Energy Storage Materials
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Room 269

Lecture Overview

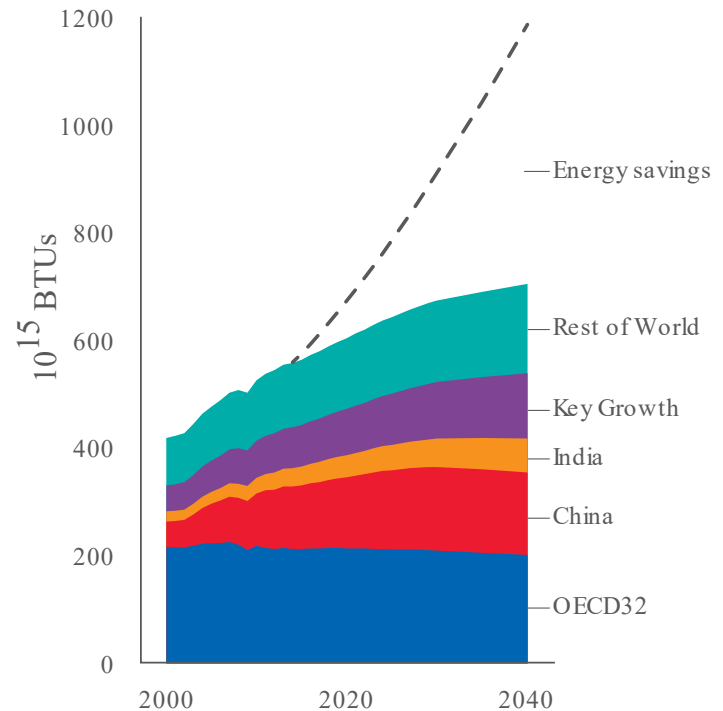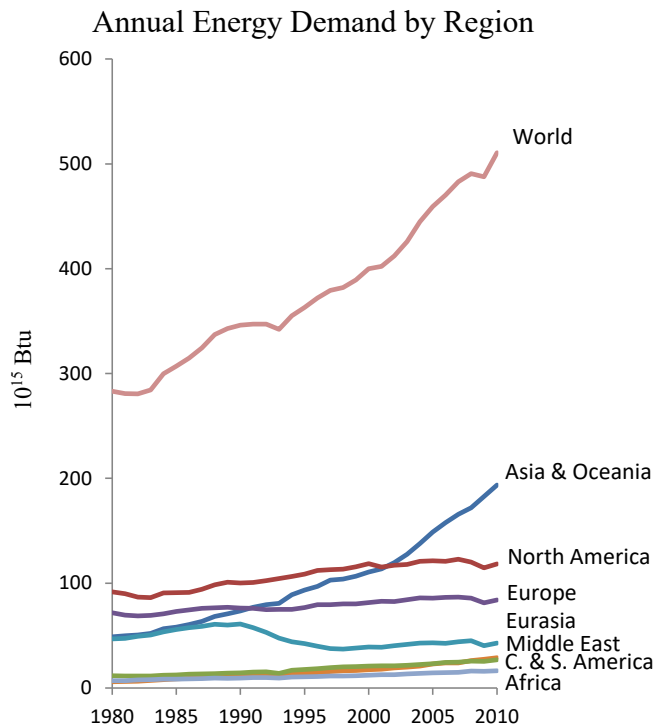| Lecture	Topic
1	Introduction to energy storage materials
1-2	Batteries
3	(Super) capacitors
4-5	Fuel Cells

Recommended Reading

Basic Solid State Chemistry, A. R. West, *Wiley*, **1988**.
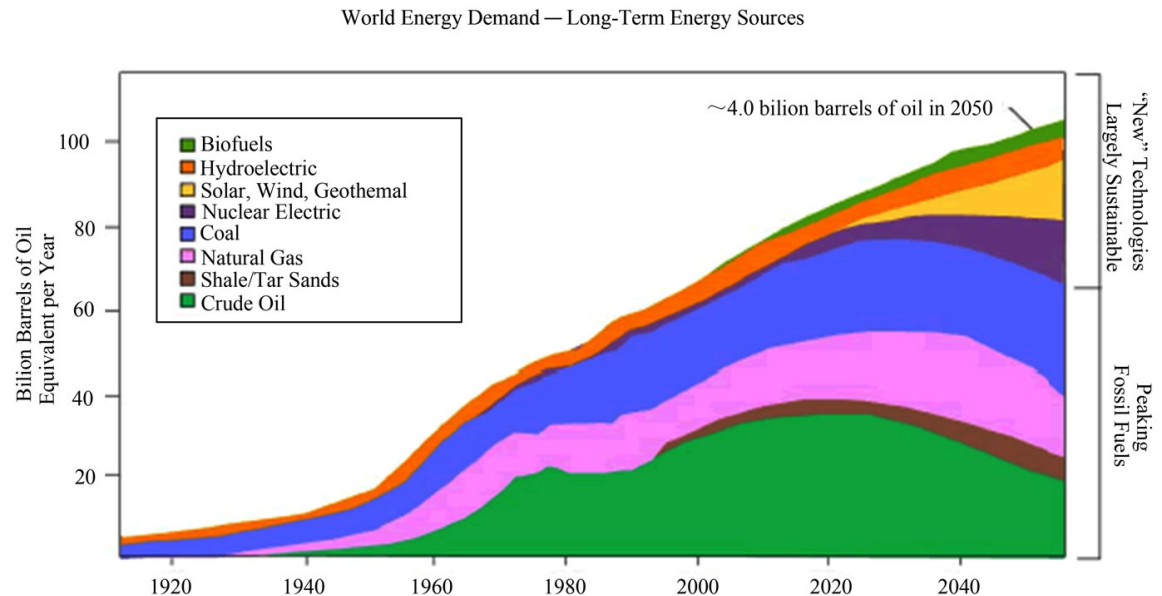
References given during course.

Introduction

Meeting global energy demand is one of the big challenges facing society.

Annual Energy Demand by Region

World

Asia & Oceania

North America

Europe

Eurasia

Middle East

C. & S. America

Africa

10^{15} Btu

600
500
400
300
200
100
0

1980 1985 1990 1995 2000 2005 2010

1200
1000
800
600
400
200
0

10^{15} BTUs

Energy savings

Rest of World

Key Growth

India

China

OECD32

2000 2020 2040

BTU = British Thermal Unit ≈ 1055 J

Energy sources

To meet this demand will require a combination of energy sources:

- Fossil Fuels
  - Coal
  - Oil
  - Gas

- Nuclear
- Renewable
  - Wind
  - Solar
  - Hydro

- ...

World Energy Demand — Long-Term Energy Sources

~4.0 bilion barrels of oil in 2050

Legend:
- Biofuels
- Hydroelectric
- Solar, Wind, Geothemal
- Nuclear Electric
- Coal
- Natural Gas
- Shale/Tar Sands
- Crude Oil

Y-axis: Bilion Barrels of Oil Equivalent per Year

"New" Technologies Largely Sustainable

Peaking Fossil Fuels

All sources have problems...

Fossil fuels

- **Finite supply**
- Environmental cost (i.e. climate change)
- Political uncertainty

Nuclear

- "Finite" supply
- Concerns over waste storage
- Political issues

Renewable

- Intermittent source
- (Relatively) expensive (although this is changing)
- Limited lifespan of components

Drivers behind change

- Problems with energy supply/demand
- Climate change
    - CO_2 emissions

- Other emissions
    - NO_x
    - SO_x
    - Particulates
    - Others

- Dwindling oil and gas resources
- Poltical aspects of fuel supply

Energy storage

If we aim to increase renewable sources, we need a way to *store* this energy.

- Supply cannot immediately respond to changes in demand
- Inefficient to waste "excess" energy (e.g. on a windy day)

How can we store this energy?

Historic approaches:

Technology	Energy conversion
- Burning wood	Chemical potential $\rightarrow$ Heat
- Firebrick (Used since the Hittites)	Heat $\rightarrow$ Heat
- Gravity!	Gravitational potential $\rightarrow$ Kinetic
e.g. Irrigation (Hanging Gardens of Babylon)	
e.g. Mill ponds (modifying existing rivers)	

Energy storage history

The discovery of electricity introduced much more variety into energy storage methods:

Technology	Energy conversion
- Burning wood	Chemical potential $\rightarrow$ Heat
- Firebrick (Used since the Hittites)	Heat $\rightarrow$ Heat
Gravity! *e.g.* Irrigation, Mill ponds	Gravitational potential $\rightarrow$ Kinetic
- Batteries	Chemical $\rightarrow$ Electrical
- (Super-) Capacitors	Electrical $\rightarrow$ Electrical
- Fuel Cells	Chemical $\rightarrow$ Electrical
- Cryogenic / Liquid air	Kinetic (from electrical) $\rightarrow$ 'Heat'
- Mechanical (*e.g.* flywheels)	Kinetic $\rightarrow$ potential

Efficient energy storage relies on *materials*

Important properties for energy storage:

- **Cost**
- (Long-term) stability; reactivity
- Durability
- Compatibility of different materials
- Material performance

  - Ionic conduction
  - Electronic conduction

Batteries

Battery History

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

- Iron and copper electrodes, filled with vinegar or wine
- Possible uses: medicinal, religious or electro-plating!

1800: Volta created the voltaic pile

- Alternating Ag and Zn discs, NaCl electrolyte
- Enabled *chemistry* e.g. $2H_2O \rightarrow H_2 + O_2$
- Corrosion limited battery life

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)

1886 The first dry cell, $Zn | NH_4Cl | MnO_2$

- NH_4Cl immobilised with plaster of Paris ($CaSO_4 \cdot 0.5\ H_2O$)

1899 The first alkaline battery $NiO(OH) | KOH | Cd$

- Higher energy density than lead-acid, but expensive
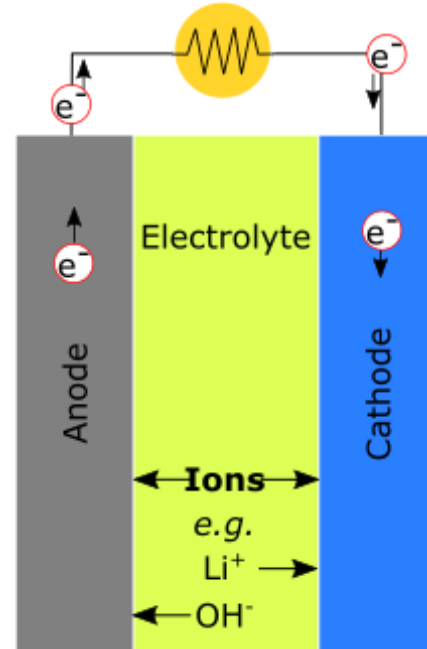
1991 Li-ion battery commercialised by Sony
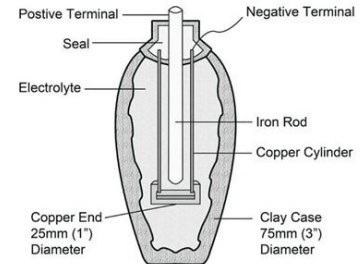
Battery Operation
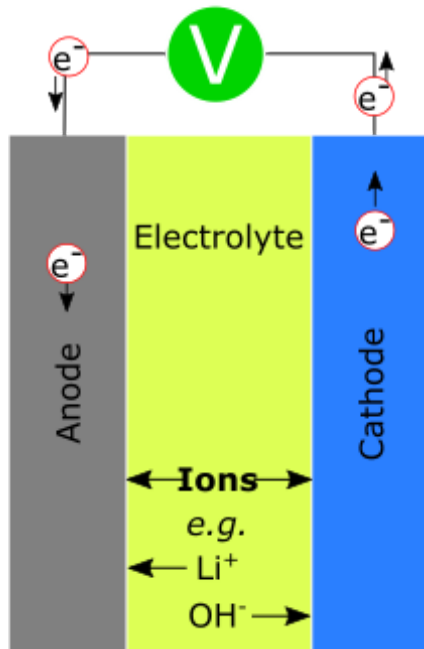
NOTE: In rechargeable cells, naming of *anode* and *cathode* is often unclear. Here we define:

- Cathode is **positive** electrode under **discharge**
- Anode is **negative** electrode under **discharge**

Improving batteries

The most important parameter in improving batteries is the total *energy capacity*, E

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

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

  Q is expressed in units of Ah (1 mAh = 3.6 C), so E_{bat} is in Wh (Watt-hours)

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

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

We want to maximise volumetric and gravimetric energy densities
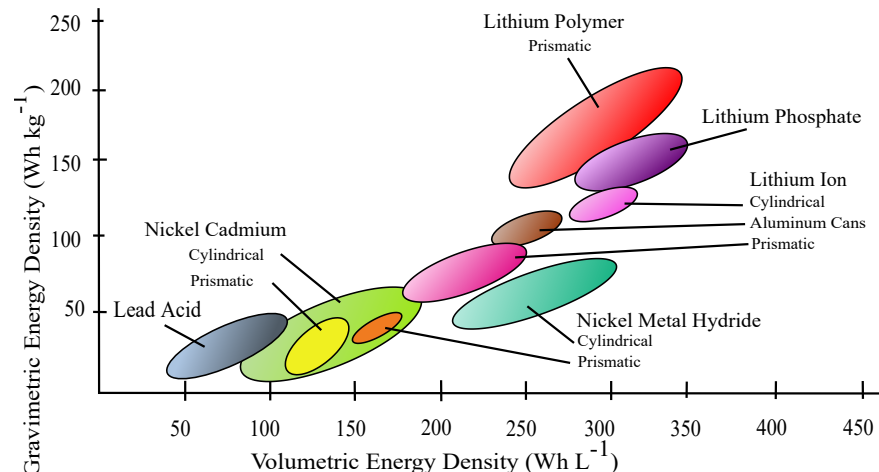
Increase E_{bat}: Increase *voltage* V
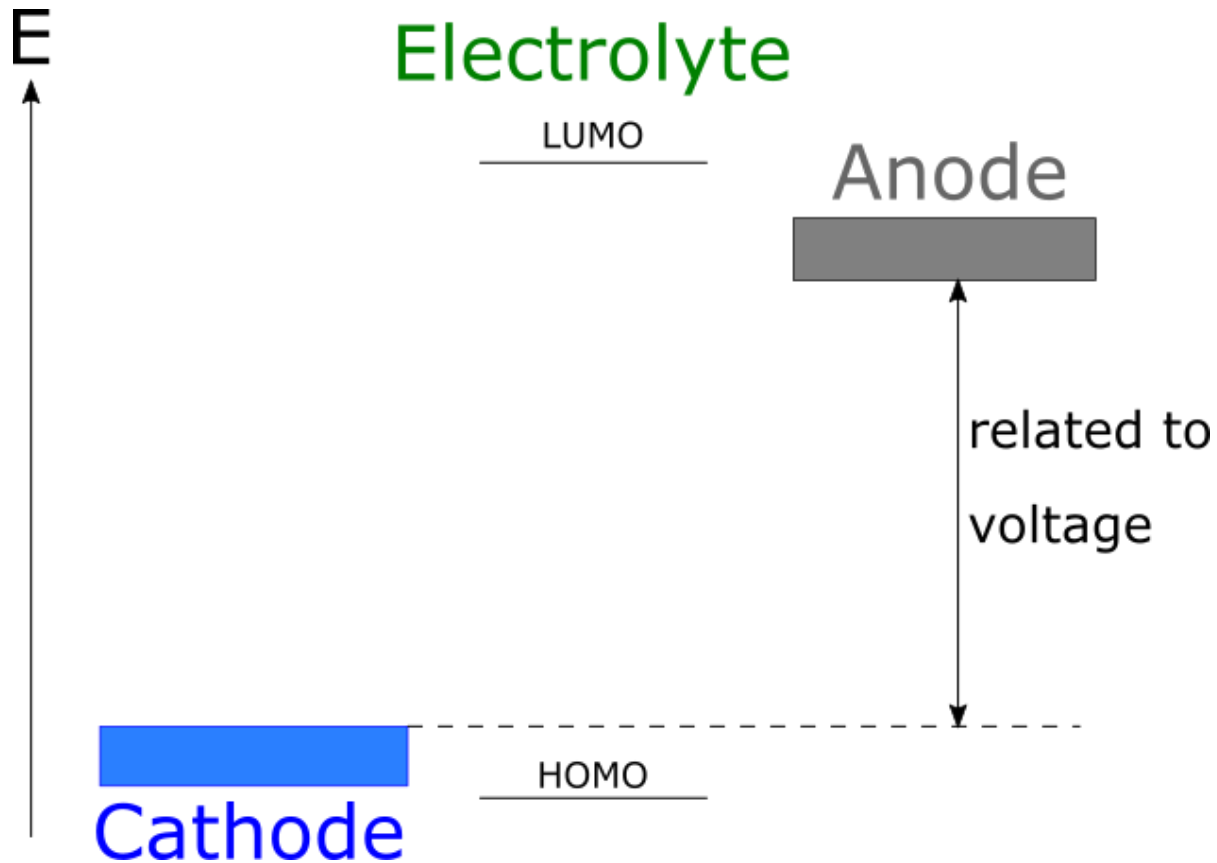
Increase E_{bat}: Increase *charge Q*

Faraday's Law:

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

e.g. for $\text{LiCoO}_2 \longrightarrow \text{Li}^+ + \text{e}^- + \text{CoO}_2$:

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

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

- For LiCoO_2, CoO_2 is *very* 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}

Charging rates

Ideally we want to charge batteries quickly

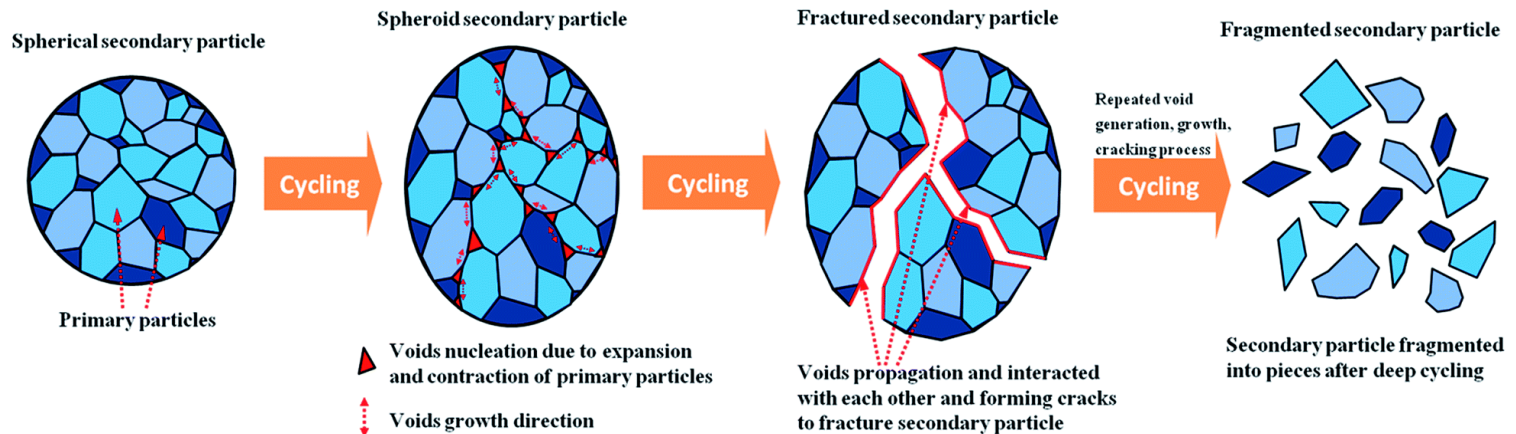Define charge rate, $C = \frac{I}{Q}$, the ratio of discharge current to capacity

- *i.e.* for a 1000 mAh (1 Ah) battery:
    - $1C$ => current of 1 A, which could be sustained for 1 hour
    - $2C$ => 2 A (for 30 mins)
    - $\frac{C}{6}$ => 0.167 A (for 6 hours)
- This allows us to describe charging rates independent of battery capacity.
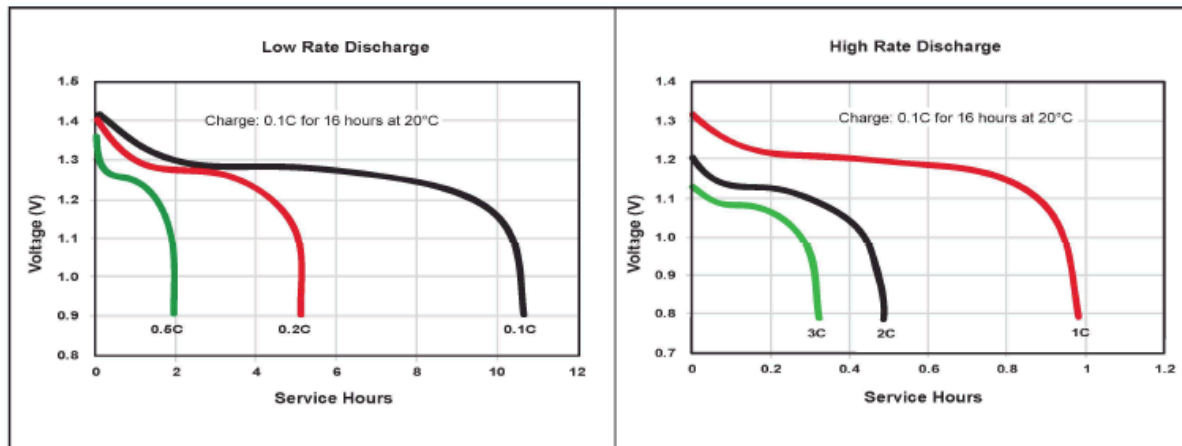
Effect of rate on capacity

High charging rates reduce capacity

- Electrons can move much faster than ions, so at high *C*-rates strain occurs in the lattice
    - Ions get stuck, reducing the overall discharge capacity
   - Irreversible damage to crystal structure and/or microstructure can occur, preventing future charging

Spherical secondary particle

Primary particles

Spheroid secondary particle

Cycling

▲ Voids nucleation due to expansion and contraction of primary particles

⇣ Voids growth direction

Fractured secondary particle

Cycling

Voids propagation and interacted with each other and forming cracks to fracture secondary particle

Repeated void generation, growth, cracking process

Cycling

Fragmented secondary particle

Secondary particle fragmented into pieces after deep cycling

B. Song, *J. Mat. Chem. A*, **2015**, 18171.

Ragone (*ru-GO-nee*) plot

Displays the relation between *specific energy* (E) and *specific power* (P):

$$E = QV(= ItV)$$ The total amount of energy available in the battery

$$P = IV$$ The rate at which energy can be used

Some applications require fast discharge over short times (e.g. electric sports car accelerating) while others need more sustained energy supply (long-range electric vehicle)


B.D. McCloskey, J. Phys. Chem. Lett., **2015**, 6, 3592-3593.
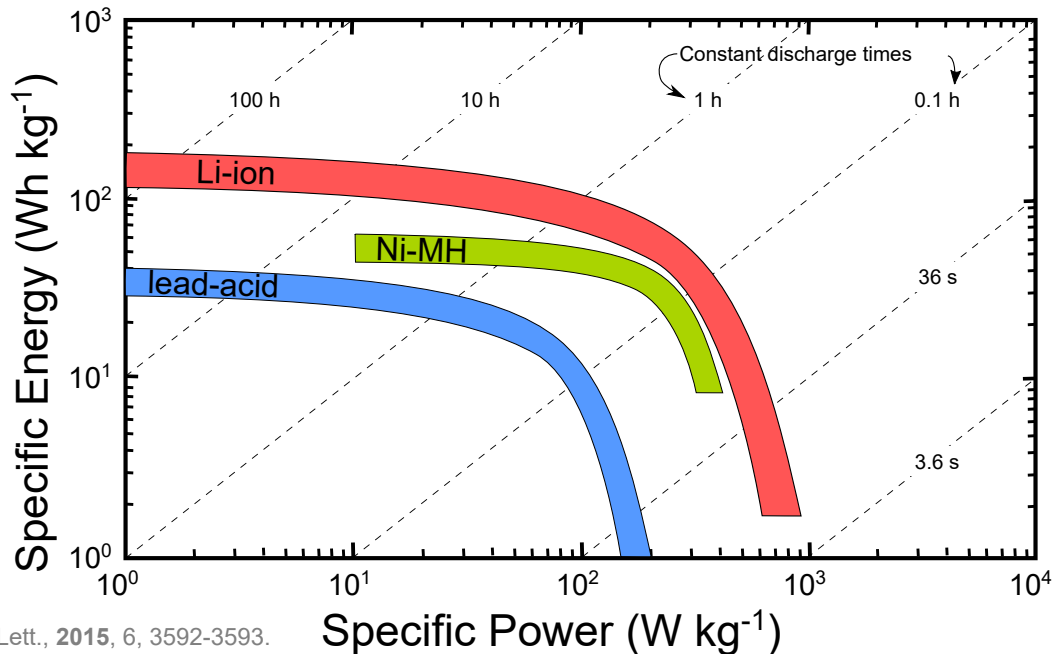
Electrochemical measurements

Typically we use *Galvanostatic* (constant current) measurements to characterise battery response, and measure the resulting voltage.

- Charging rates have a big impact on device performance, so *potentiostatic* (*i.e.* constant voltage) measurements would be difficult to attribute to chemistry *vs.* rate effects.
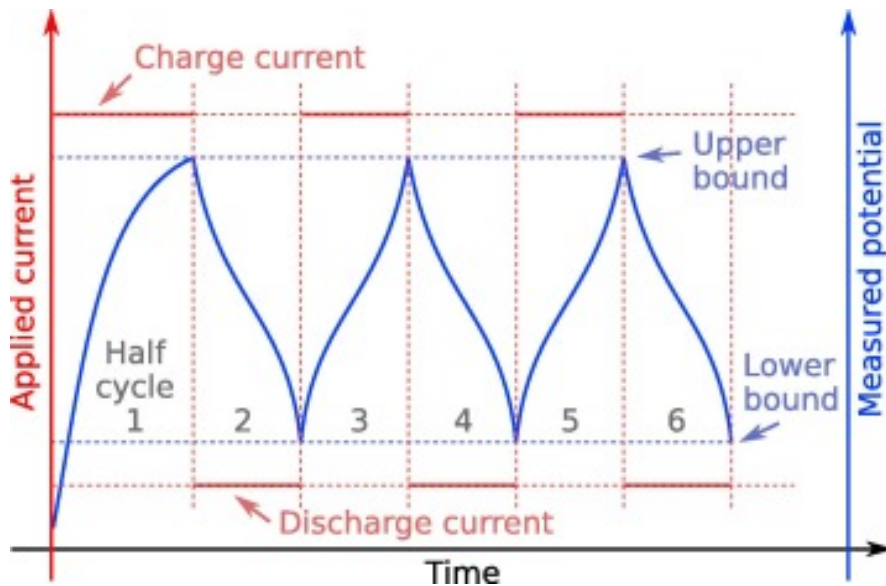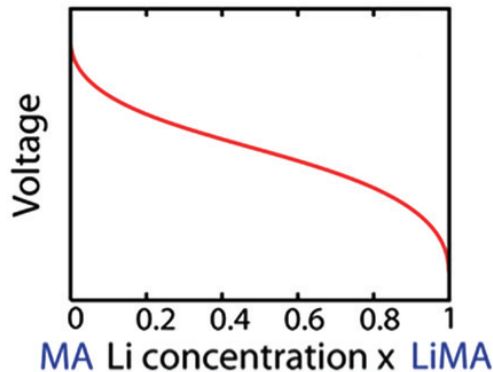
Electrochemical measurements

e.g. for a 2.2 Ah battery:
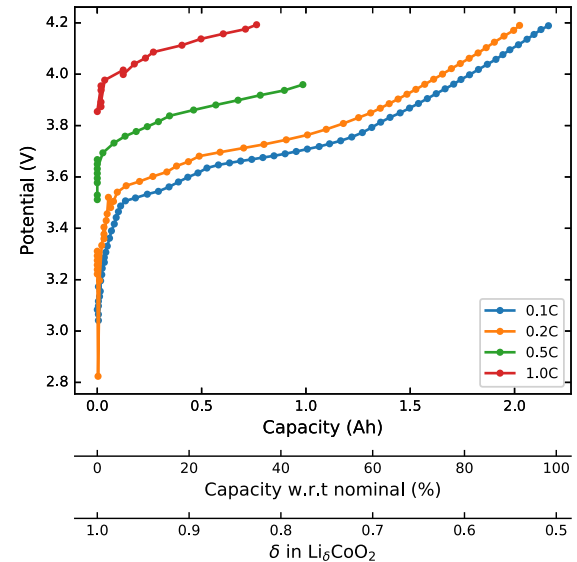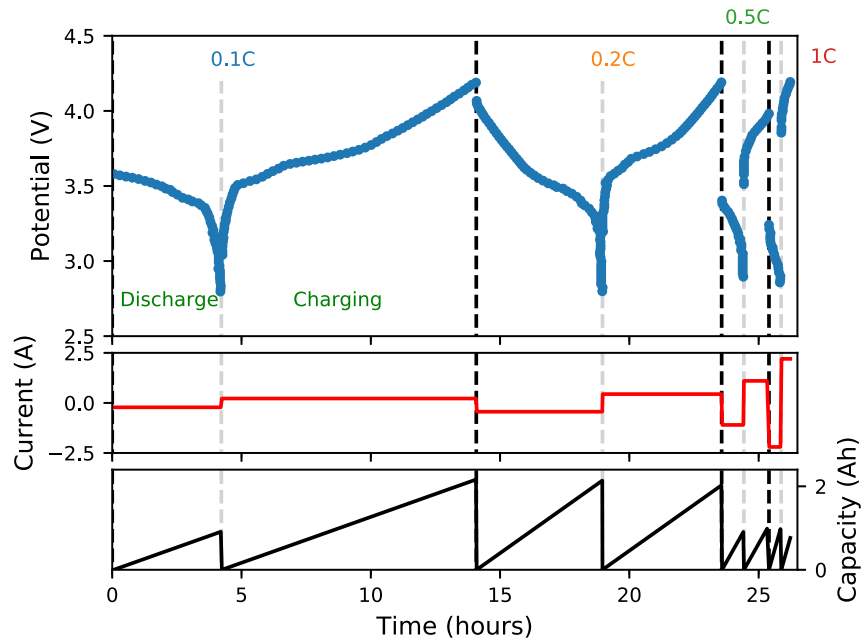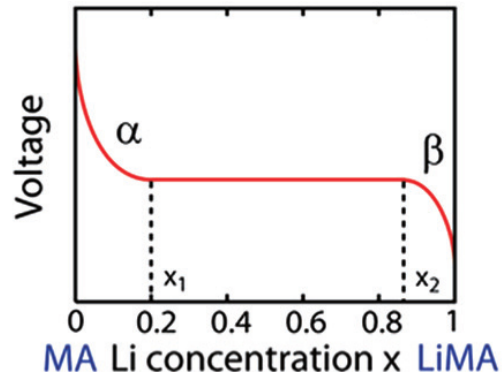

Capacity can be expressed in a number of formats

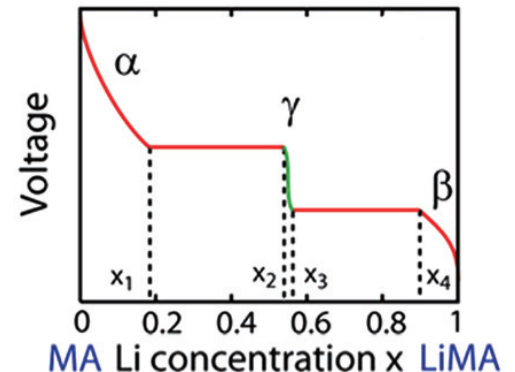# What can we learn from galvanostats?

Solid Solution

Two-phase region

Phase change

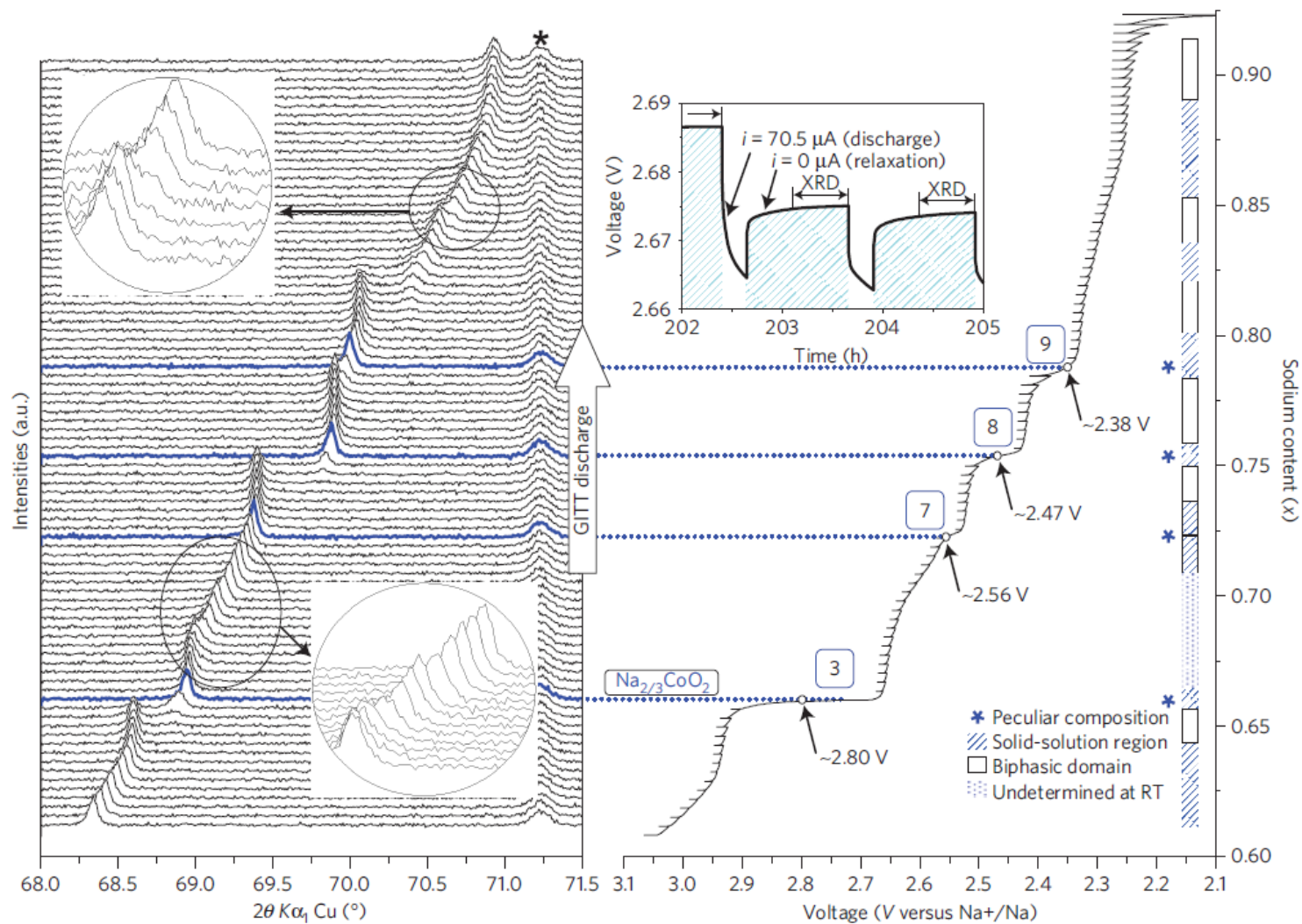Ions can be continously added/removed from the material without a structural transition

Two distinct compositions exist together, and the relative proportions change with x

Abrupt voltage (and structure) change between α and β due to a more-stable γ phase with narrow composition window.

Example: Na$_x$CoO$_2$

Berthelot *et al*, *Nature Materials*, **2010**, 74-80.

Key materials properties

Anode

- Good electronic conductor
- Good ionic conductor
- Structural stability on ionic movement

Electrolyte

- Good ionic conductor
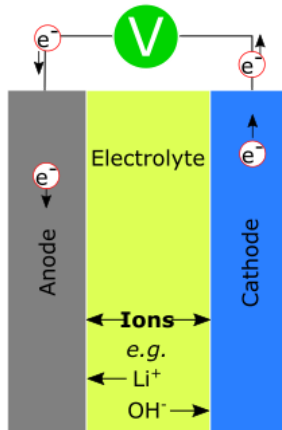- *Negligible* electronic conduction

Cathode

- Good electronic conductor
- Good ionic conductor
- Structural stability on ionic movement

Overall

- Compatibility between materials (particularly under volume changes during charge/discharge)