Future Directions in Metal Ion battery Research

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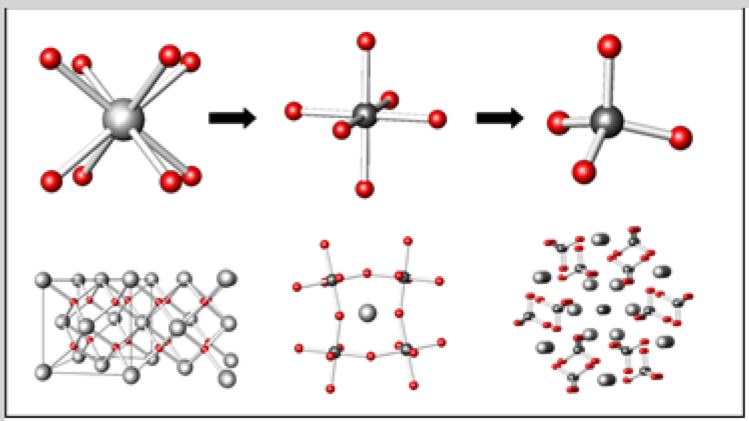


Solid State Chemistry Unit

Introduction

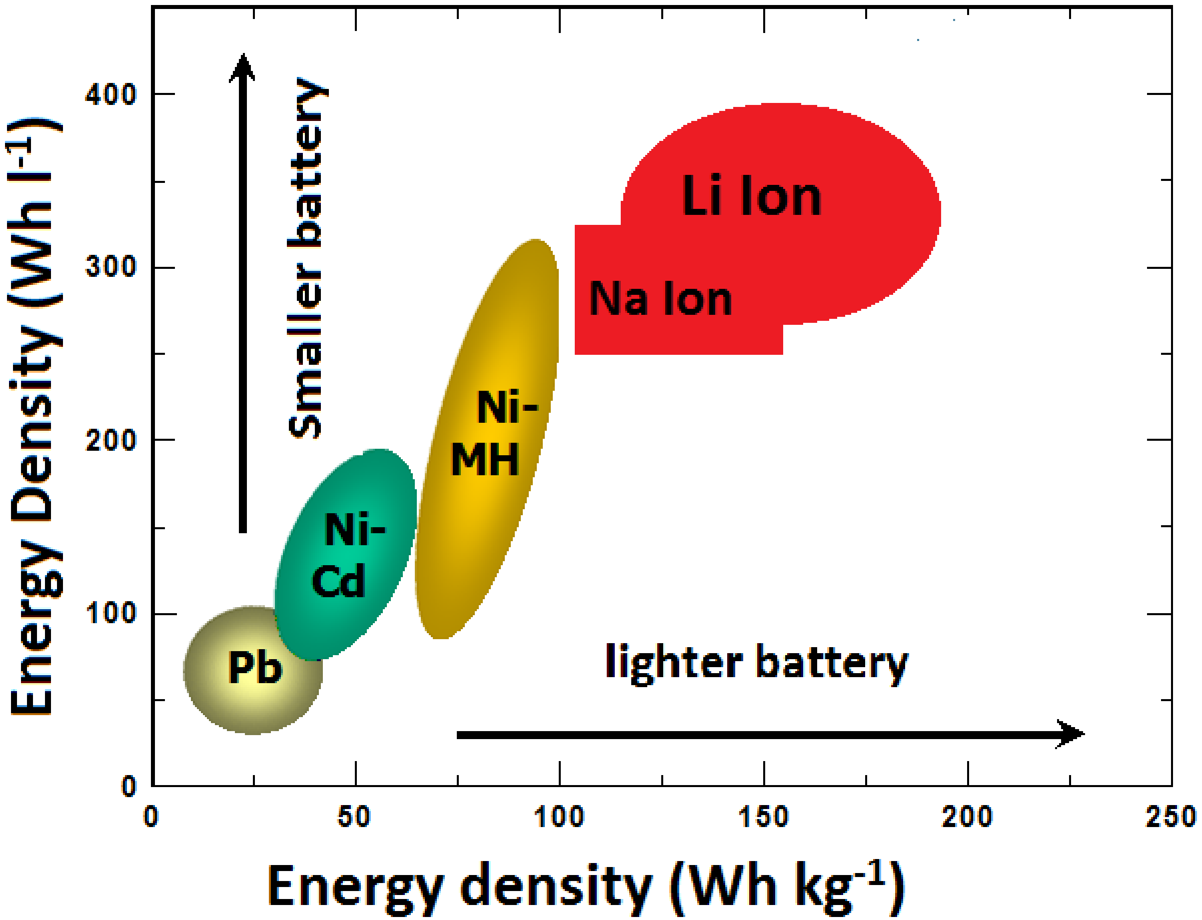
Growing Concerns regarding diminishing fuel reserves, and increasing greenhouse gas emissions

These concerns are driving research into cleaner energy technologies

In order to effectively utilise such technologies:-efficient electrical energy storage is vital:- **i.e. high power batteries.**

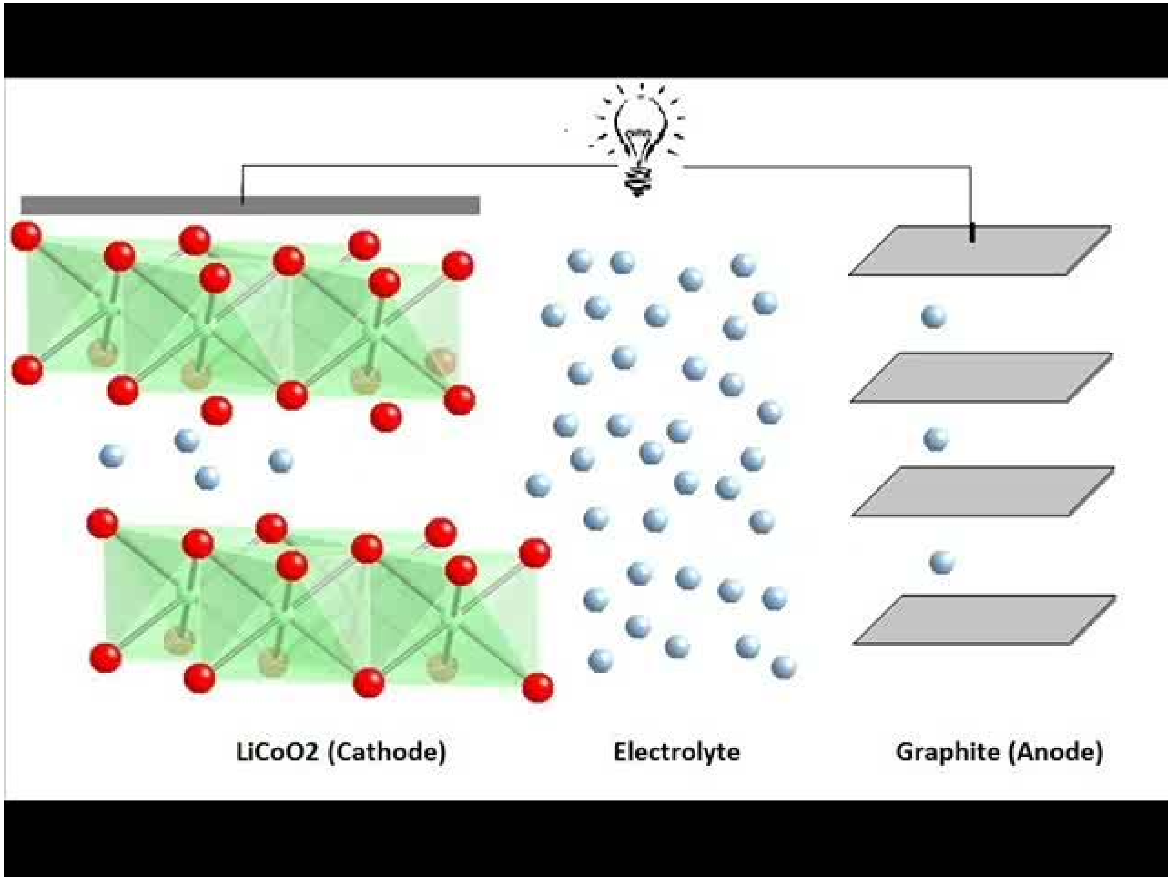
Battery technologies

Drive to develop smaller lighter weight batteries.



Li Ion Batteries: How they work

Small high power batteries:- applications in portable devices plus hybrid and all electric cars



Li ion Battery: Key Requirements

An ideal Li ion battery will have

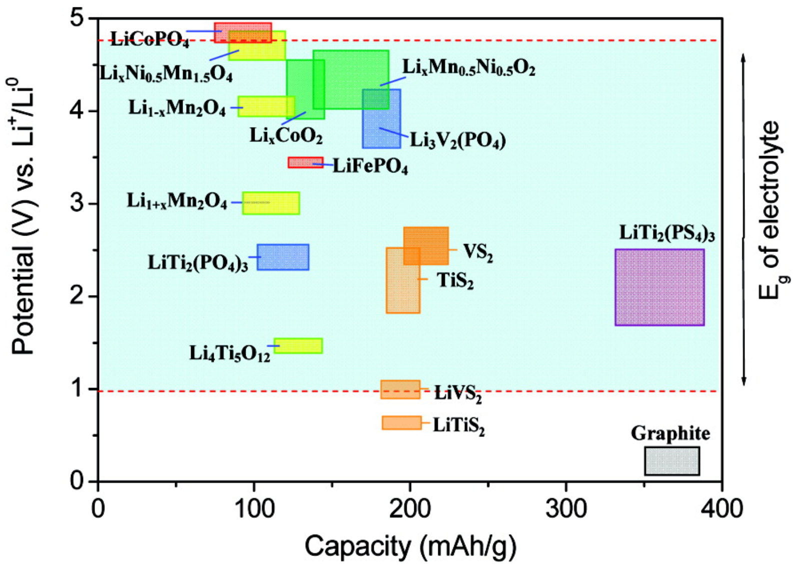
- High capacity
- Low weight, volume

High Energy Density

- Low cost
- Excellent safety:- non toxic materials, and safe operation
- High charge/discharge rates possible
- Long service life

Also perhaps most important
we need the anode and cathode
potentials to be within the stability
window of the electrolyte

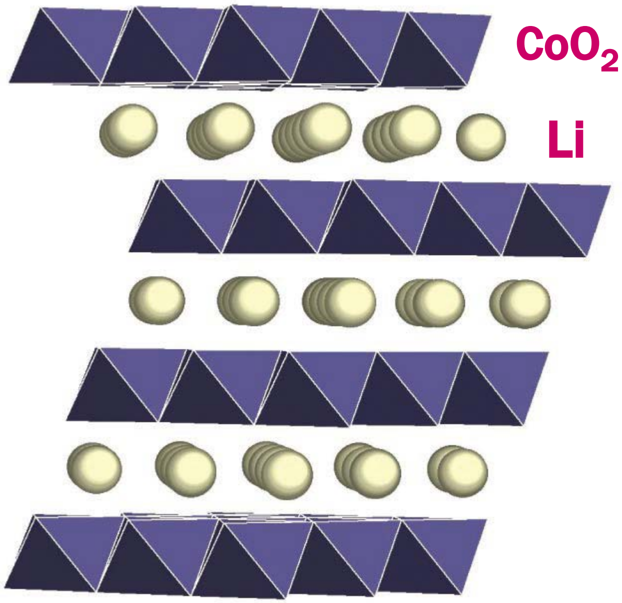
Can overcome this constraint
if a SEI layer develops
(blocks electron transfer
between electrode and electrolyte)



John B. Goodenough; Youngsik Kim; *Chem. Mater.* 2010, 22, 587-603

Lithium Ion battery cathode materials

The First commercial Lithium Ion battery Cathode Material was $LiCoO_2$, and this material (or a variant containing other transition metals, e.g. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$: NMC) is still most widely used



However, there are issues with this material; e.g. cost and toxicity of Co, capacity not high enough.

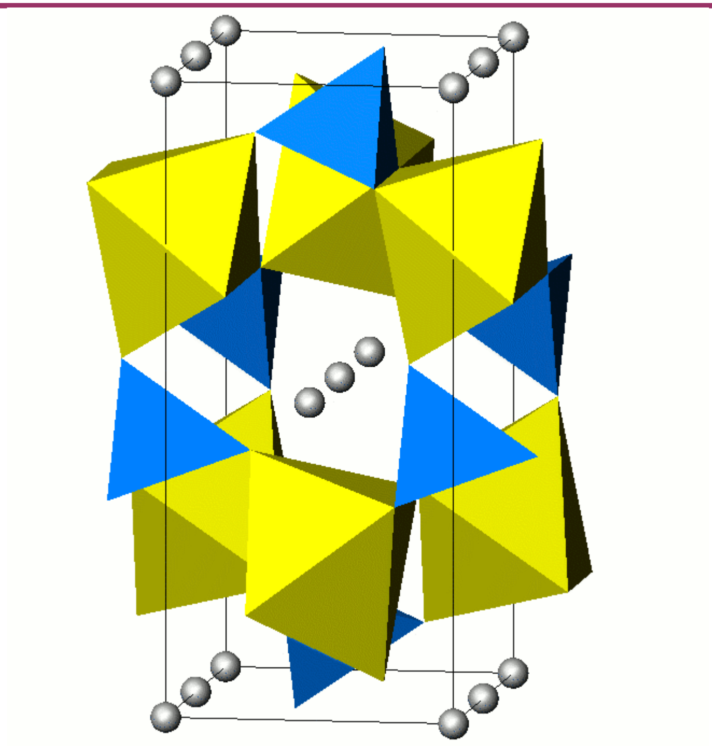
Newer Systems: Lithium Iron Phosphate

Large interest in Fe based cathode materials; e.g.

$LiFePO_4$

Li_2FeSiO_4

$LiFeSO_4F$



PO_4 tetrahedra (blue)
FeO_6 octahedra (yellow)

Lower cost raw materials, improved safety on rapid cycling; although typically higher cost to synthesise, and poor electronic conduction

Anode and Electrolyte Systems

Anode: commonly graphite, although growing interest in higher capacity anode materials

Key issues: understanding the SEI layer that forms

Electrolyte: typically a Li salt in an non-aqueous solvent

Key issues: flammability, stability (especially towards higher voltage cathode materials)

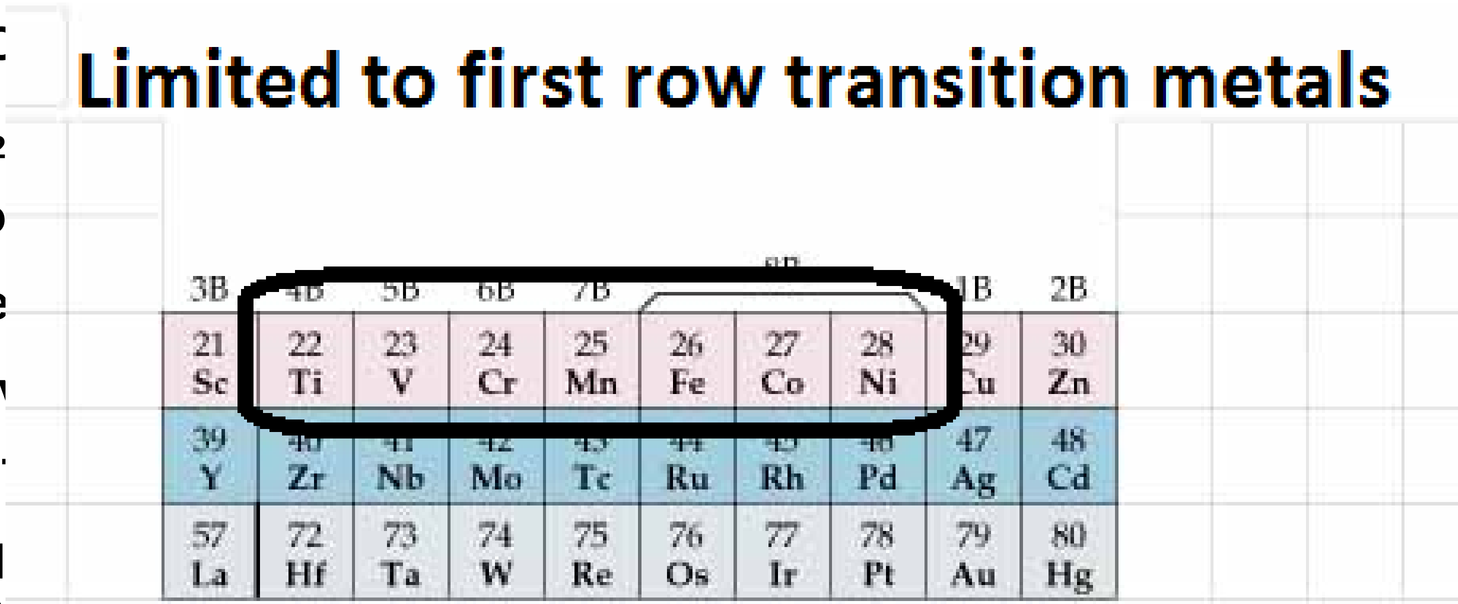
What determines the capacity ?

How can we work out the theoretical capacity of an electrode material ?

e.g. LiC

$LiCoO_2$

therefo



472 C

Charge

To conv

→(985.

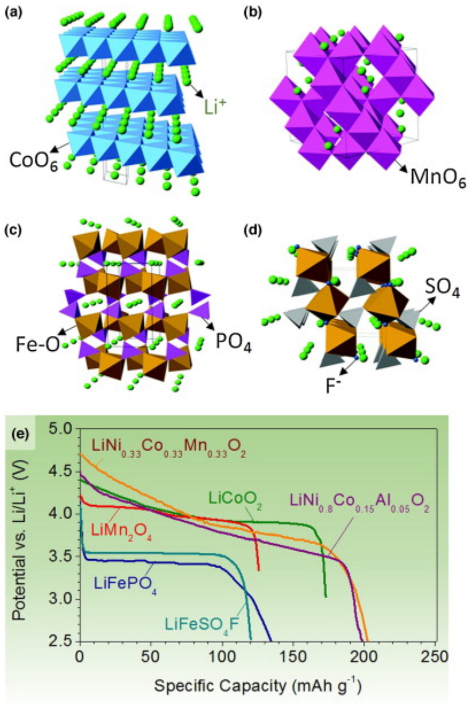
Typical **bility**
issues)

Thus capacity is determined by the amount of Li that can be reversibly intercalated/deintercalated and the weight of the material

Future targets (Cathodes)

How can we increase the capacity ?

Increase the amount of Li that can be reversibly intercalated/deintercalated



N. Nitta et al. : Materials Today 18, 2015, 252

Reduce the weight (e.g. reduce the amount of transition metal ?)

Exploiting Anion Redox Chemistry

Conventional materials reversibly intercalate/deintercalate Lithium through changes to the transition metal oxidation state

i.e. $Li(Co^{3+})O_2 \leftrightarrow Li_{1-x}(Co^{3+})_{1-x}(Co^{4+})_xO_2 + x\ Li^+ + x\ e^-$

$Li_{2-x}MnO_{3-x/2}$: Mn^{4+} : should not be an active cathode material

Research has shown activity in this material and related doped variants, e.g. $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$, $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$

→ high capacities (>200 Ah kg^{-1}): attributed to anion redox

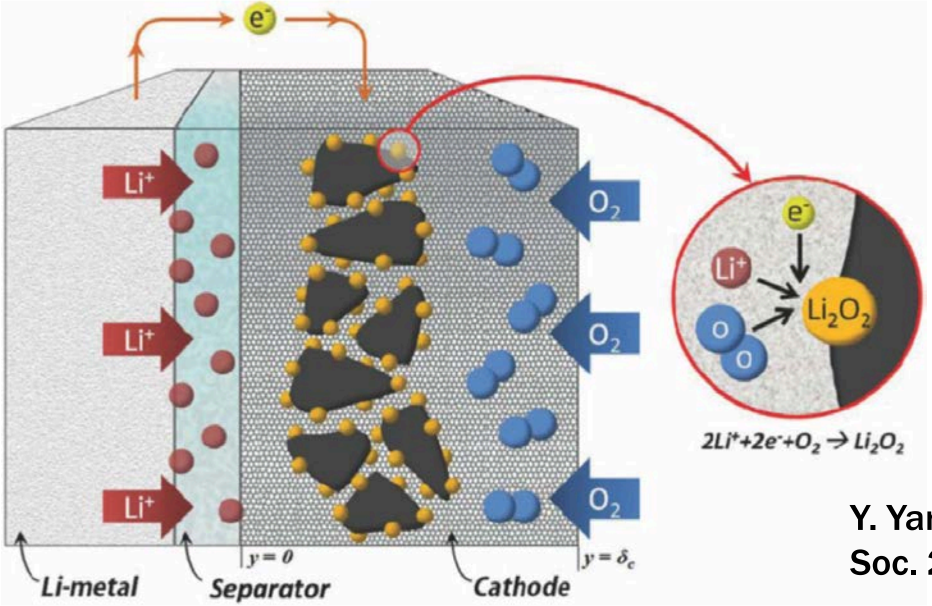
$Li_{1.2}Ti_{0.4}Mn^{4+}{}_{0.4}(O^{2-})_2 \leftrightarrow Li_{1.2-x}Ti_{0.4}Mn^{4+}{}_{0.4}(O^{2-})_{2-x}(O^{-})_x + x\ Li^+ + x\ e^-$

$Li\text{-}O_2$ battery

Can we eliminate the transition metal altogether ?

Li – oxygen (O_2) battery: This is commonly referred to by the somewhat misleading name: the Li-air battery

$2\ Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$ Anion redox ($O_2 + 2e^- \leftrightarrow O_2^{2-}$)



Y. Yang et al. : J. Electrochem. Soc. 2013, 160, A1847-A1855

- Benefits: high capacity- assuming the formation of Li_2O_2, the capacity is 1168 Ah kg^{-1} (8 times higher than that of $LiCoO_2$)
- Problems:
- Actually Li-O_2 , **NOT** Li-air, hence need to remove water, CO_2, and even N_2.
- Also need an electronic conducting matrix (to allow for electron transfer/removal)
- Issues with stability of the electrolyte (common electrolytes readily oxidised by the peroxide that forms).
- Need a Li containing anode (safety concerns if Li metal used).
- Needs to be open to the O_2 tank to allow O_2 in and out

Li- S battery

While O_2 is a gas, Sulphur is a solid, so the issues regarding needing an open battery to allow reversible gas intake/release can be avoided

Lithium-sulphur battery:- attracting significant interest

- Equivalent to Li-air, but with S in place of O
- Issues with solubility of LiS_x in common battery liquid electrolyte systems

Future Targets: Solid State Electrolytes

Issues with current liquid electrolytes: flammability, unstable towards higher voltage (>5 V) cathodes.

A lot of interest in new electrolytes:- polymer or **solid state** systems → **all solid state** batteries

Benefits: **Safety, higher voltage** cathodes useable, **cell simplification** (potential for the production of bipolar-type cells in which the cathode and anode of adjacent cells share the same current collector).

A further advantage of solid state batteries is their **low leakage currents**, which delivers other potential applications in terms of energy harvesting devices.

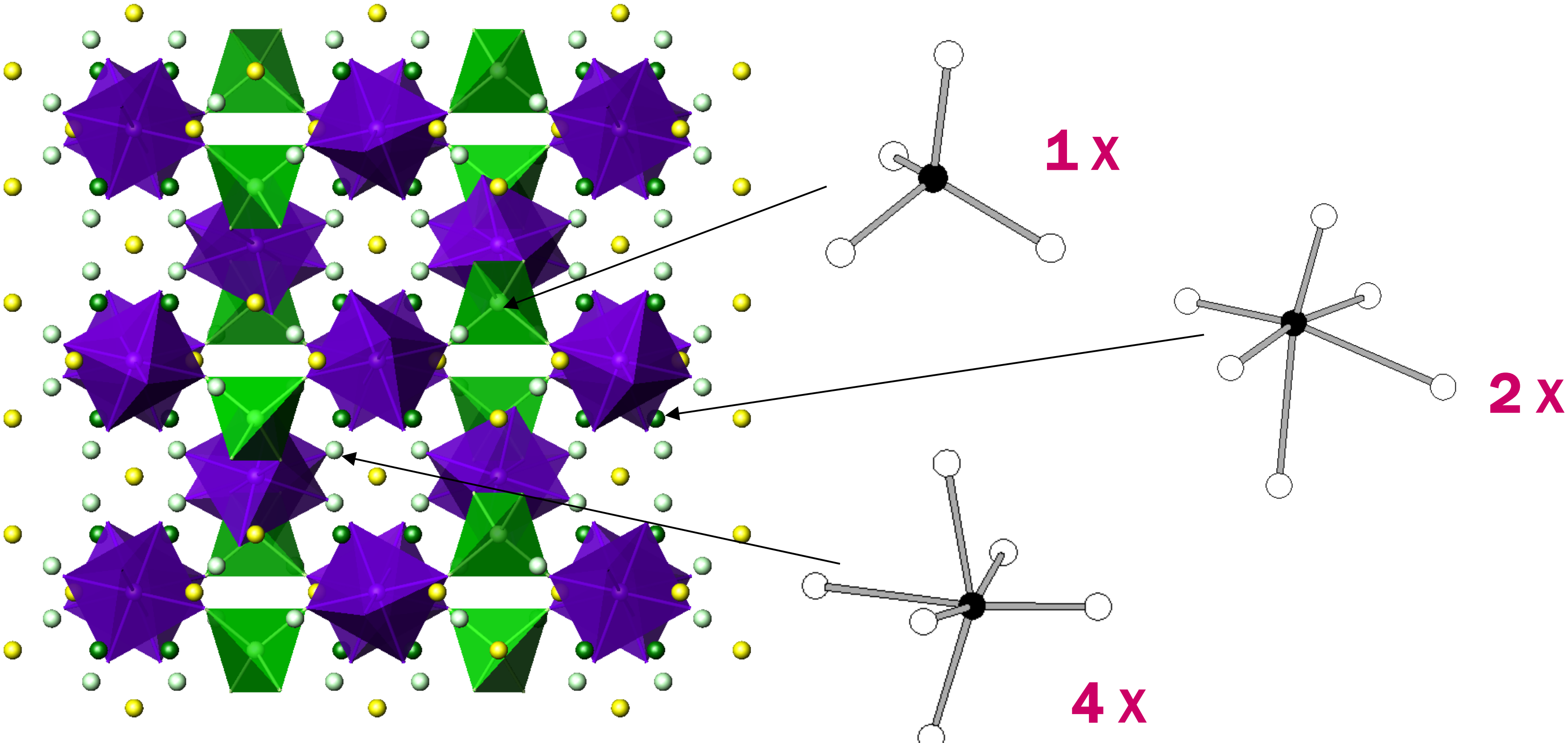
Future Targets: Solid State Electrolytes

Key requirements for an electrolyte material

- High Li ion conductivity ($>10^{-4}$ Scm^{-1})
- Low electronic conductivity ($<10^{-10}$ Scm^{-1})
- Chemical stability under operation
- Low cost and Safe materials (preferably non flammable)
- **Retention of electrode/electrolyte interface during cycling (volume changes)**

Garnet solid state electrolytes

Large interest in $La_3Zr_2Li_7O_{12}$, which possesses the garnet structure:- Three different Li sites filled in an ordered arrangement (low Li ion conductivity)

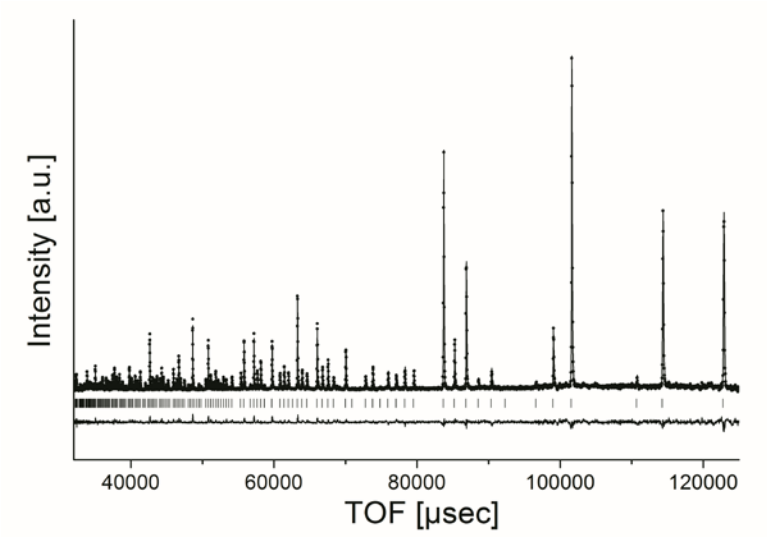


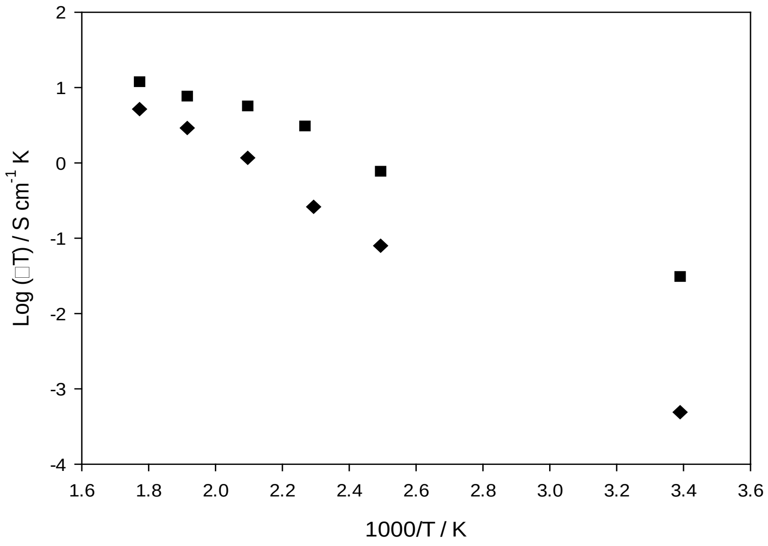
La: Yellow spheres

Optimisation of the conductivity

We can optimise the conductivity through doping studies, e.g.

Al, Ga doping





$La_3Zr_2Ga_{0.5}Li_{5.5}O_{12}$

Can also exchange Li^+ by H^+ → Fuel cell applications ?

Future targets (Anodes)

Graphite is a very good anode material, but it is limited to the incorporation of 1 Li per 6 C

There is therefore interest in alternative anode materials having higher capacities:- e.g. Silicon, Tin – much higher capacity, but do have problems due to the large volume change on Li incorporation and removal

Sodium Ion Batteries

Li ion batteries are too costly for stationary power applications (e.g. energy storage linked to renewables). For these applications, Na ion batteries are attracting interest (Na :- 4th most abundant element in earth's crust)

For the cathode, use Na analogues of Li ion battery materials, e.g. $NaFePO_4$, $Na_3V_2(PO_4)_3$, $NaFe(SO_4)_2$, $Na_{2+x}Fe_{2-y}(SO_4)_3$, Na_xMO_2 (M= 1st row transition metal)

For the Anode: **can't use graphite**, so current research into hard carbons and other anode materials

The key benefit of Na ion batteries is the much lower cost, while the limitations are in terms of slightly lower capacity (Na is heavier than Li), moisture sensitivity, slower cycling rates.

Nevertheless they have great potential for stationary power applications

Also interest in **K ion** batteries

Future Targets: Mg ion batteries

- Mg ion batteries
  - Higher capacity (two electrons per Mg)
  - However, significantly lower ionic conductivity
  - Current lack of suitable insertion electrode materials

Future Targets: Recycling

- Current Petrol/Diesel Cars have a target of ≈95% recyclability
- Need to develop methods to recycle the batteries in electric cars
  - Re-use in e.g. Stationary applications
  - Re-cycle/recover the materials :- currently (a) very difficult and (b) not cost-effective
  - Need for rational design of batteries to allow for easy recycling

Summary

- Li ion batteries a multibillion dollar industry
- Applications in cars → substantial increase in value of this industry
- Current key research issues: improved cell safety, improved cell capacity, improved cell cycling at rapid charge rates, battery recycling.
- For stationary power applications, Li ion batteries are too costly, and so other batteries, e.g. Na ion, are being targeted.