Energy Storage Materials

Dr. James Cumby

james.cumby@ed.ac.uk

Room 269

Lecture Overview

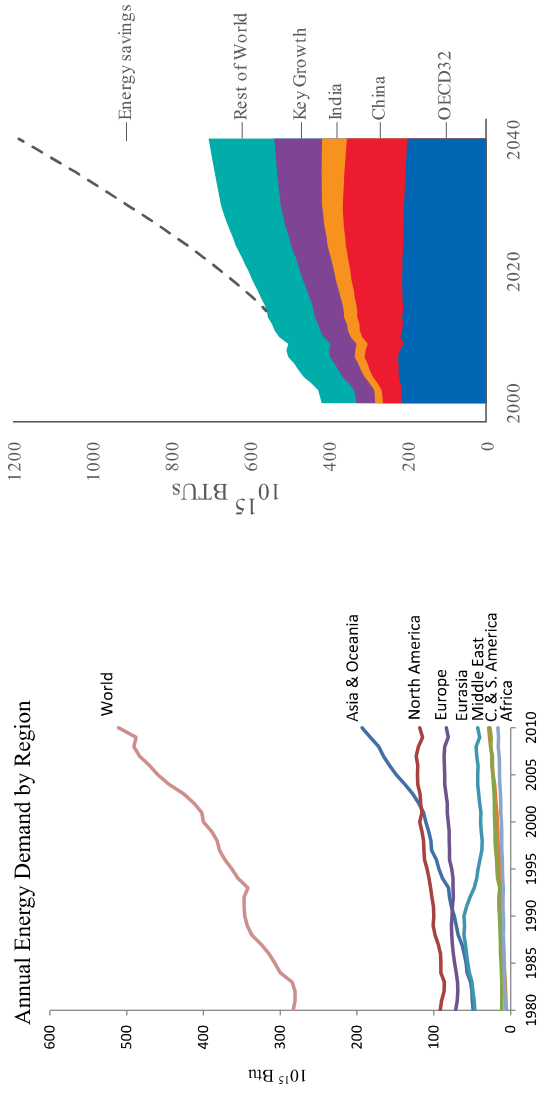| Lecture	Topic
1	Introduction to energy storage materials
1-2	Batteries
3	(Super) capacitors
4-5	Fuel Cells

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

10^{15} Btu

600
500
400
300
200
100
0

1980 1985 1990 1995 2000 2005 2010

World

Asia & Oceania

North America

Europe
Eurasia
Middle East
C. & S. America
Africa

10^{15} BTUs

1200
1000
800
600
400
200
0

2000 2020 2040

Energy savings

Rest of World

Key Growth

India

China

OECD32

BTU = British Thermal Unit ≈ 1055 J
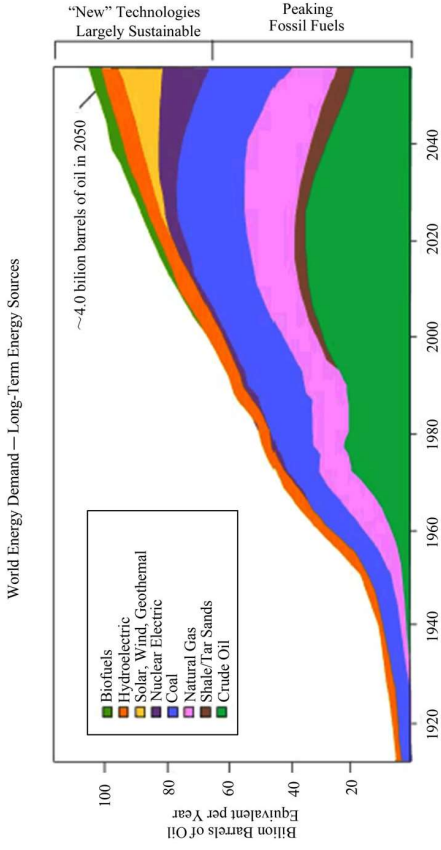
Energy sources

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

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

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  - Solar
  - Hydro

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World Energy Demand — Long-Term Energy Sources

"New" Technologies Largely Sustainable

Peaking Fossil Fuels

~4.0 bilion barrels of oil in 2050

Biofuels
Hydroelectric
Solar, Wind, Geothermal
Nuclear Electric
Coal
Natural Gas
Shale/Tar Sands
Crude Oil

Billion Barrels of Oil Equivalent per Year

100
80
60
40
20

1920 1940 1960 1980 2000 2020 2040

All sources have problems...

Fossil fuels

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

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- "Finite" supply
- Concerns over waste storage
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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_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?

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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: $Zn|Zn^{2+},SO_4^{2-} \parallel SO_4^{2-}|Cu^{2+}|Cu$

- First practical electricity source (used to power telegraphs)

1859 Lead-acid battery (first rechargeable)

1886 The first dry cell, $Zn \mid NH_4Cl \mid MnO_2$

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

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

- Higher energy density than lead-acid, but expensive

1991 Li-ion battery commercialised by Sony
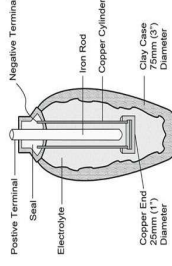
Battery Operation

Charge
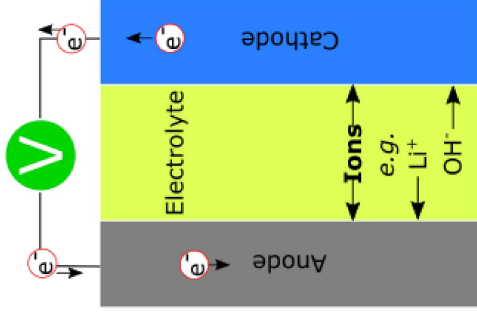
Discharge
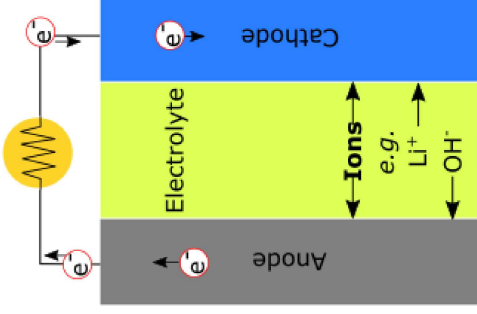
NOTE: In rechargeable cells, naming of *anode* and *cathode* is often unclear. Here we define:

- 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:

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

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

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

  o *Gravimetric* energy density (Wh g^{-1}): Q is charge per unit mass (Ah g^{-1})
  o *Volumetric* energy density (Wh L^{-1}): Q is charge per unit volume (Ah L^{-1})

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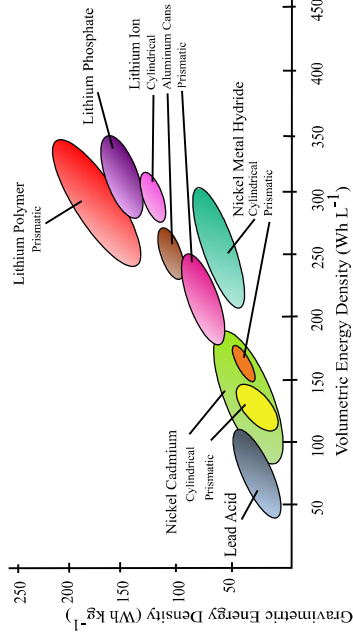
Increase E_{bat}: *voltage*
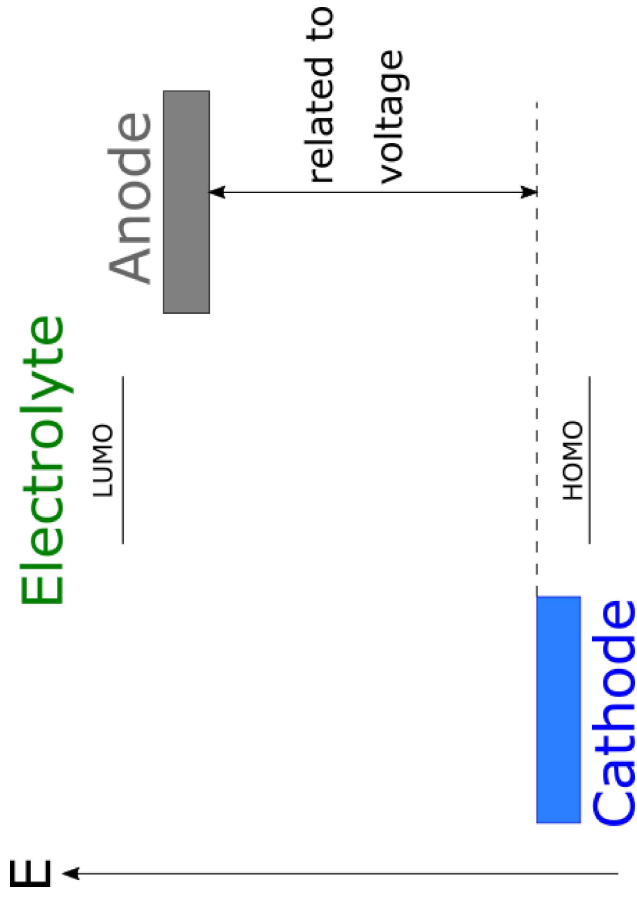
Increase E_{bat}: *charge stored*

Faraday's Law:

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

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$$n = 1, F = 96485.3 \, \text{sA mol}^{-1}$$

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$$\therefore Q = 274 \, \text{mAh g}^{-1}$$

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$$\therefore Q = 274 \text{ mAh g}^{-1}$$

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 100 mAh battery:
  - $1C$ => current of 100 A, which could be sustained for 1 hour
  - $2C$ => 200 A (for 30 mins)
  - $\frac{1}{6}C$ => 50 A (for 2 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 can occur, preventing future charging

Spherical secondary particle — **Primary particles**

Cycling

Spheroid secondary particle — Voids nucleation due to expansion and contraction of primary particles / Voids growth direction

Cycling

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

Cycling — Repeated void generation, growth, cracking process

Fragmented secondary particle — Secondary particle fragmented into pieces after deep cycling

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

Ragone (*ru-GO-nee*) plot

Quantifies the trade-off between energy density (E) and power density (P)

- $P = IV$, whereas $E = QV$

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)
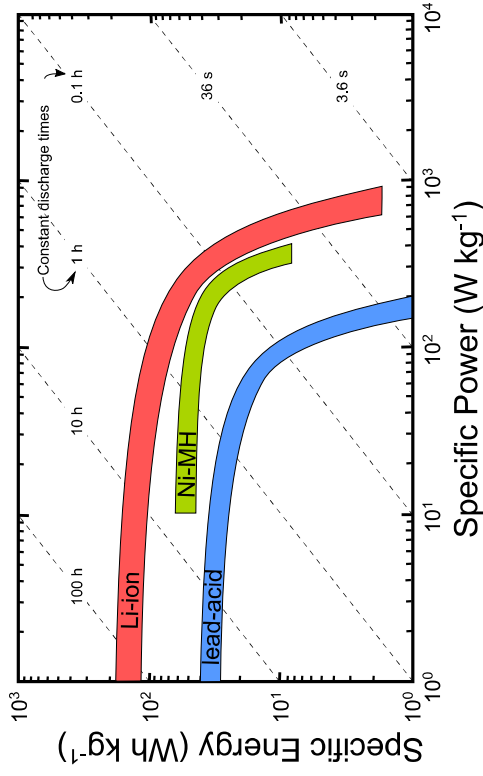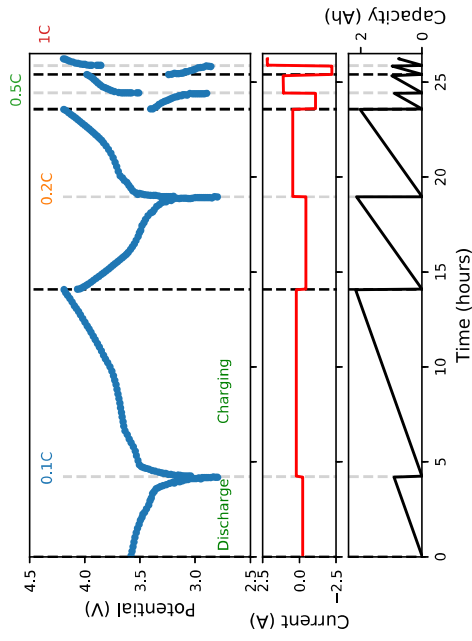
Characterising capacity

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.
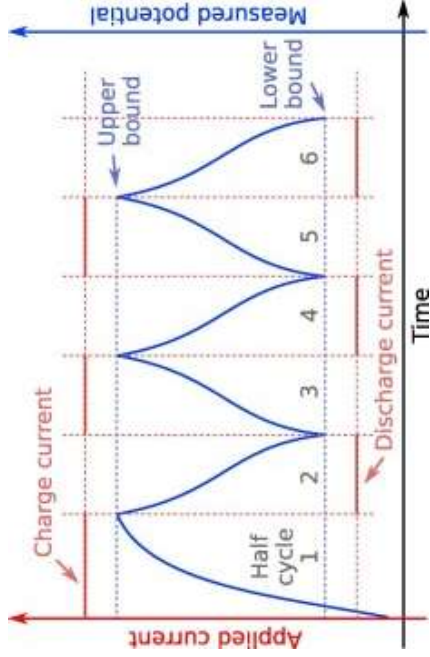
Characterising capacity

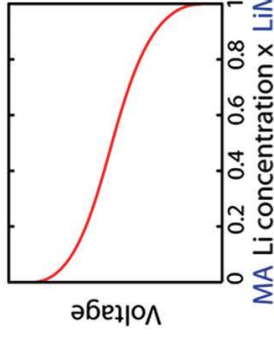e.g. for a 2.2 Ah battery:

Characterising capacity

e.g. for a 2.2 Ah battery:
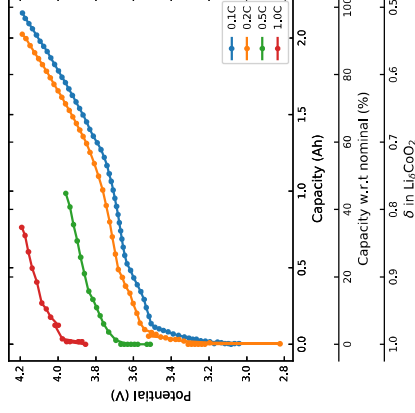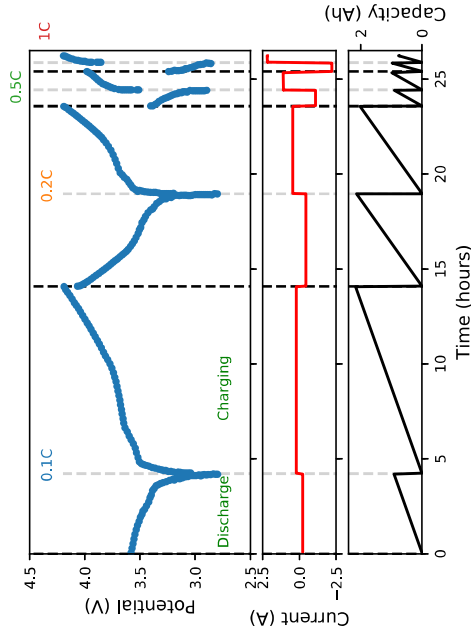
Capacity can be expressed in a number of formats
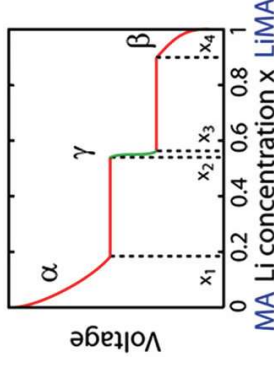
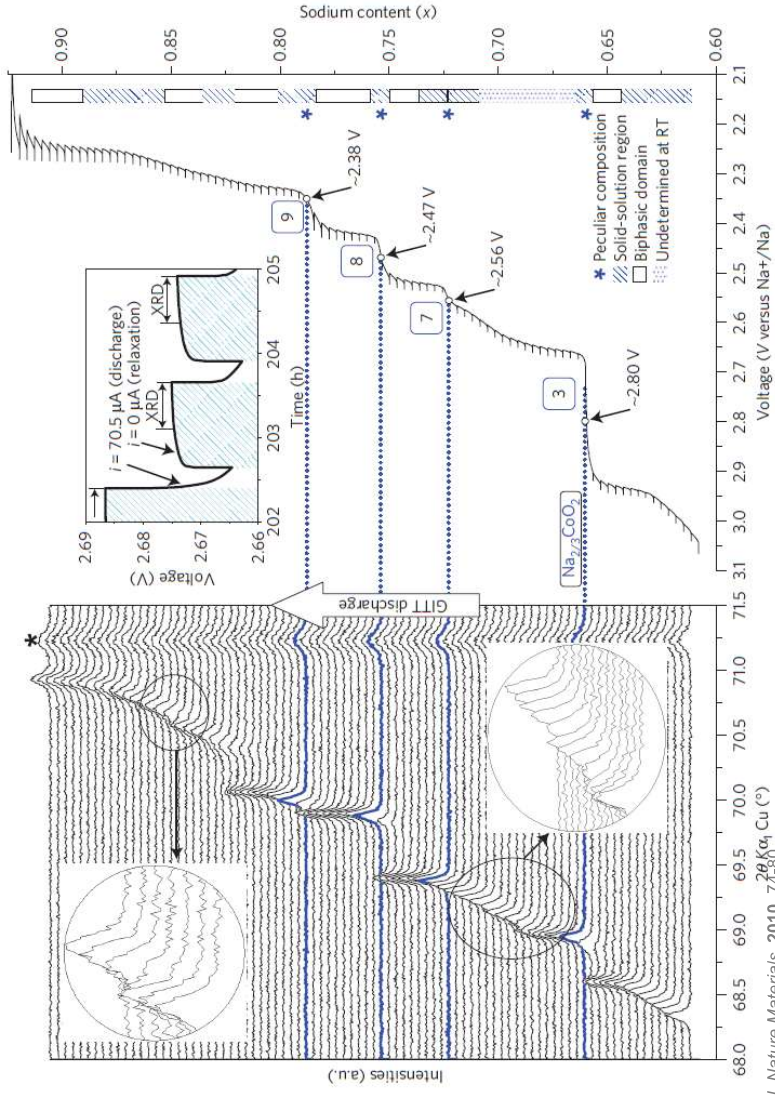# What can we learn from galvanostats?

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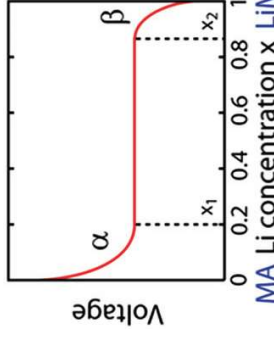
Ions can be continuously added/removed from the material without a structural transition

Two-phase region

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

Phase change

Abrupt voltage (and structure) change between α and β due to a more-stable γ phase with narrow composition window.
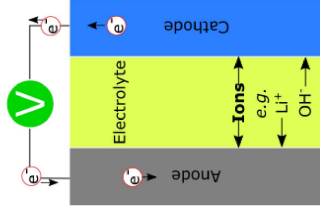
Example: Na$_x$CoO$_2$

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)

Charge

Discharge