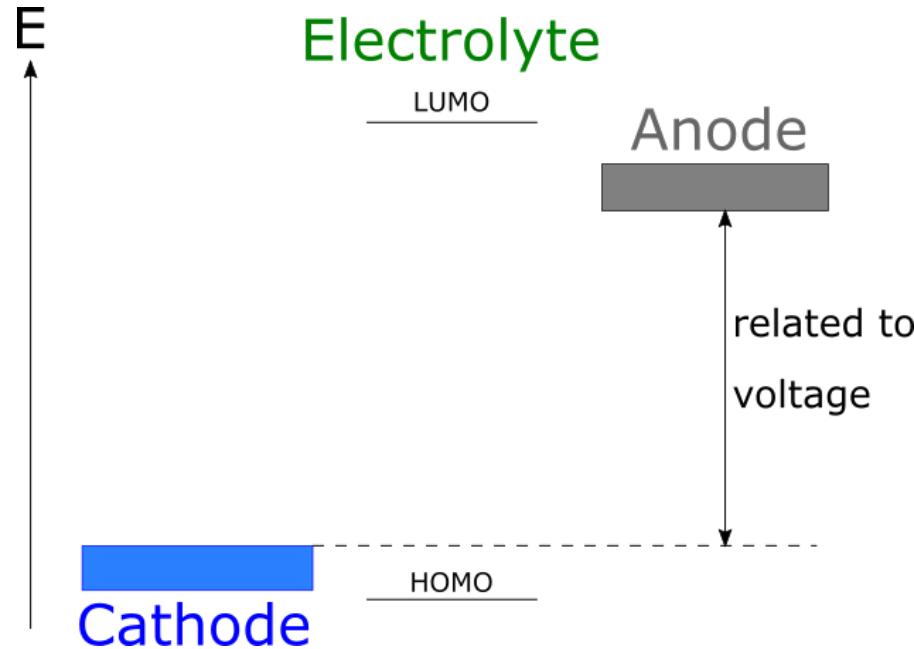
Improving batteries

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



Approaches 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:

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

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

- CoO_2 is unstable: $2 \text{Co}^{\text{IV}}\text{O}_2 \rightarrow \text{Co}_2^{\text{III}}\text{O}_3 + \frac{1}{2}\text{O}_2$
 - We can only safely reach $\text{Li}_{0.5}\text{CoO}_2$, so the useful capacity is 137 mAh g^{-1}

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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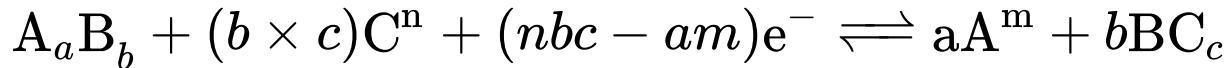
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Electrode materials fall into two categories:

- Conversion
- Intercalation

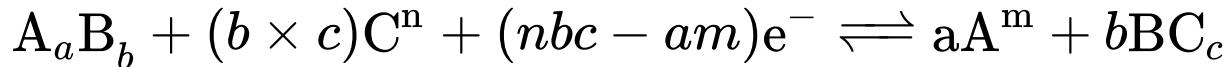
Conversion electrodes

Electrochemical reaction proceeds during charge/discharge.
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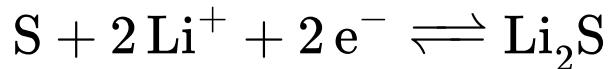


Examples:

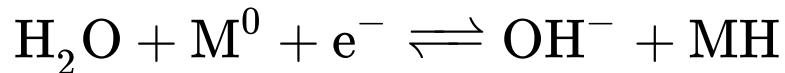
Chloride-ion battery cathodes:



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 BiCl₃ example)

Conversion electrodes (2)

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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

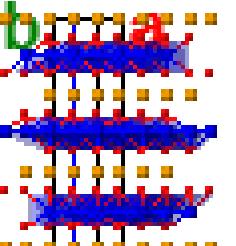
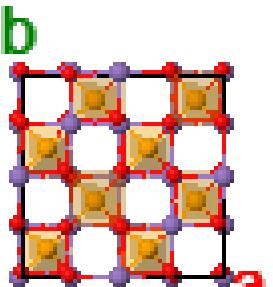
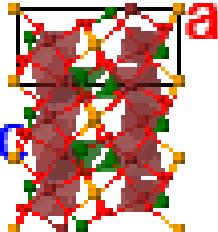
No chemical 'reaction'; mobile species is 'inserted' into a material able to accommodate its charge/size.

Example: Li_xCoO_2



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

Intercalation cathode families

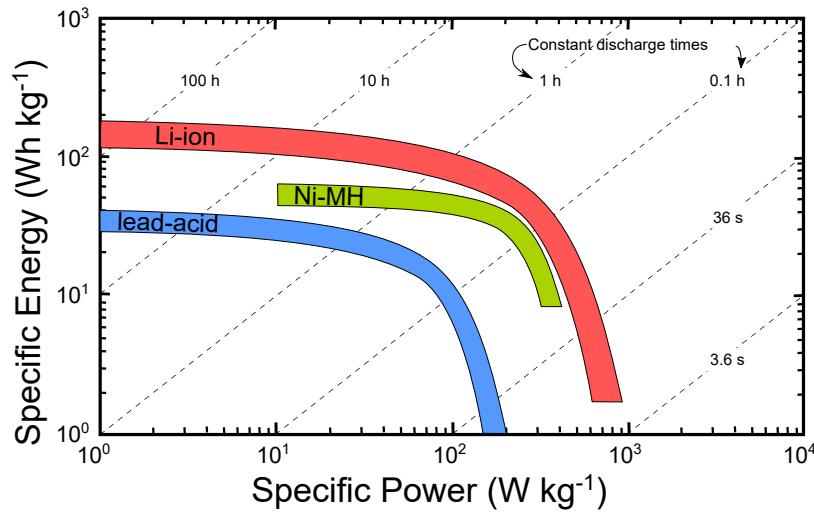
	2D conductor	3D conductor	1D conductor
Type	$\alpha\text{--NaFeO}_2$	spinel	olivine
Structure	 a b c JSmol	 b a JSmol	 a c JSmol
Formula	LiCoO_2	LiMn_2O_4	LiFePO_4
$Q_{\text{theo.}} / \text{mAh g}^{-1}$	274	148	170

←-----→ Better Li conduction ←-----→
 →-----→ Safer →-----→
 ←-----→ (Higher cost) ←-----→

Charging rates

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

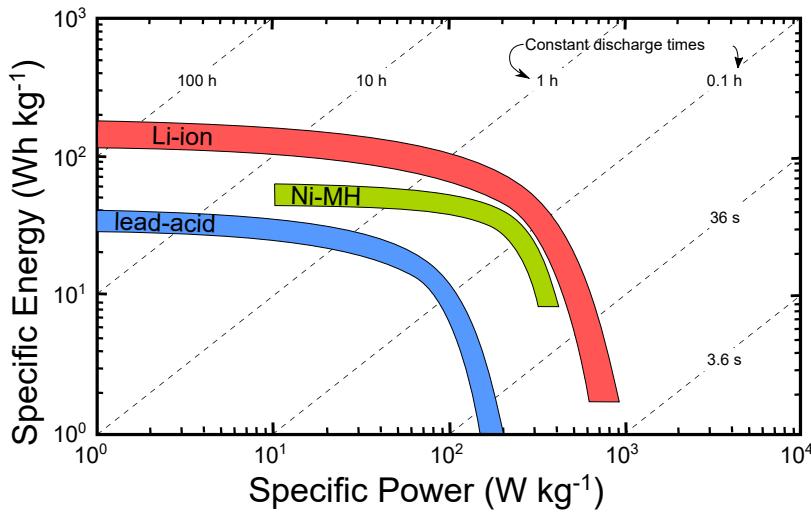
- Tradeoff between *Power* ($P = IV$) and $E_{\text{bat}} (= ItV)$
- Seen on a Ragone plot:



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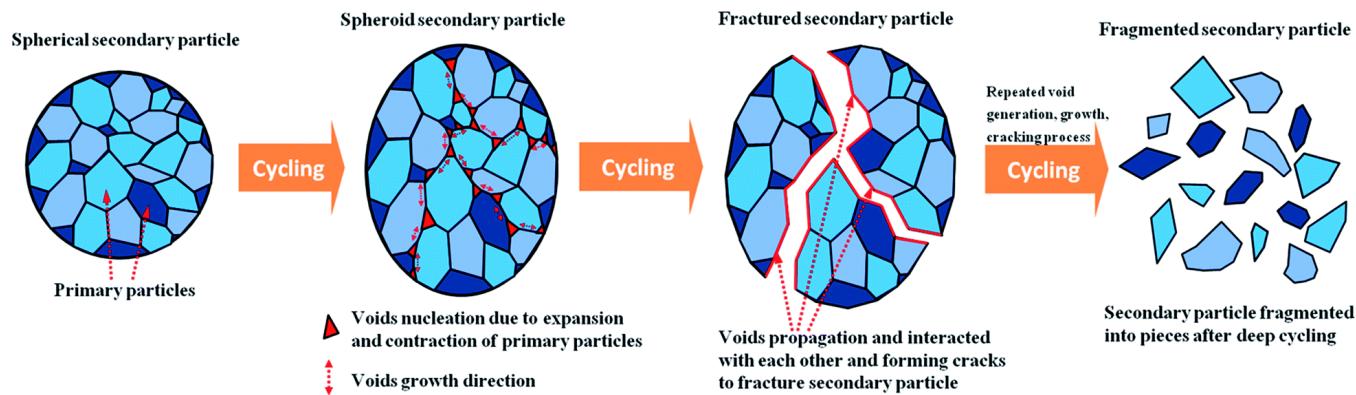
E_{bat} depends on the (dis)charge rate, so to compare different materials we use the C —rate = $\frac{I}{Q}$

- 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.

High charging rates reduce E_{bat}

Rapid charging causes problems over a range of length scales:

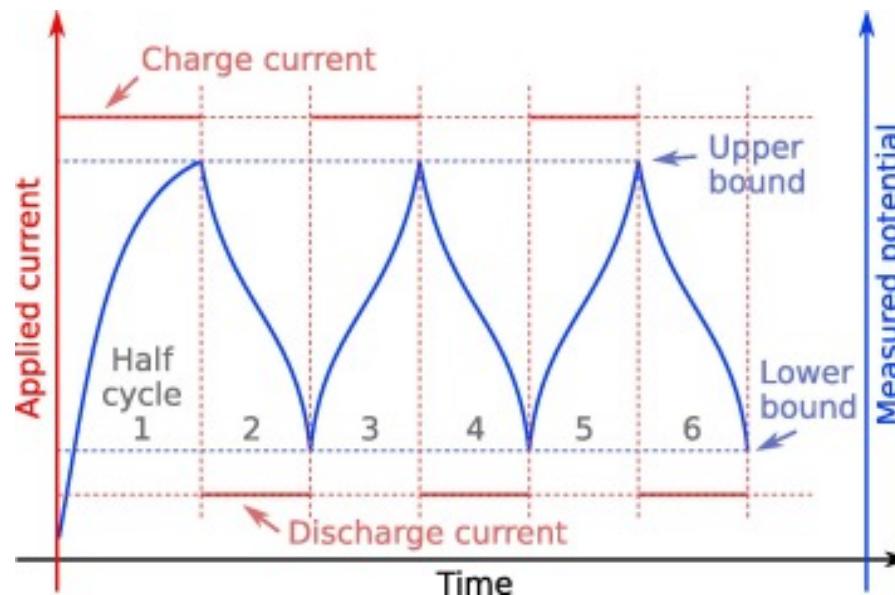
- inhomogeneous lattice strain traps mobile ions
 - Defects can become 'pinned'
- Irreversible damage to microstructure can occur
- thermal gradients can cause additional side-reactions (engineering problem)



Electrochemical measurements

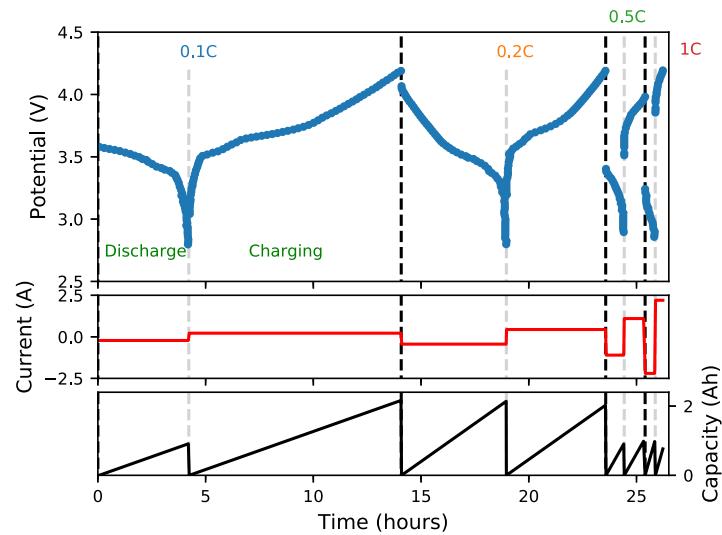
To avoid variations in rate, battery analysis uses *Galvanostatic* (constant current) electrochemistry

- measure the resulting potential.
- easier to separate chemistry effects from rate effects



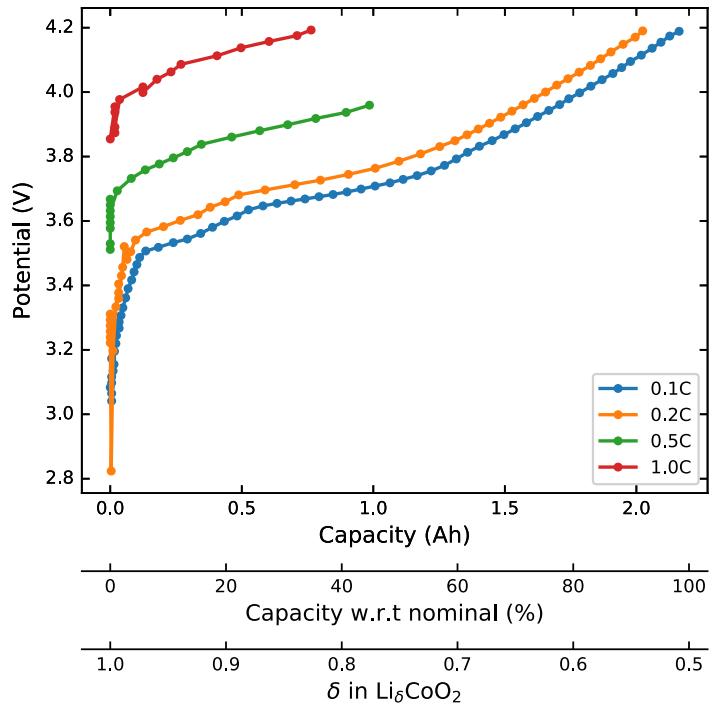
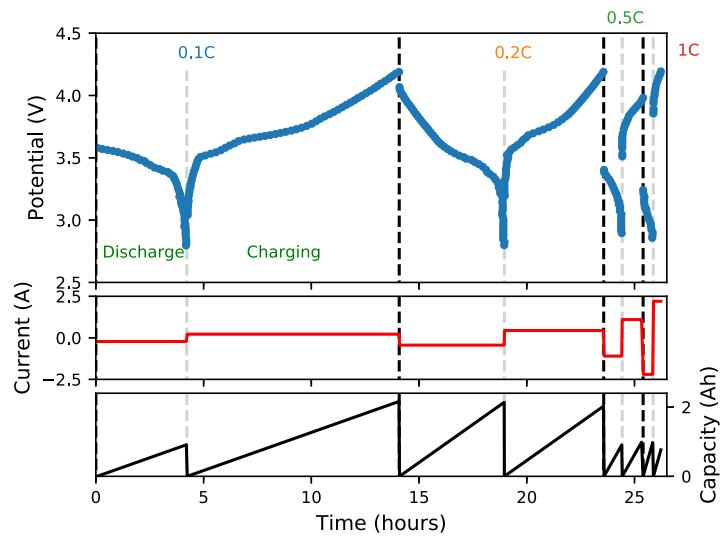
Electrochemical measurements (2)

e.g. for a 2.2 Ah battery:



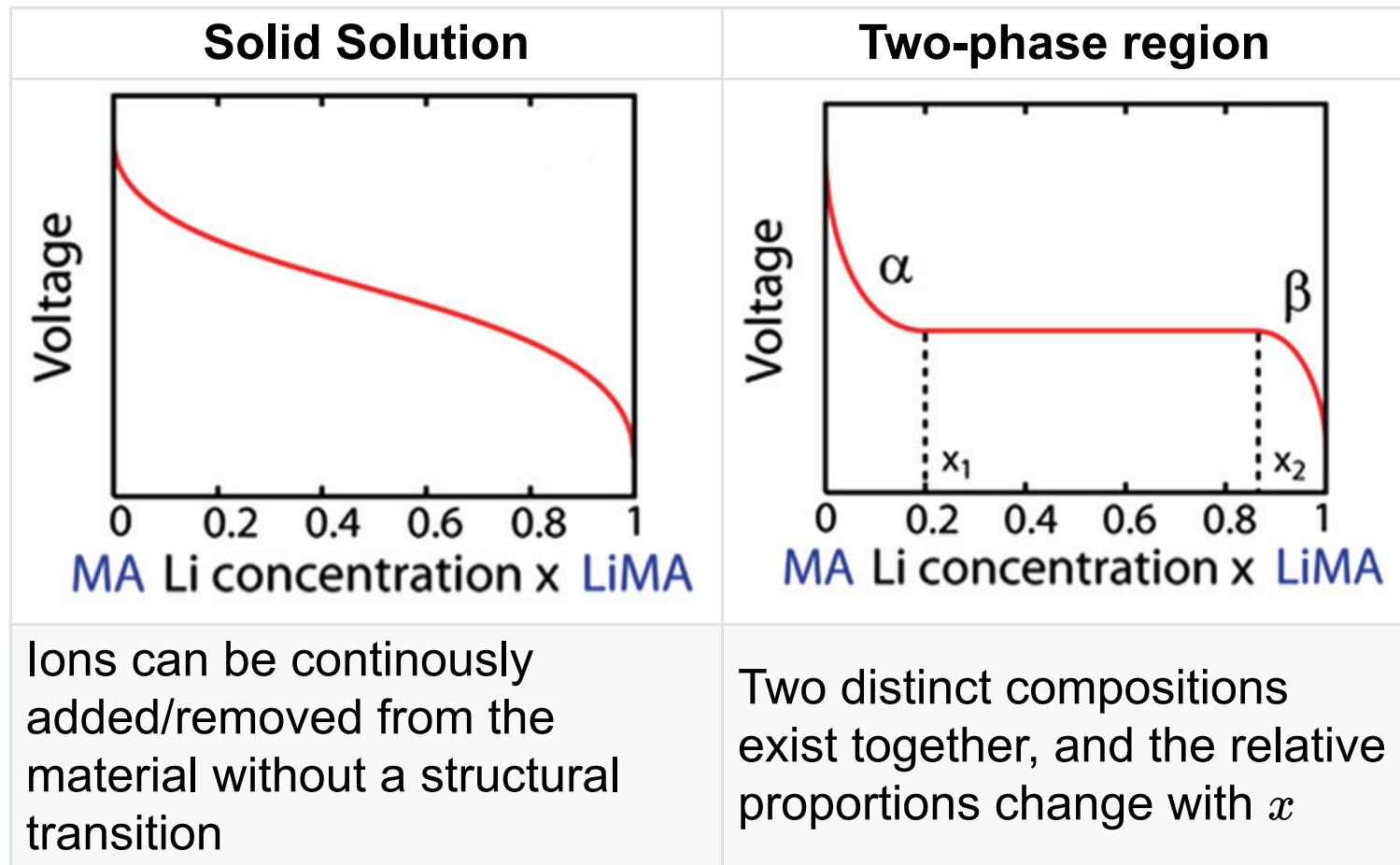
Electrochemical measurements (2)

e.g. for a 2.2 Ah battery:



Capacity is often expressed in a number of formats

Material insights from galvanostats



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
- high (dis)charge rates reduce capacity
 - problems over different length scales
- we can use galvanostatic measurements to learn a lot