

# Energy Storage Materials

## Dr. James Cumby

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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

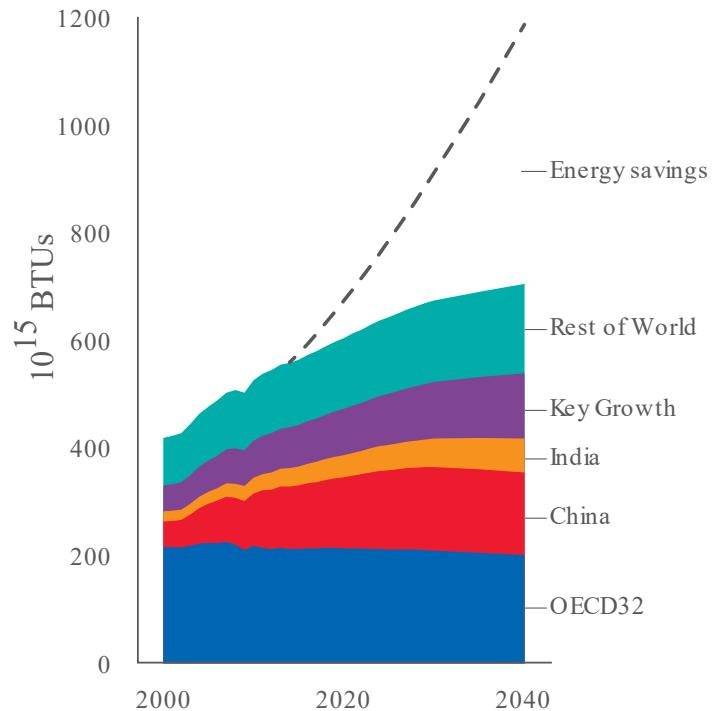
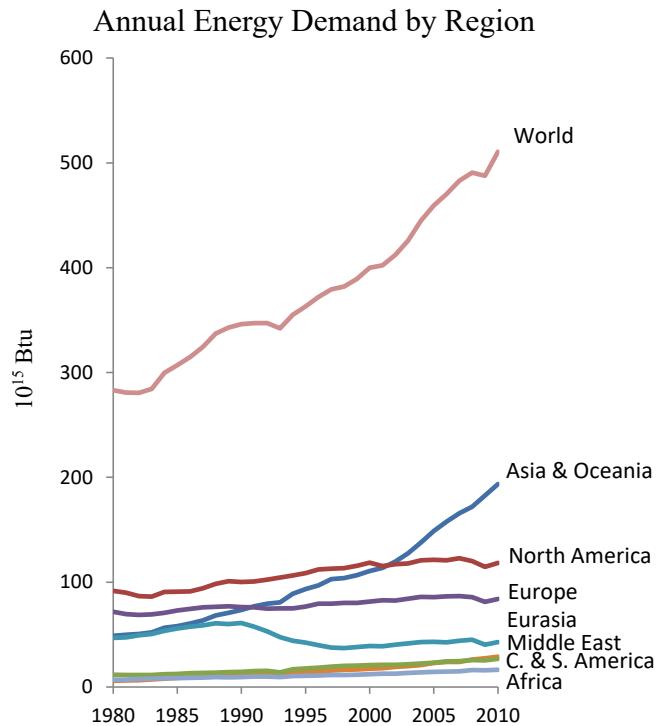
## Recommended Reading

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.



# Energy sources

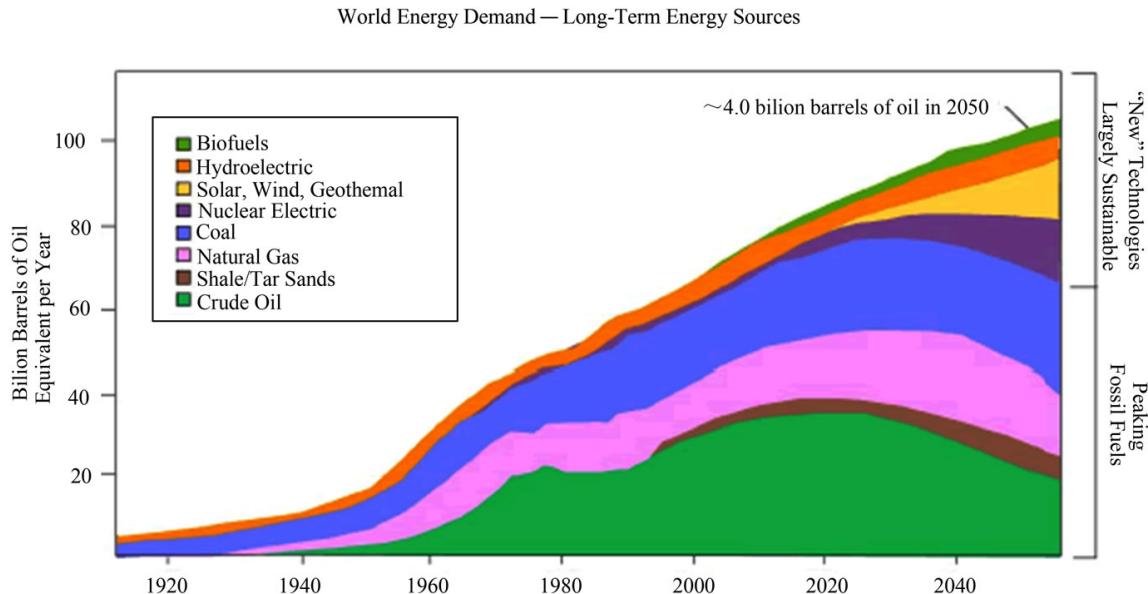
To meet this demand will require a combination of energy sources:

- Fossil Fuels
  - Coal
  - Oil
  - Gas
- Nuclear
- Renewable
  - Wind
  - Solar
  - Hydro
- ...

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- **Finite supply**
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## Renewable

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



# Drivers behind change

- Problems with energy supply/demand
- Climate change
  - CO<sub>2</sub> emissions
- Other emissions
  - NO<sub>x</sub>
  - SO<sub>x</sub>
  - Particulates
  - Others
- Dwindling oil and gas resources
- Political 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?

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## How can we store this energy?

Historic approaches:

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

# Energy storage history

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

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

# Efficient energy storage relies on *materials*

Important properties for energy storage:

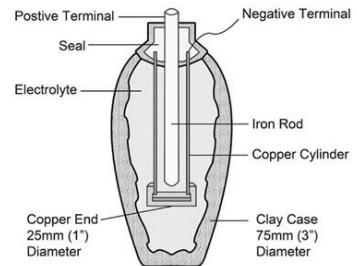
- **Cost**
- (Long-term) stability; reactivity
- Durability
- Compatibility of different materials
- Material performance
  - Ionic conduction
  - Electronic conduction

# 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!



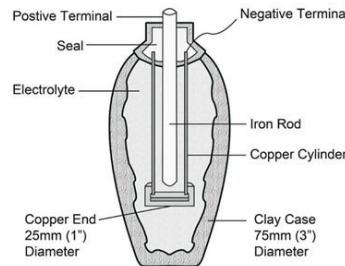
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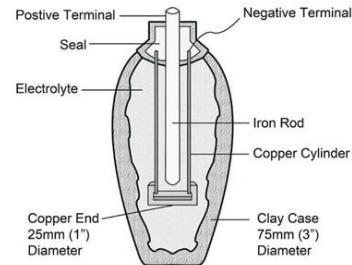
- Alternating Ag and Zn discs, NaCl electrolyte
- Enabled *chemistry* e.g.  $2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$
- Corrosion limited battery life



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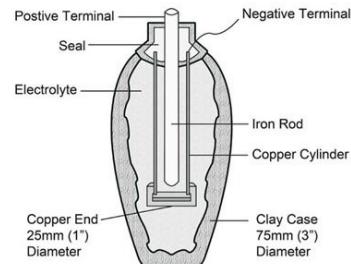
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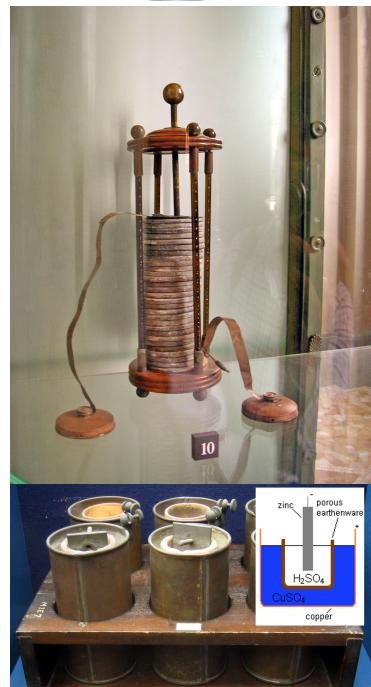
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**1886** The first dry cell,  $\text{Zn} | \text{NH}_4\text{Cl} | \text{MnO}_2$

- $\text{NH}_4\text{Cl}$  immobilised with plaster of Paris ( $\text{CaSO}_4 \cdot 0.5 \text{ H}_2\text{O}$ )

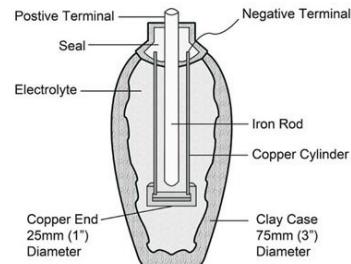
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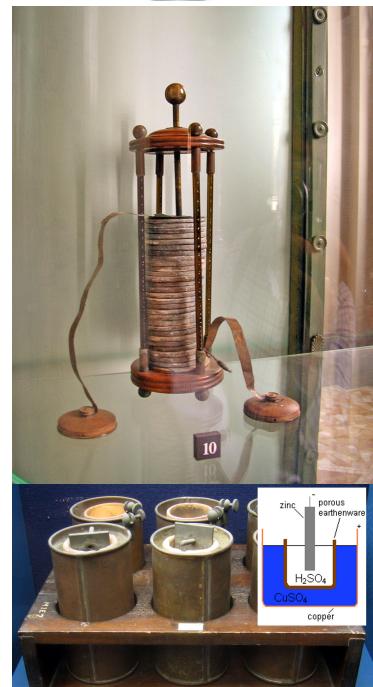
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**1991** Li-ion battery commercialised by Sony



Akira Yoshino



John B. Goodenough



M. Stanley Whittingham

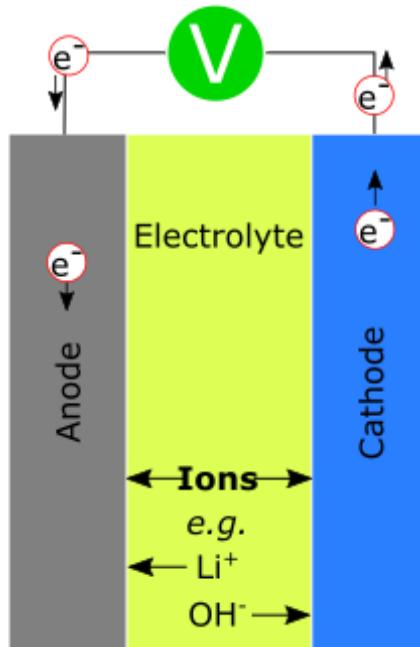


Our exclusive interview with 2019 Nobel laureate John B Goodenough

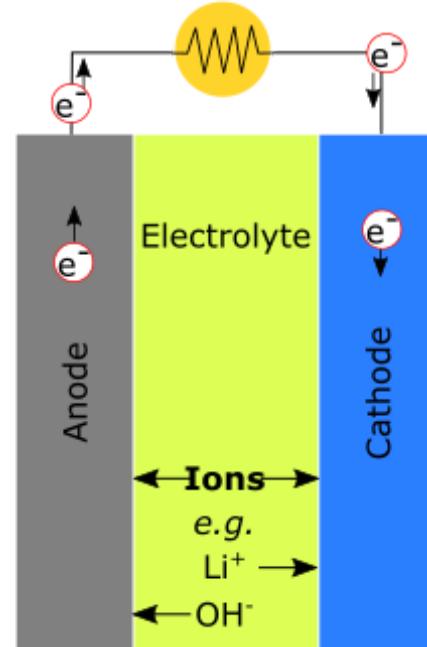


# Battery Operation

## Charge



## Discharge



**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:

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

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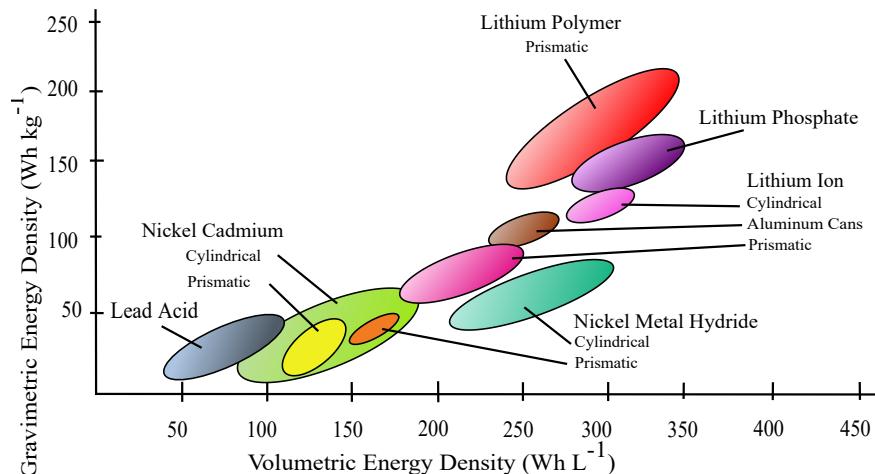
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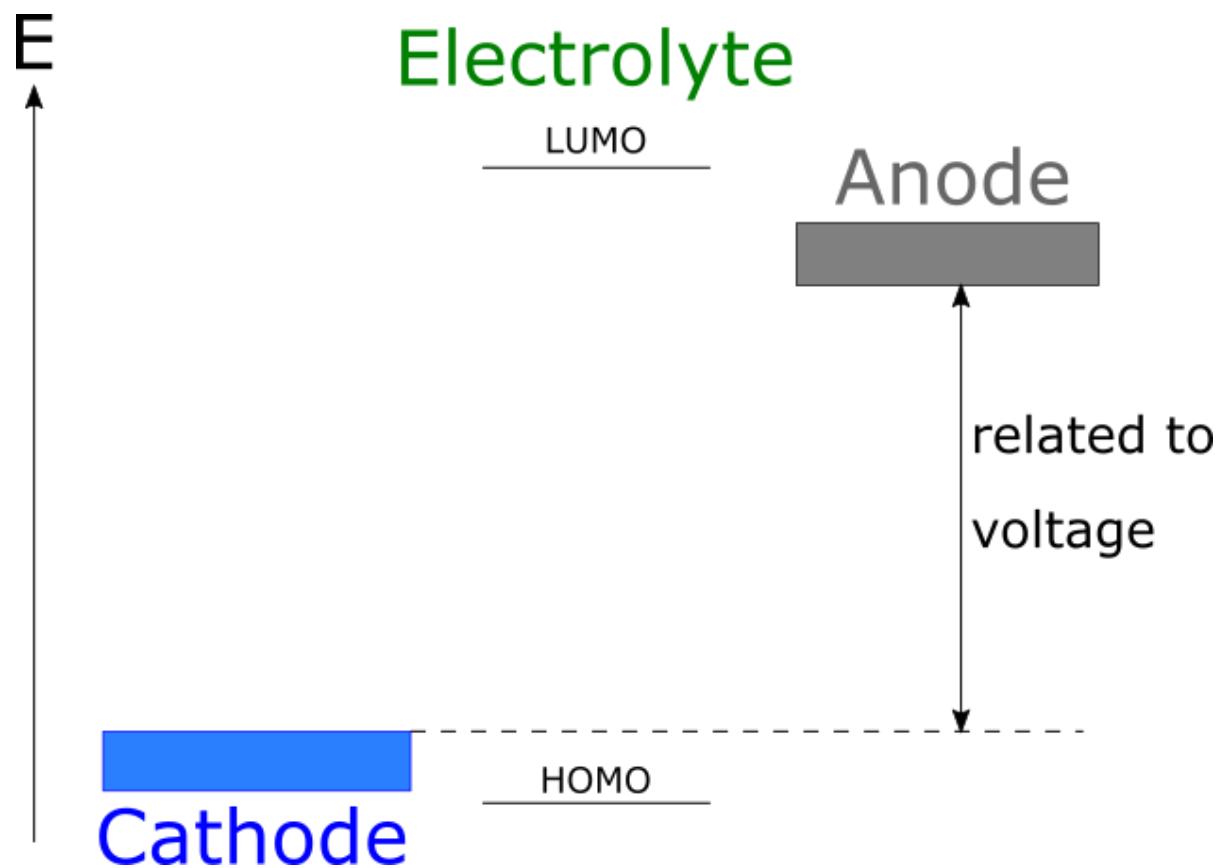
- $E_{\text{bat}}$  is dependent on the amount of battery material. More useful are:

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

We want to maximise  
volumetric and  
gravimetric energy  
densities



Increase  $E_{\text{bat}}$ : Increase voltage  $V$



# Increase $E_{\text{bat}}$ : Increase charge $Q$

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

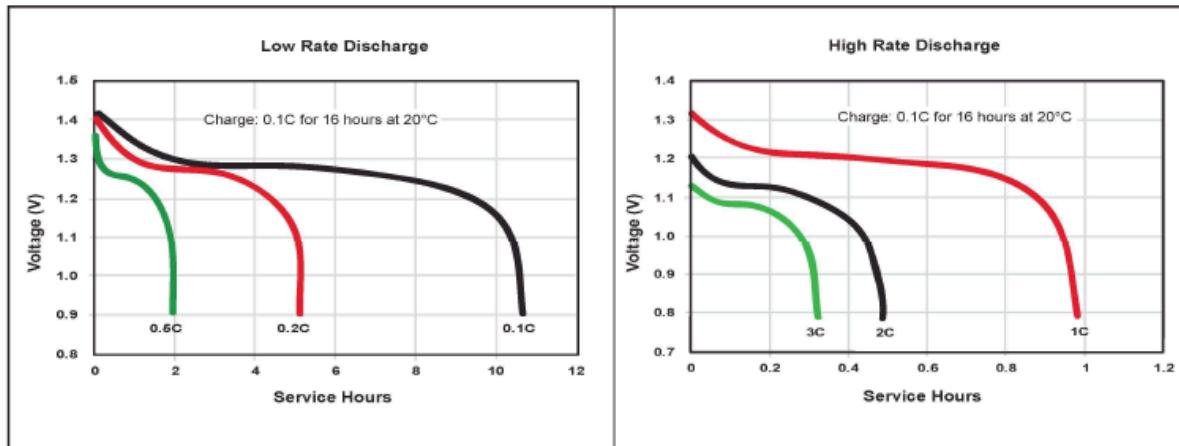
- For  $\text{LiCoO}_2$ ,  $\text{CoO}_2$  is *very* unstable:  $2 \text{Co}^{\text{IV}}\text{O}_2 \rightarrow \text{Co}_2^{\text{III}}\text{O}_3 + \frac{1}{2}\text{O}_2$ 
  - We can only safely reach  $\text{Li}_{0.5}\text{CoO}_2$ , so the useful capacity is  $137 \text{ mAh g}^{-1}$

# Charging rates

Ideally we want to charge batteries quickly

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

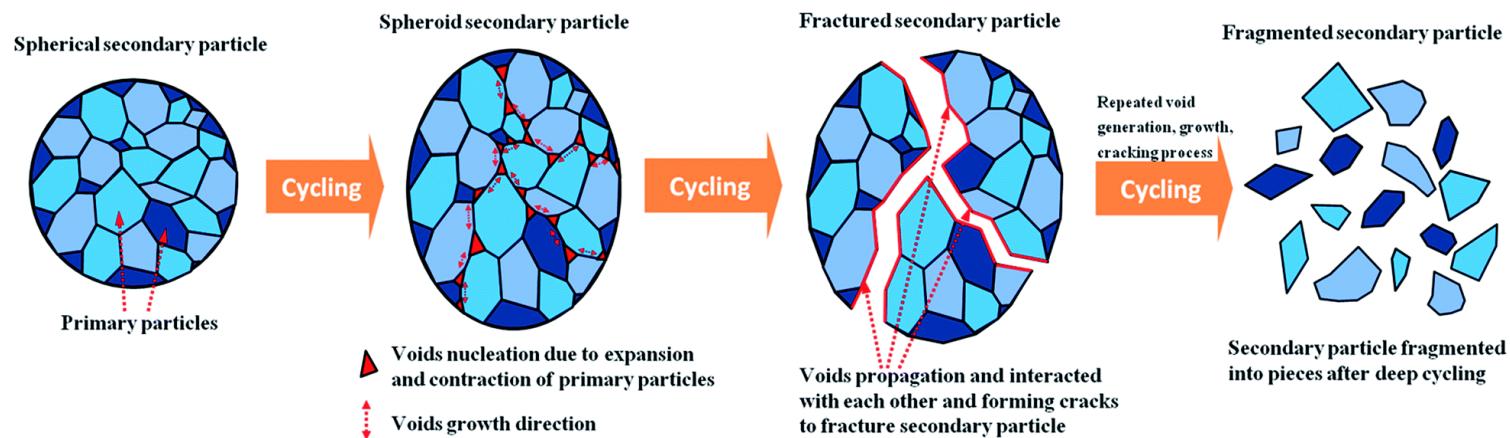
- i.e. for a 1000 mAh (1 Ah) battery:
  - $1C \Rightarrow$  current of 1 A, which could be sustained for 1 hour
  - $2C \Rightarrow$  2 A (for 30 mins)
  - $\frac{C}{6} \Rightarrow 0.167$  A (for 6 hours)
- This allows us to describe charging rates independent of battery capacity.



# 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



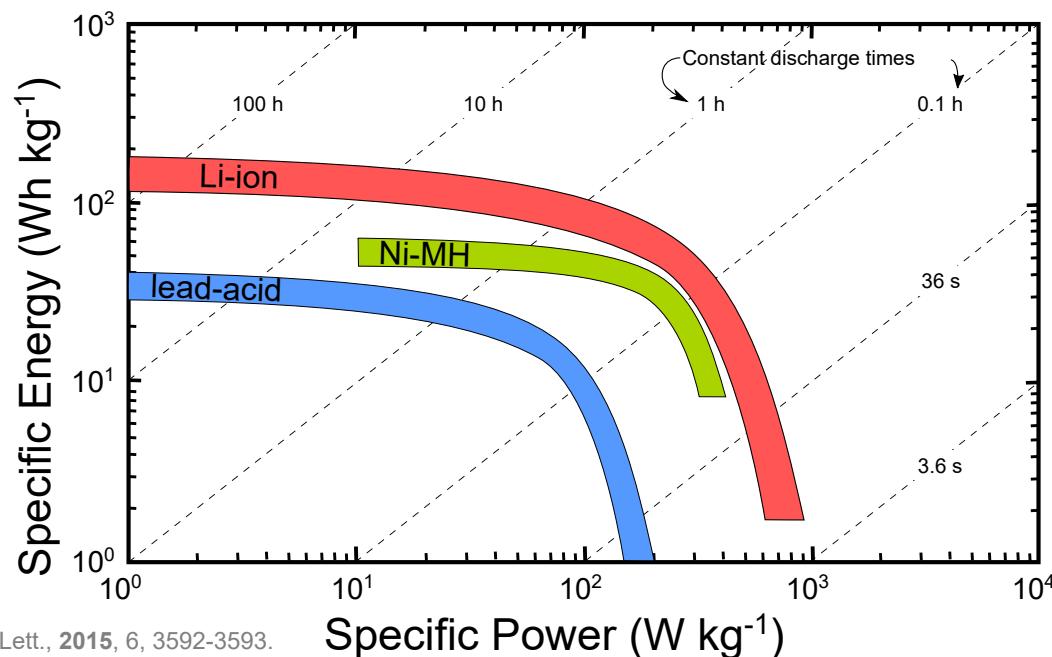
# Ragone (*ru-GO-nee*) plot

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

$$E = QV (= ItV) \quad \text{The total amount of energy available in the battery}$$

$$P = IV \quad \text{The rate at which energy can be used}$$

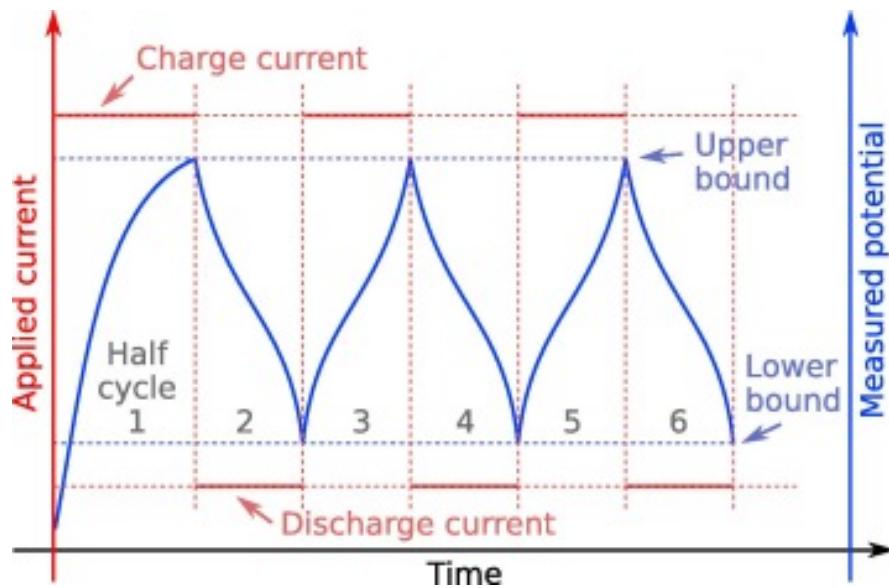
Some applications require fast discharge over short times (e.g. electric sports car accelerating) while others need more sustained energy supply (long-range electric vehicle)



# Electrochemical measurements

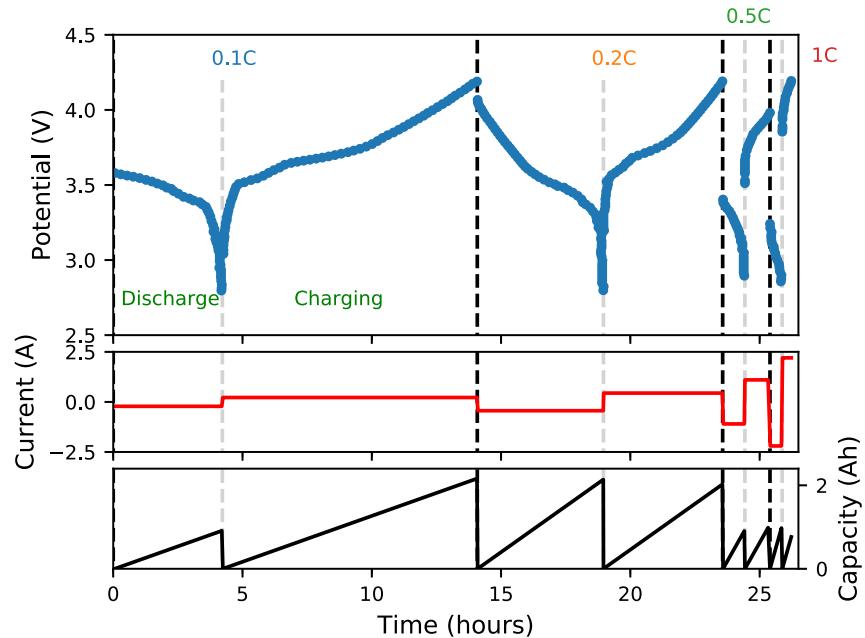
Typically we use *Galvanostatic* (constant current) measurements to characterise battery response, and measure the resulting voltage.

- 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.



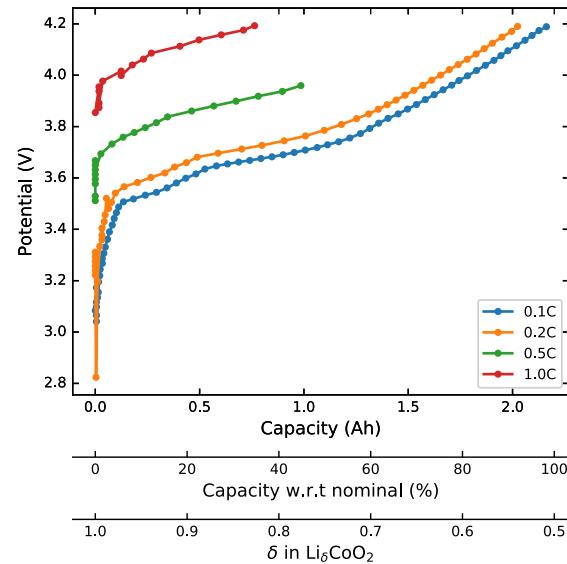
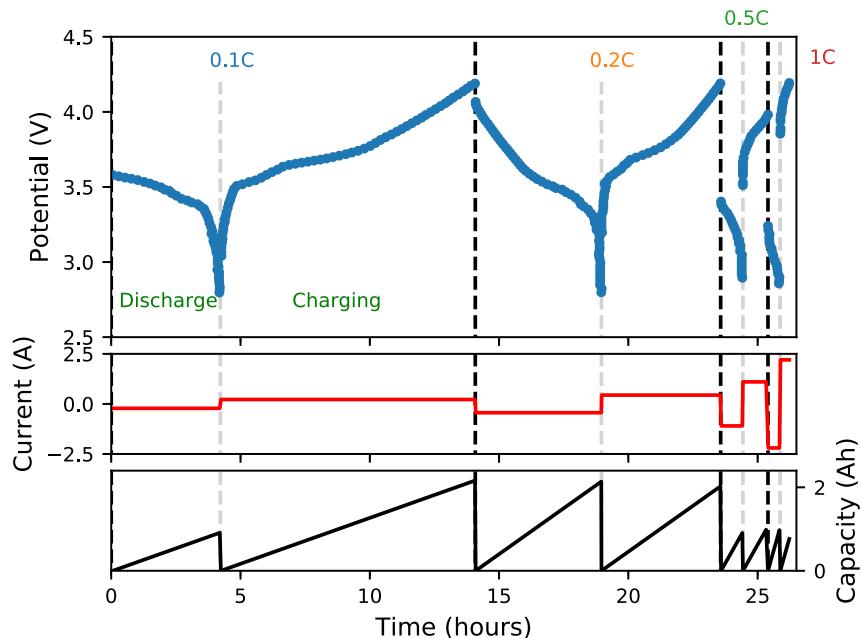
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e.g. for a 2.2 Ah battery:



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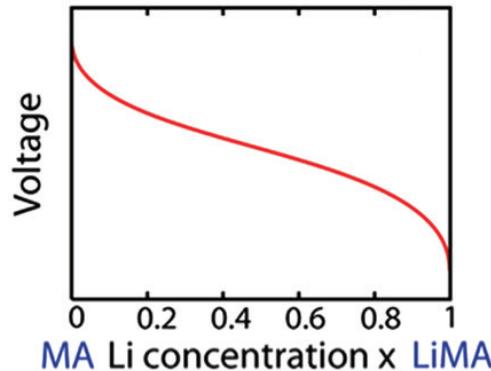
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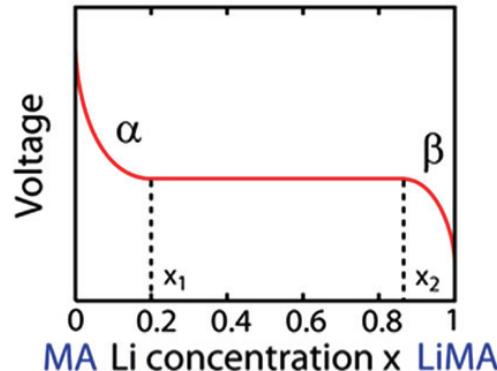
Capacity can be expressed in a number of formats

# What can we learn from galvanostats?

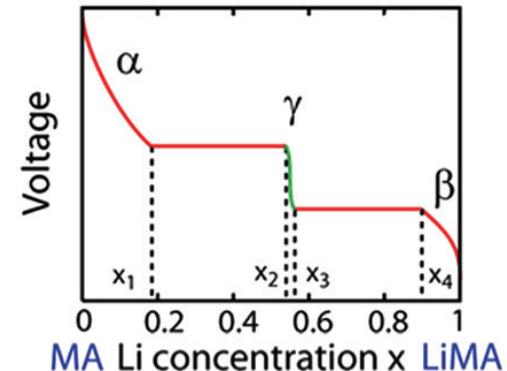
Solid Solution



Two-phase region



Phase change

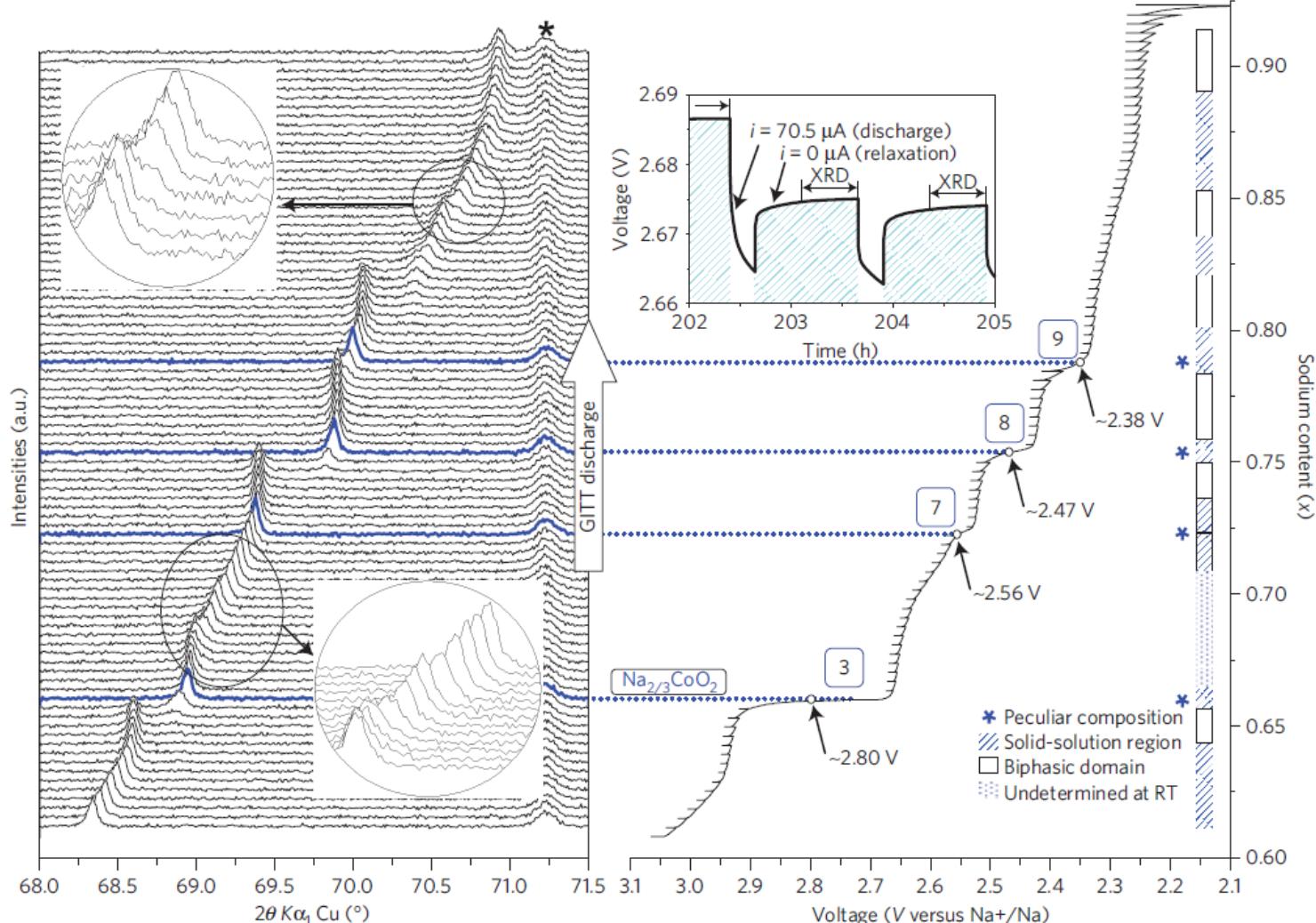


Ions can be continuously added/removed from the material without a structural transition

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

Abrupt voltage (and structure) change between  $\alpha$  and  $\beta$  due to a more-stable  $\gamma$  phase with narrow composition window.

# Example: $\text{Na}_x\text{CoO}_2$



# Key materials properties

## Anode

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

## Electrolyte

- Good ionic conductor
- *Negligible* electronic conduction

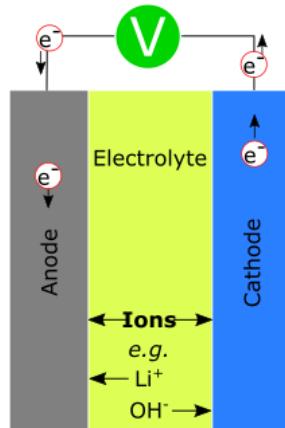
## Cathode

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

## Overall

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

## Charge



## Discharge

