How Neutrons Benefit Next Generation Battery Systems.

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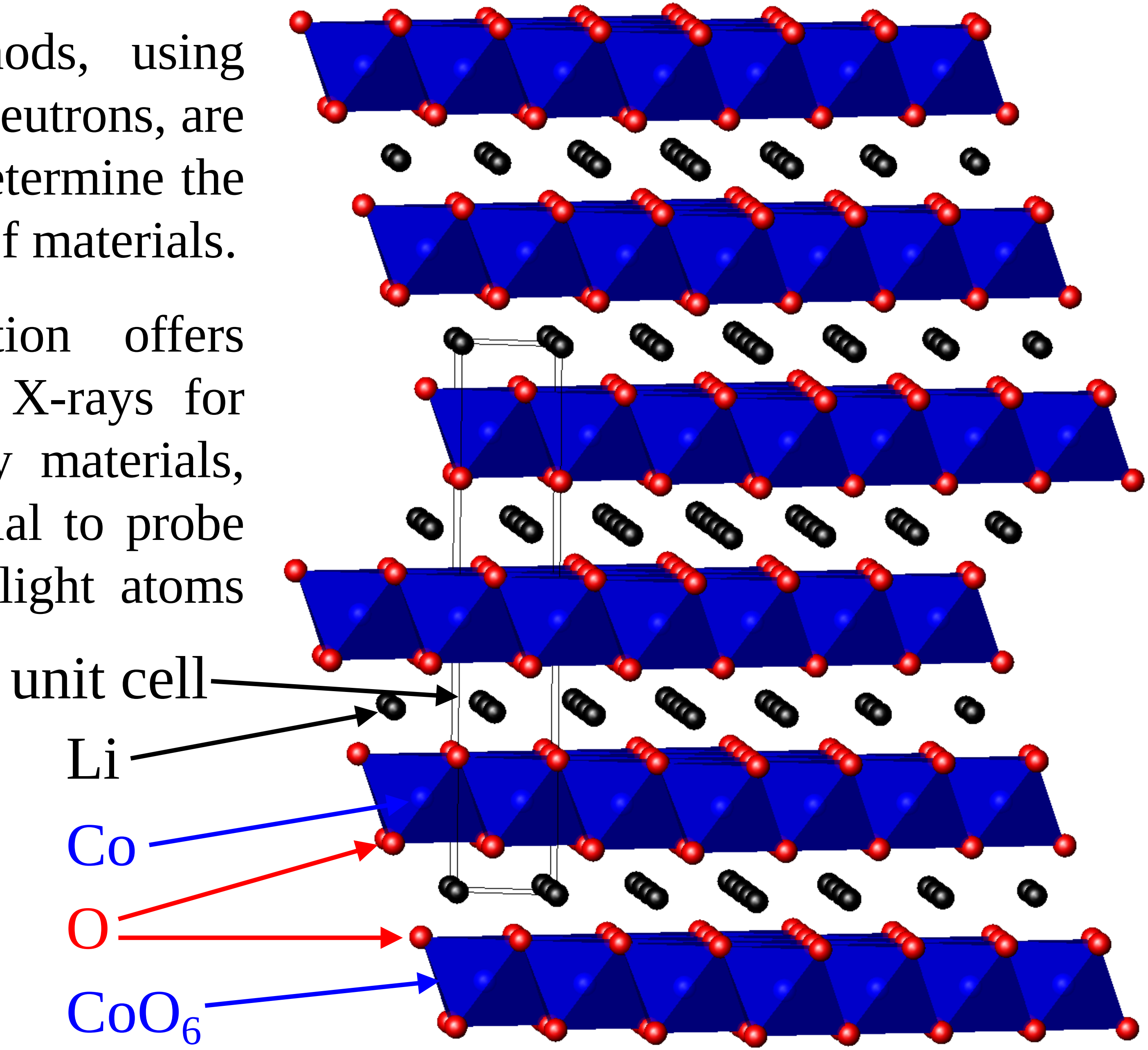
Talk will (briefly) cover.....

- Introduction to neutron diffraction.
- Current battery materials. } What neutrons can (and hopefully will) do.
- Future battery materials.

THE DIFFRACTION TECHNIQUE

Diffraction methods, using either X-rays or neutrons, are widely used to determine the crystal structure of materials.

Neutron diffraction offers advantages over X-rays for studies of energy materials, since it is essential to probe the locations of light atoms such as H, Li, O, *etc*.

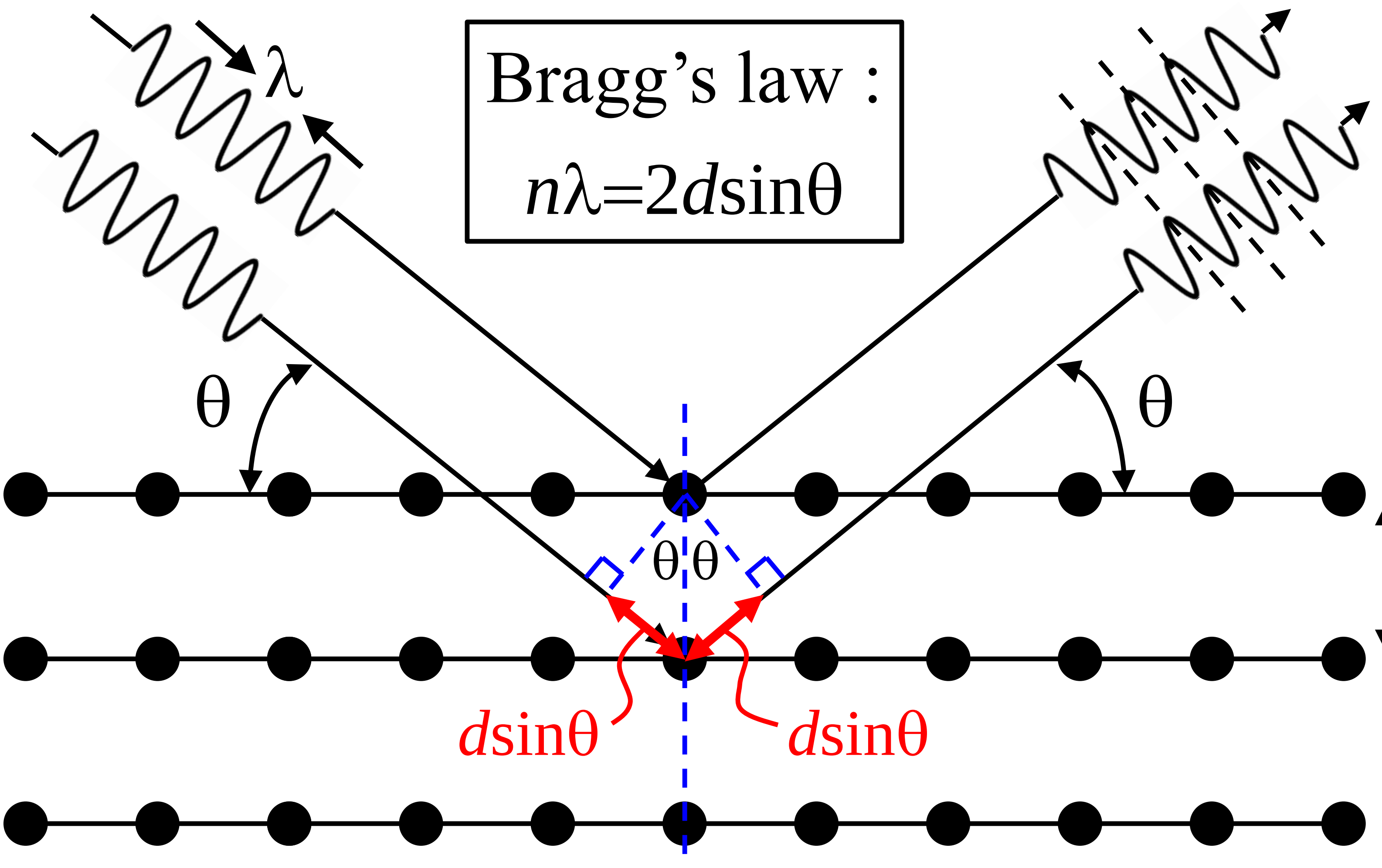


Lithium battery cathode material $LiCoO_2$.

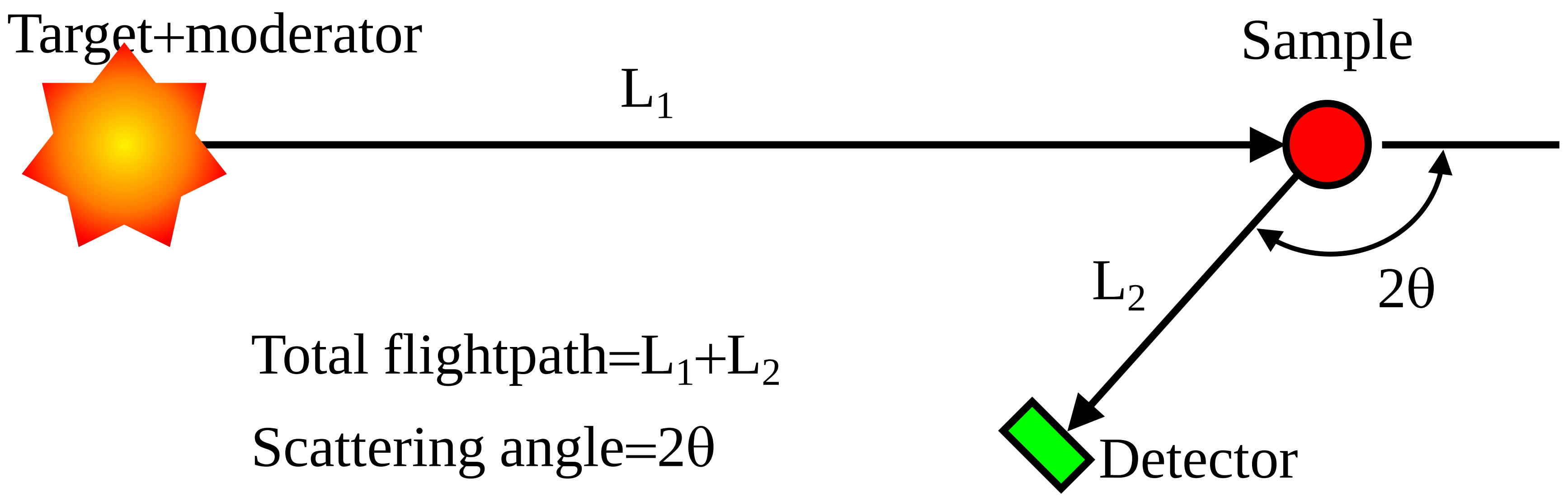
BRAGG'S LAW OF DIFFRACTION

Planes of atoms of separation *d*.

Neutrons of wavelength λ, at incident angle θ.



POWDER DIFFRACTION AT A PULSED SOURCE



Total flightpath=L_1+L_2

Scattering angle=2θ

Measure time, *t*, taken by neutron to travel source to sample to detector

$\Rightarrow$ velocity, $v=(L_1+L_2)/t$ $\Rightarrow$ energy, $E=\frac{1}{2}mv^2$, *m* is the neutron's mass.

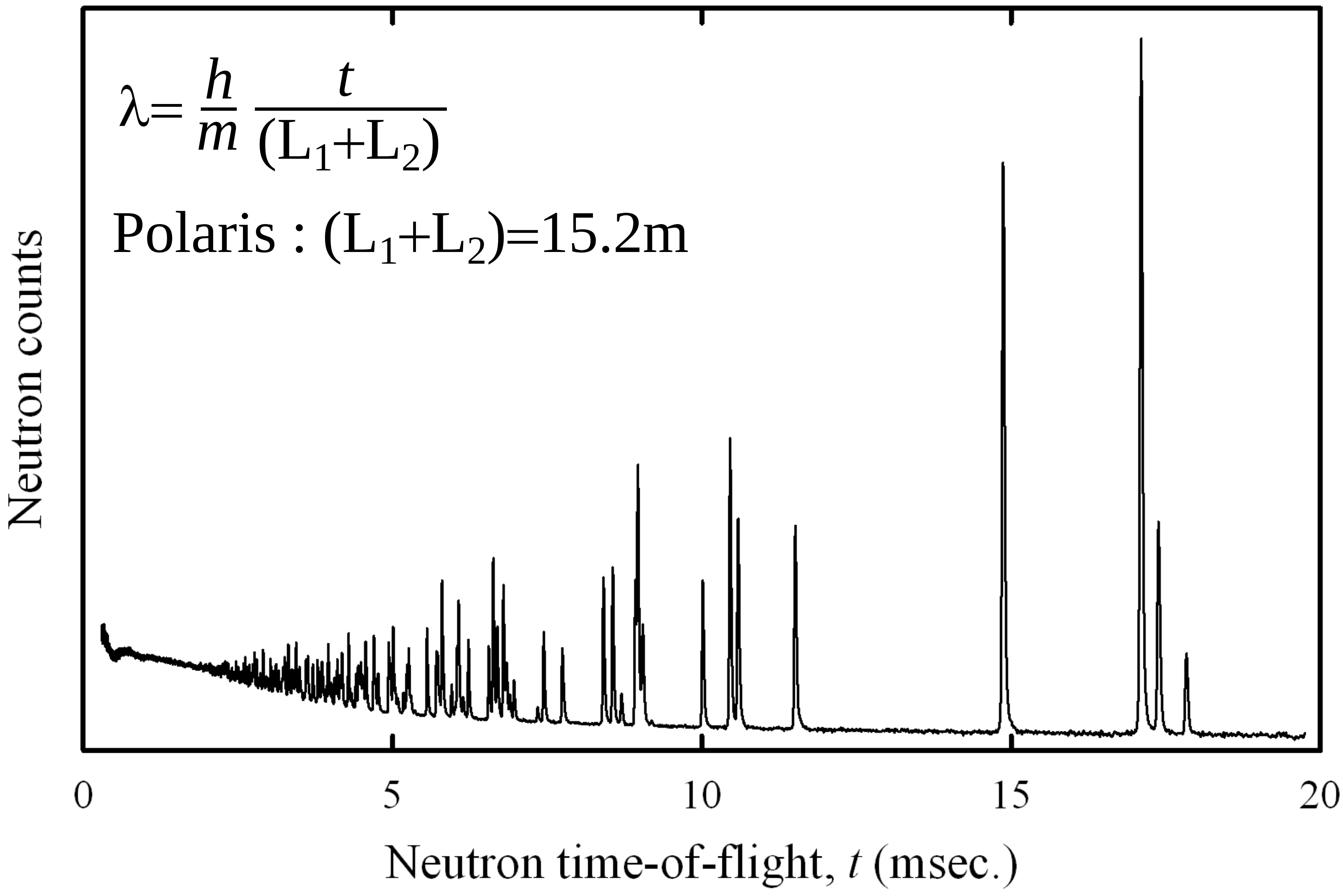
Also, energy, $E= h^2/2m\lambda^2$, where *h* is Planck's constant.

$$\Rightarrow \lambda=\frac{h}{m}\frac{t}{(L_1+L_2)} \qquad \text{Bragg's law : } d=\frac{\lambda}{2\sin\theta}$$

Measure diffraction pattern at fixed 2θ (*c.f.* reactor source).

TIME-OF-FLIGHT POWDER DIFFRACTION

Example : $LiCoO_2$ cathode material, data from Polaris at ISIS.....



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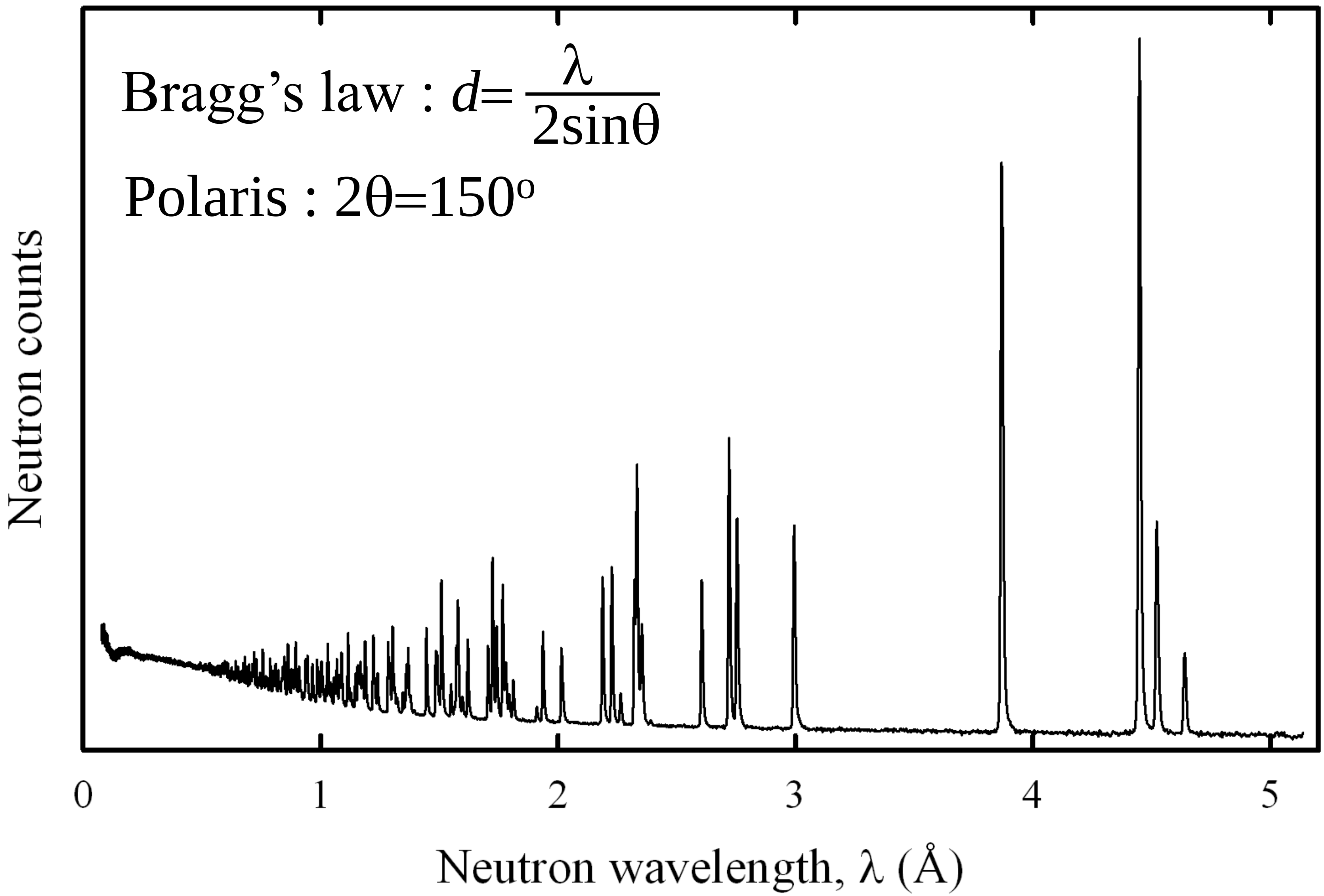

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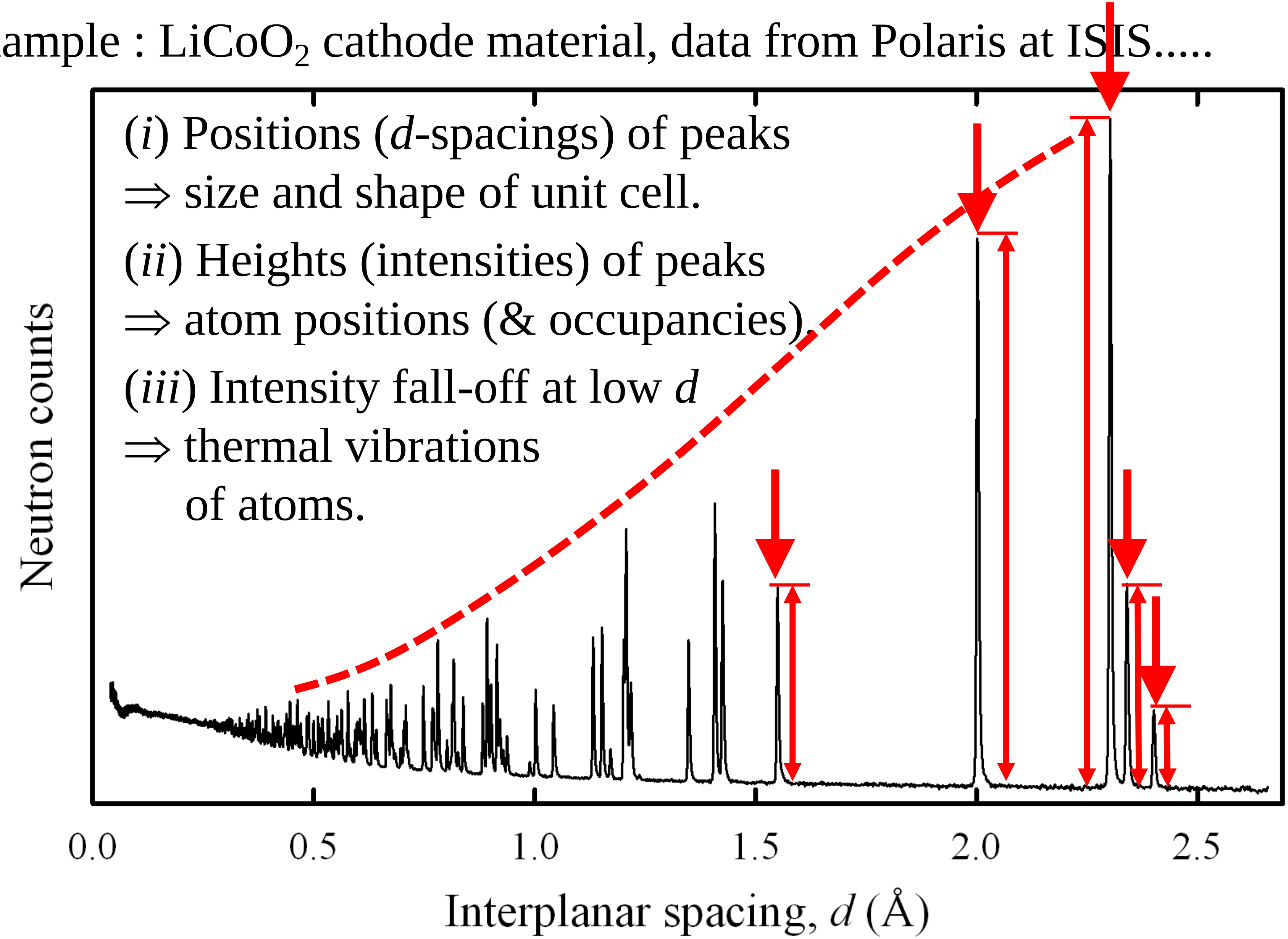
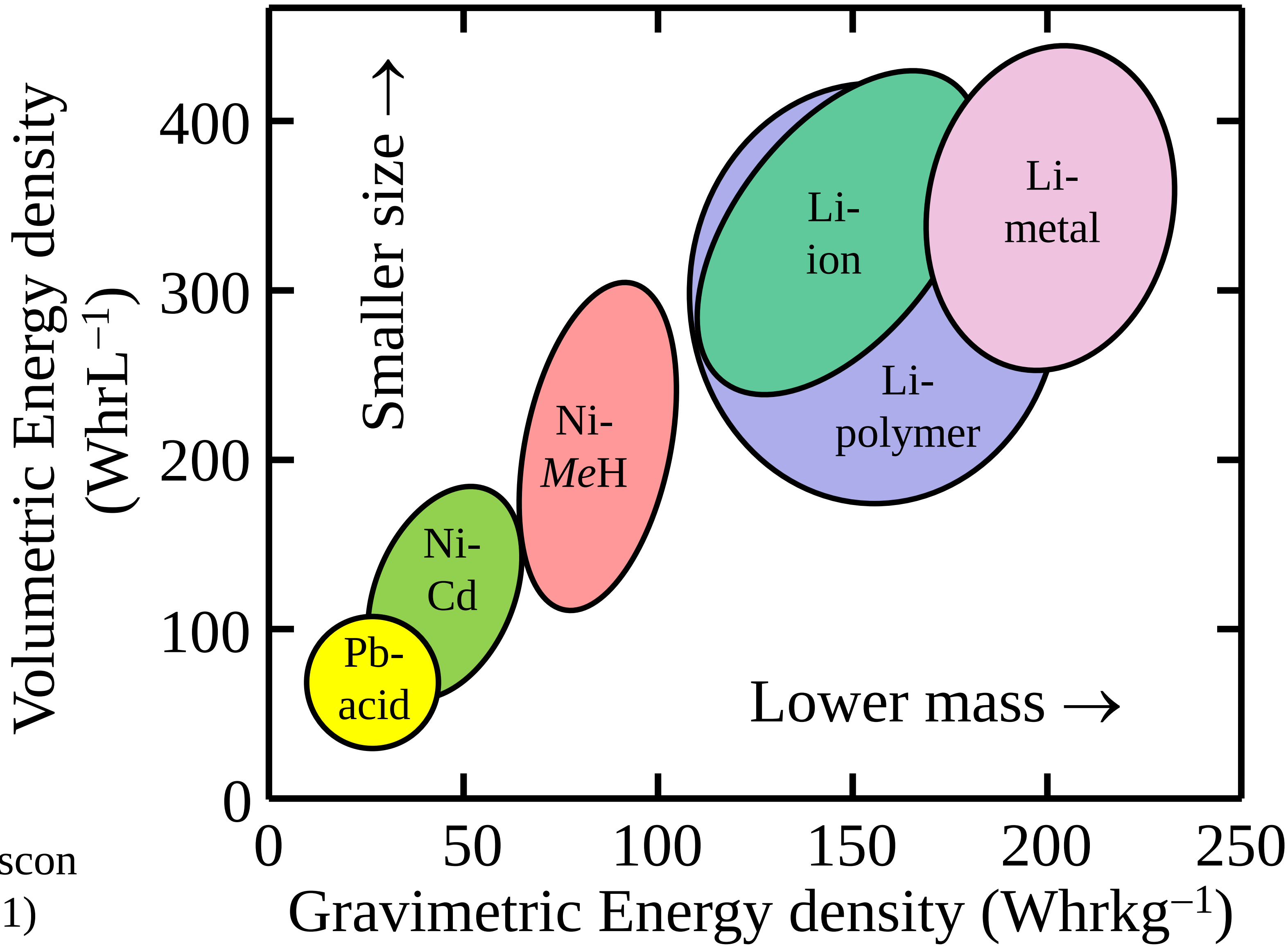
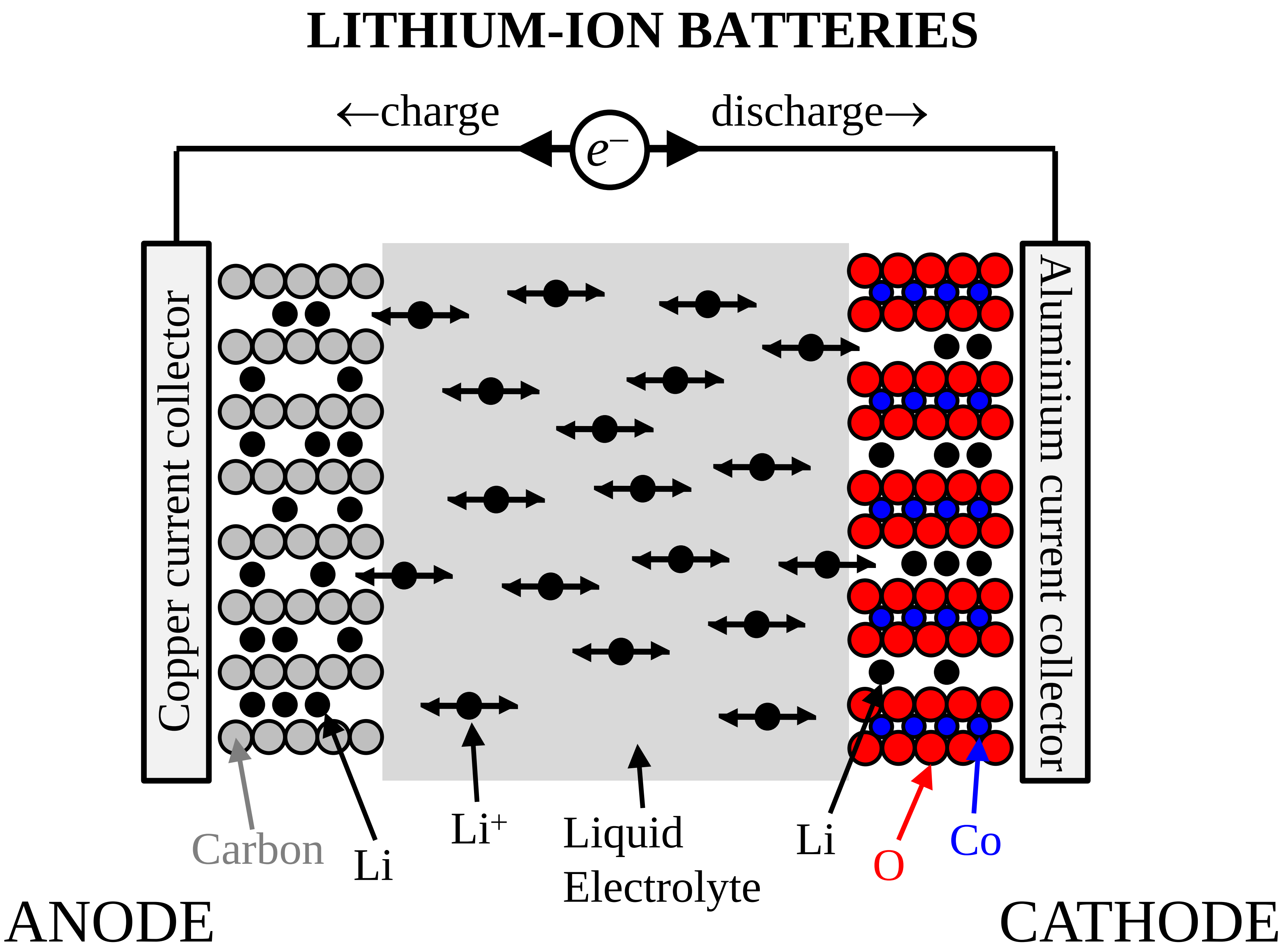


RECHARGEABLE BATTERIES

Currently, the major focus of research is on lithium batteries.



Tarascon (2001)


LITHIUM-ION BATTERIES
←charge
e⁻
discharge→
Copper current collector
Aluminium current collector
Carbon
Li
Li+
Liquid Electrolyte
Li
O
Co
ANODE
CATHODE

LITHIUM-ION BATTERIES

Increasing demand for new, high capacity, lightweight, batteries.

Faraday Challenge - £246M on battery development for electric cars.

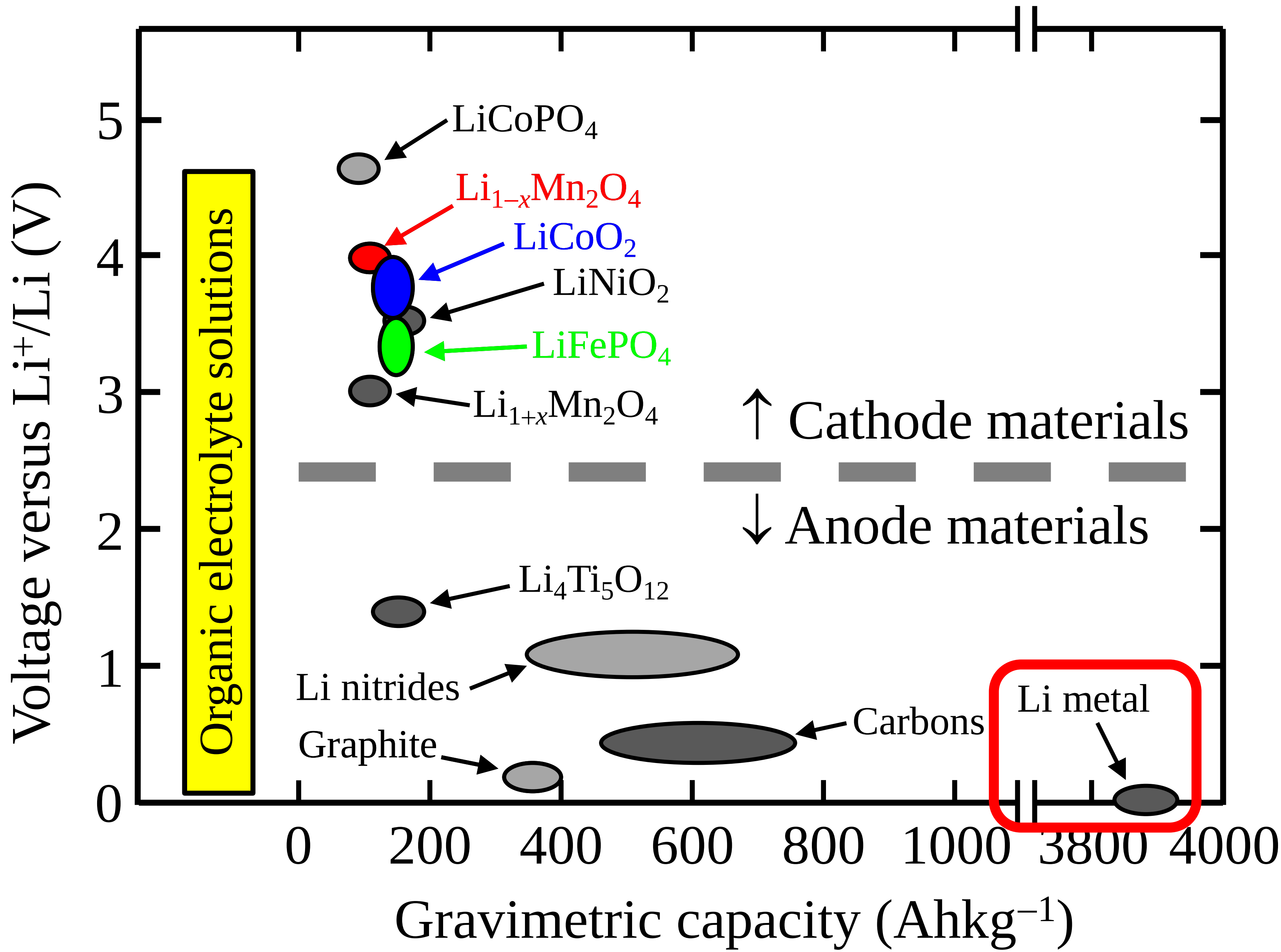
There are a number of issues to be addres

- Relatively low capacity ⇒ limited rang
- Relatively long charge times.
- Safety concerns (*e.g.* fires).
- Capacity fade on repeated charge-disch
- Environmental impact (*e.g.* recyclability
- Availability/distribution of lithium reser

.....and others.

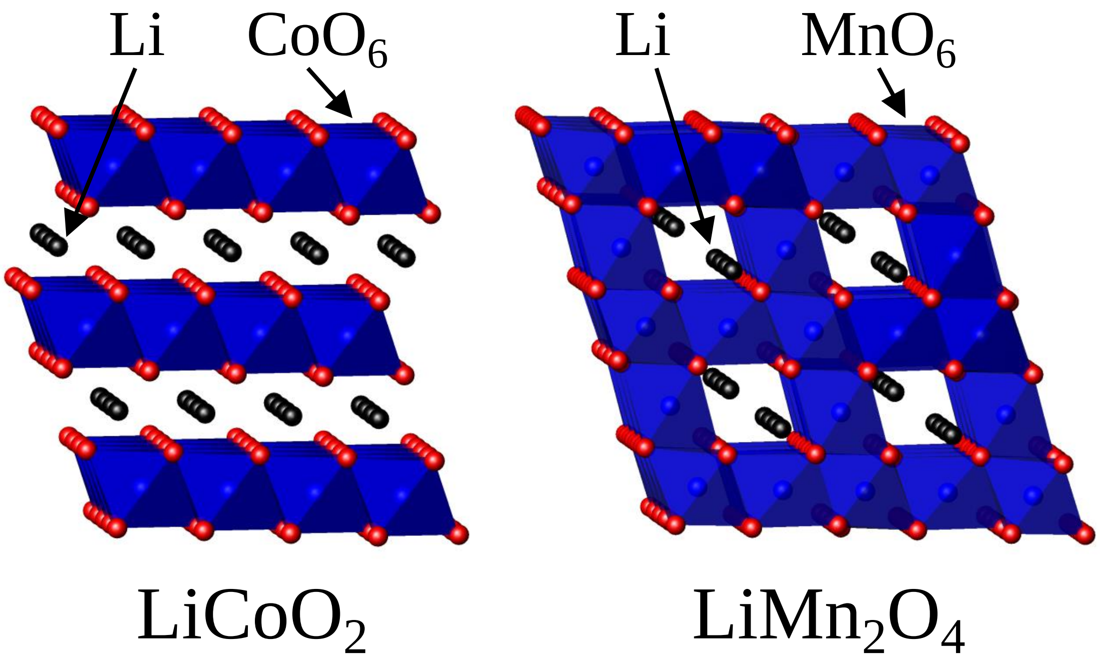
⇒ Essential to optimise performance of current materials and identify new candidate compounds for future battery systems.

LITHIUM-ION BATTERIES



CATHODE MATERIALS

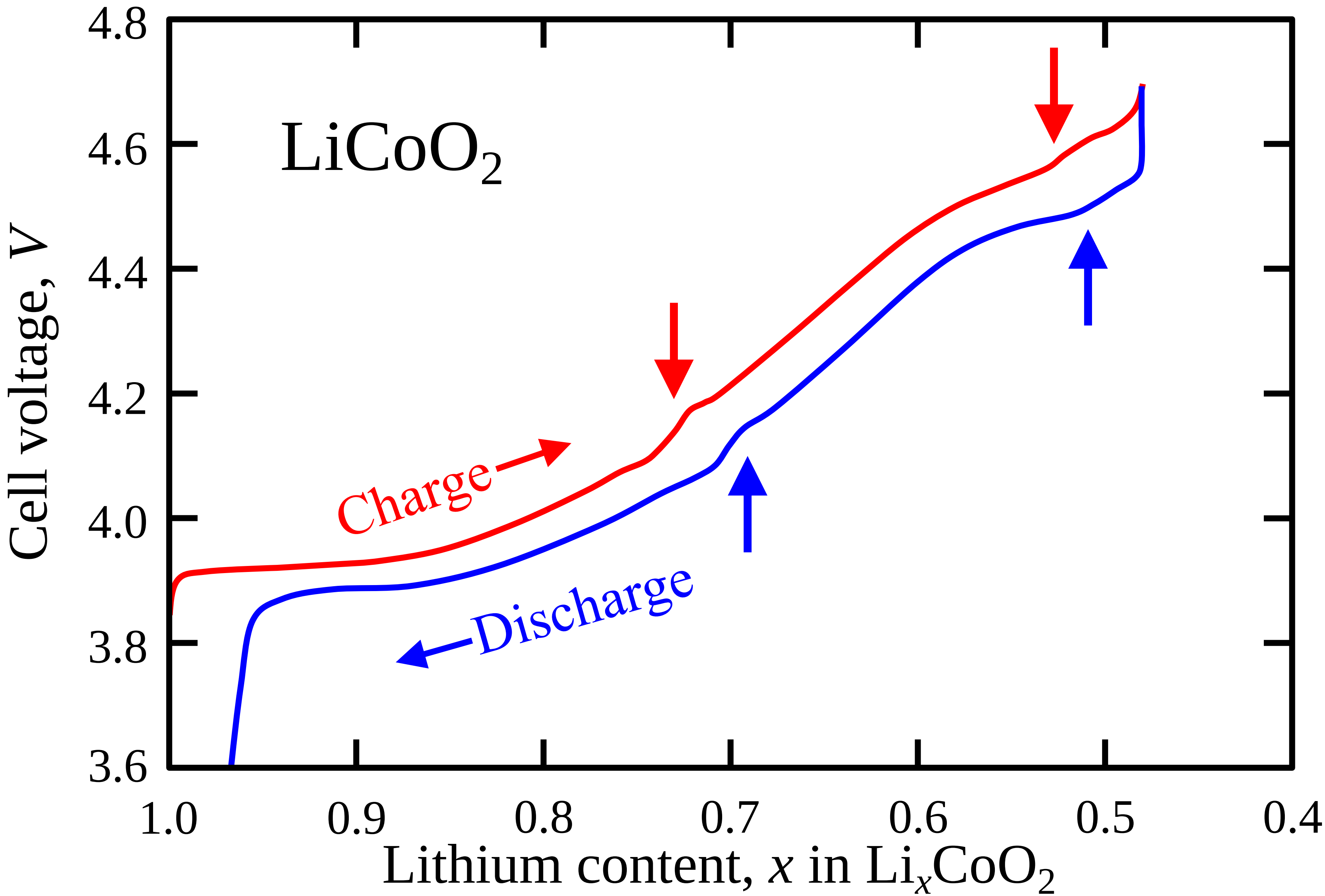
At present, three compounds (and their derivatives) have found commercial application as cathodes within lithium-ion batteries.....



From a crystal structure point-of-view, ease of lithium removal/ insertion is facilitated by Li layers ($LiCoO_2$) or Li channels ($LiMn_2O_4$ and $LiFePO_4$).

But it is not that simple.....

VOLTAGE PROFILES

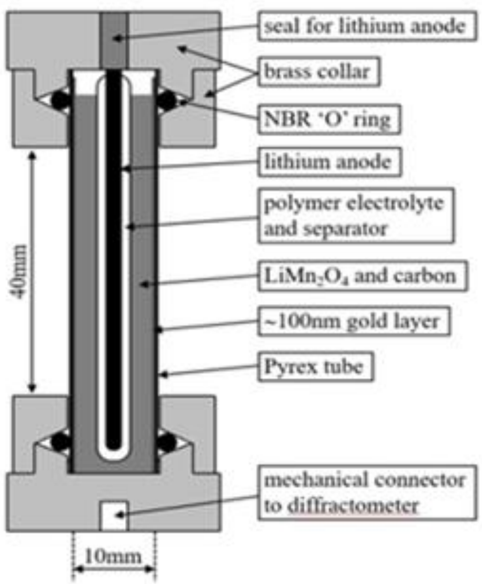


⇒ need (neutron) diffraction to study this behaviour.....

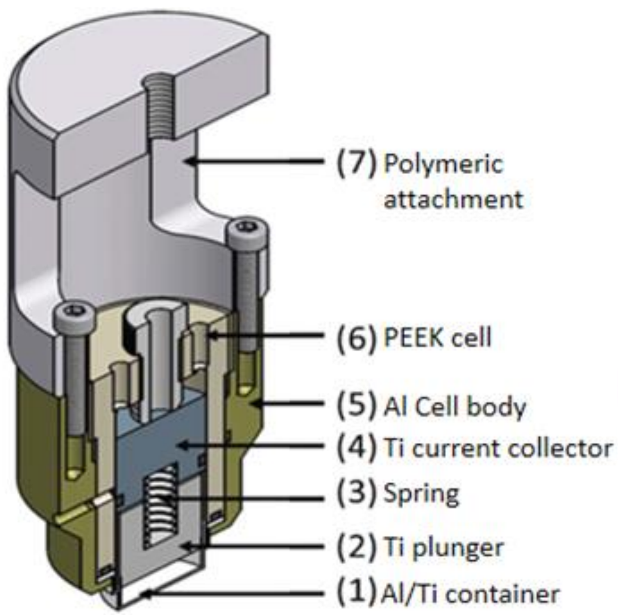
IN-SITU ELECTROCHEMICAL CELLS

Traditionally, neutron diffraction studies of battery materials were performed ex-situ on samples removed from batteries.

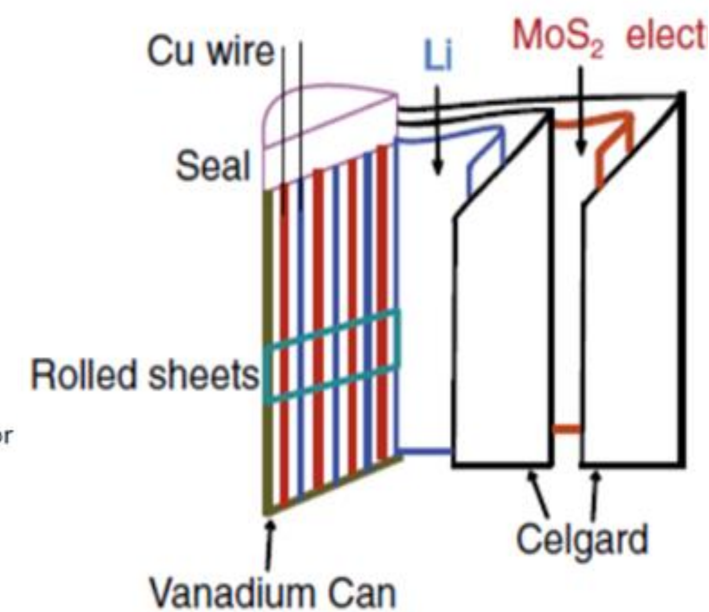
Today, almost all neutron facilities in the world have a programme to develop in-situ electrochemical cells for time-resolved neutron diffraction studies of battery materials during charge / discharge.....



Bergström *et al* (1998)



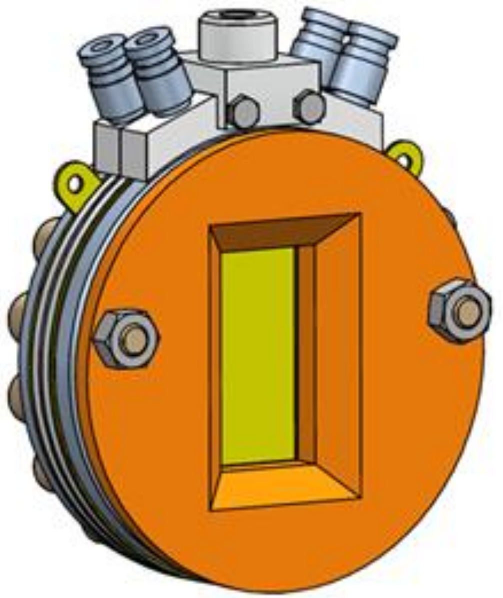
Novák *et al* (2013)

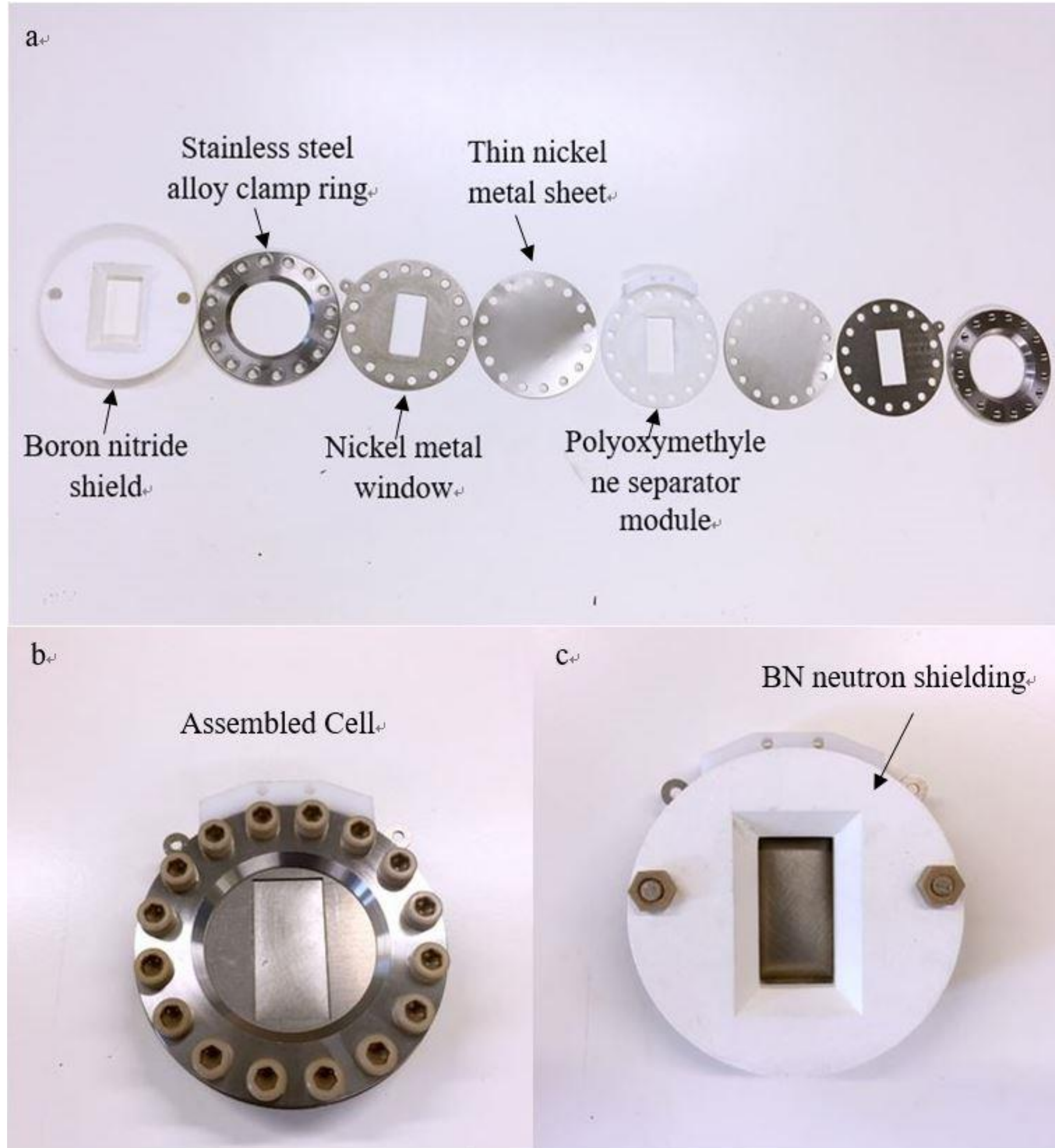


Sharma *et al* (2011)

At ISIS, we exploit the advantage of fixed scattering geometry.....

IN-SITU ELECTROCHEMICAL CELLS





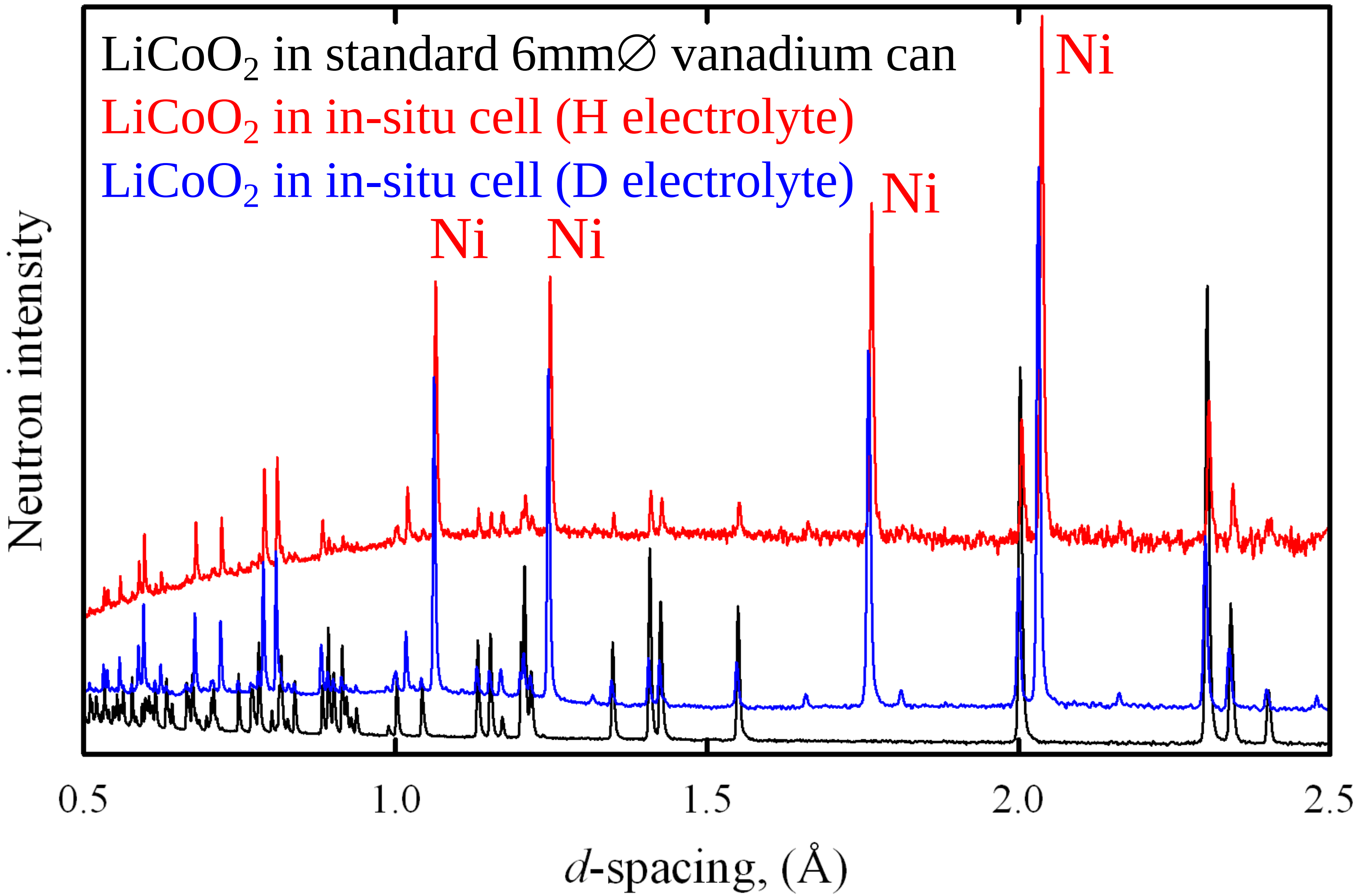
Modular in-situ ‘coin cell’, designed as part of collaborative project with Sheffield and Stockholm Universities.

Used to study Ni-Me-H and Li battery systems.

Dong *et al* (2018).

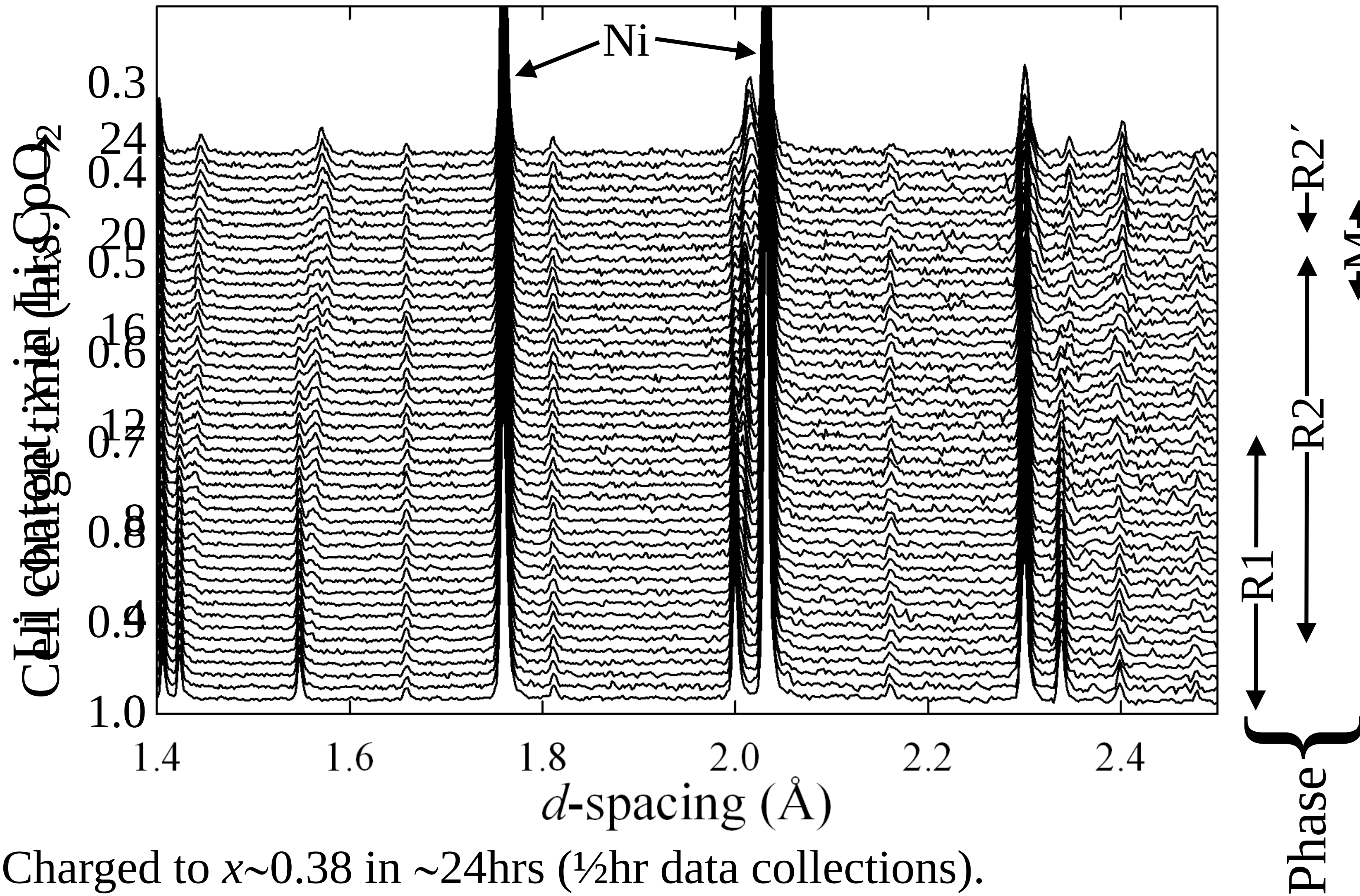
IN-SITU ELECTROCHEMICAL CELLS

Quality of diffraction data collected using an in-situ cell.....



IN-SITU ELECTROCHEMICAL CELLS

Example of Li_xCoO_2 studied on Polaris diffractometer at ISIS.....



Charged to *x*~0.38 in ~24hrs (½hr data collections).

IN-SITU ELECTROCHEMICAL CELLS

Challenge with the design of in-situ electrochemical cells is to study the material under conditions that mimic those found in the real battery.

So why not just use a real battery?

(*i*) Current neutron fluxes require ~½g of material to be used in an in-situ cell, ~10^2-10^3× more than in a commercial coin cell.

(*ii*) Even so, it typically takes ~30mins to collect a diffraction pattern of good statistical quality, so can't study fast charge processes.

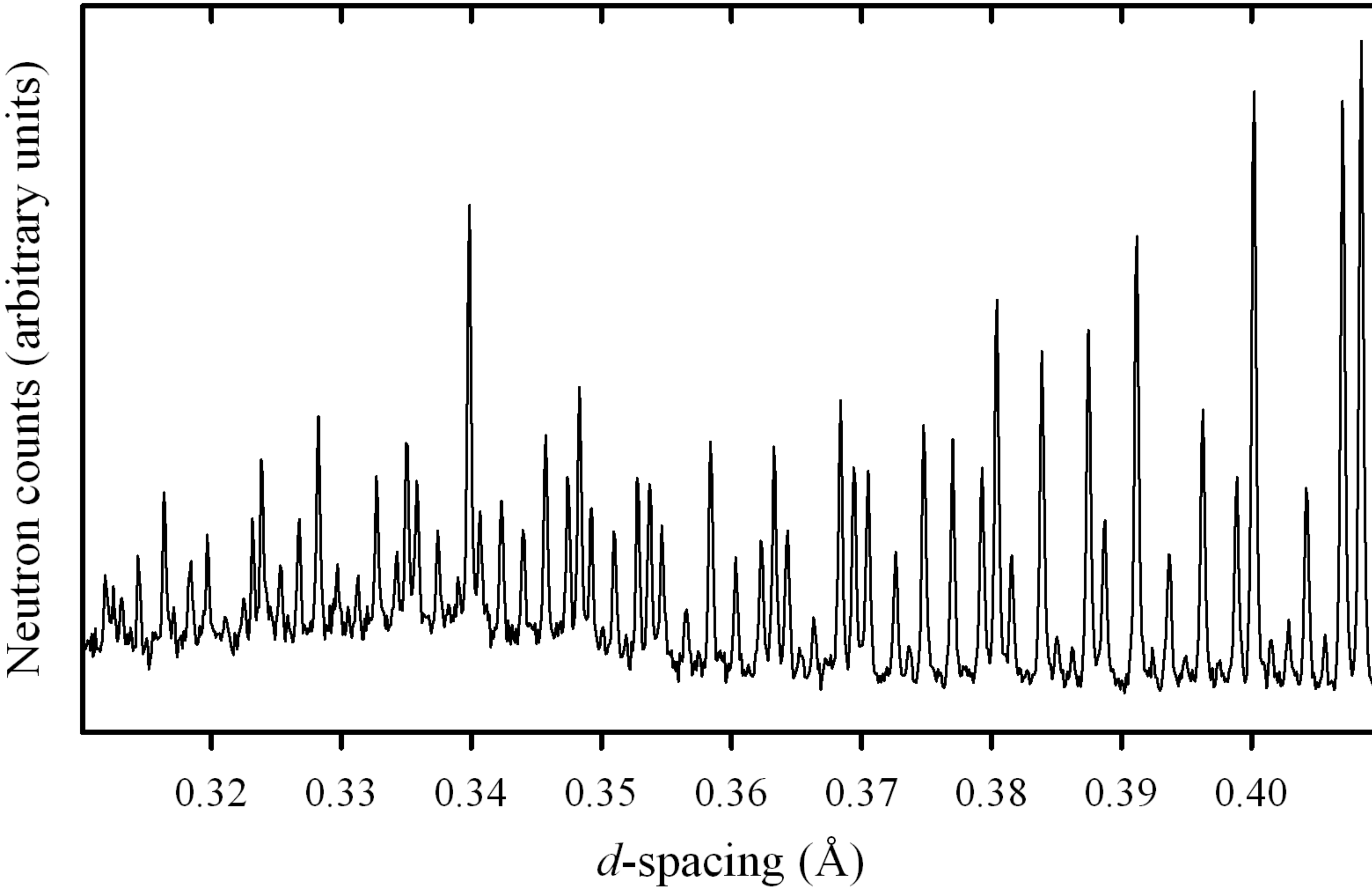
⇒ need higher neutron flux.

(*iii*) Commercial cells are constructed of many different materials, which will give a complicated diffraction pattern.

⇒ need Δ*d*/*d* resolution as well!

HIGH RESOLUTION POWDER DIFFRACTION

Demonstration of high Δ*d*/*d* resolution at low *d*-spacings.....



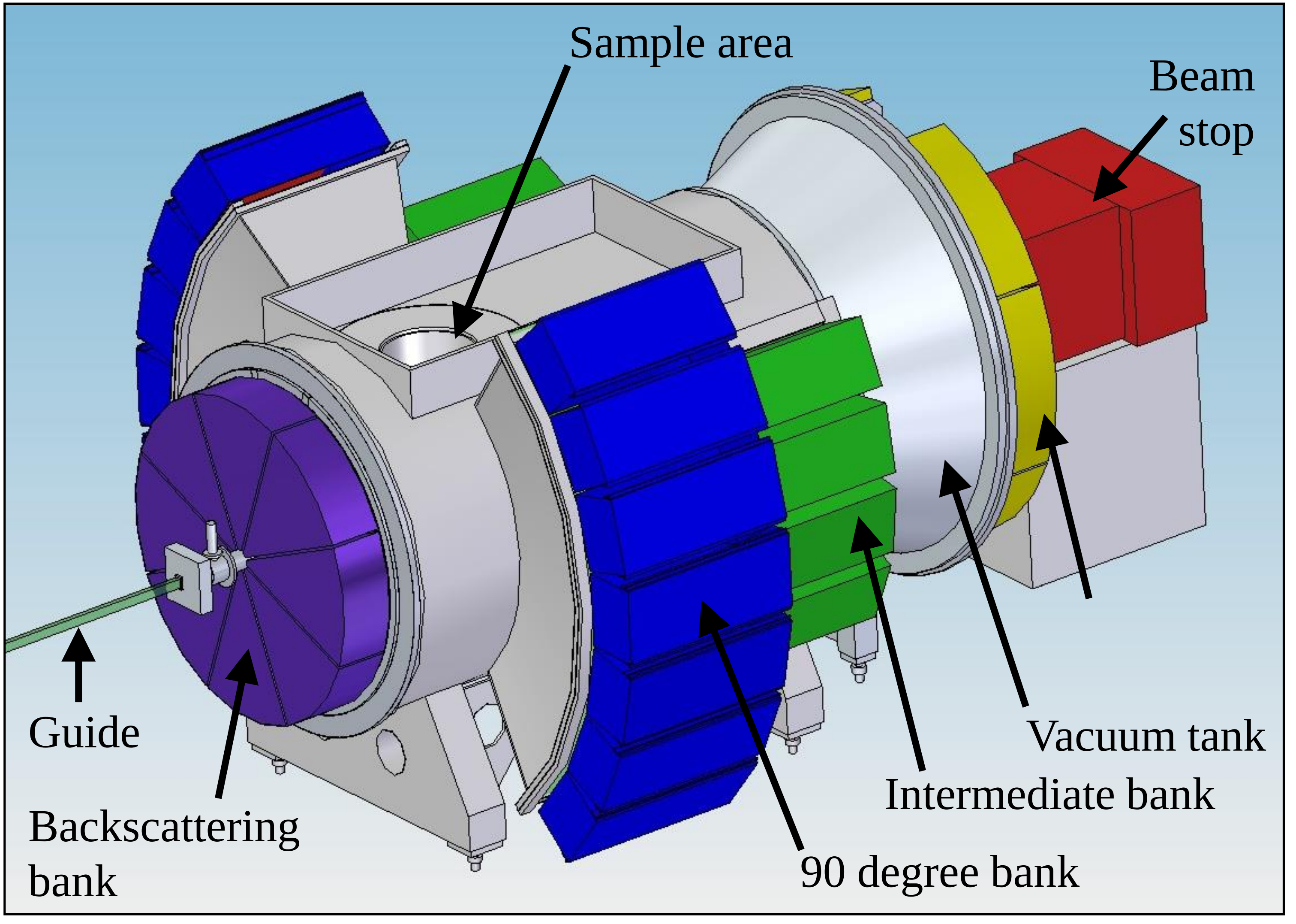
HIGH RESOLUTION POWDER DIFFRACTION

The High Resolution Powder Diffractometer, HRPD, at ISIS is one the highest resolution powder diffractometers in the world.

But doesn’t currently have sufficient countrate for in-situ studies.

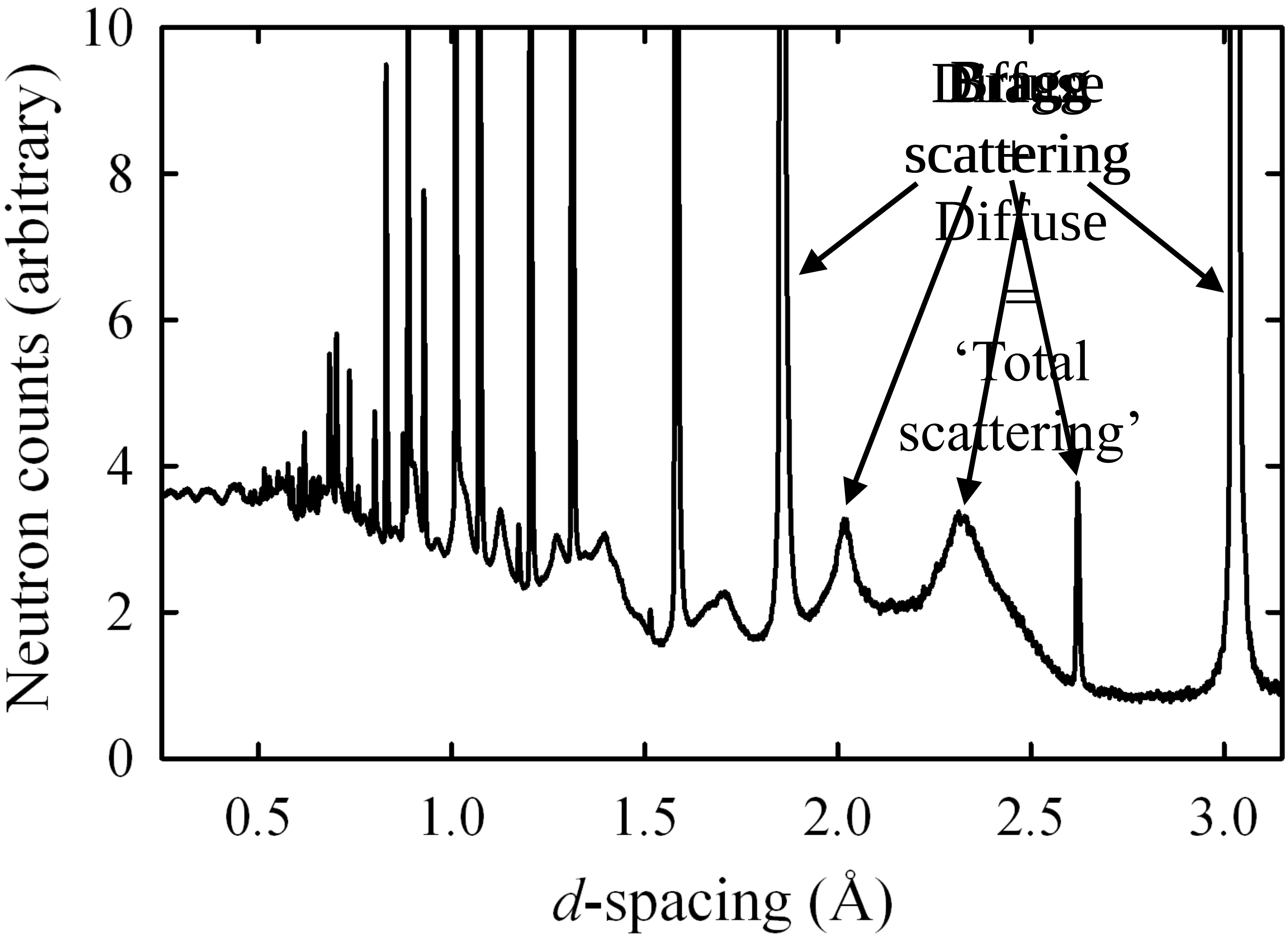
HIGH RESOLUTION POWDER DIFFRACTION

Planned HRPD upgrade to maximize countrate at high $\Delta d/d$ resolution.



But low background & wide range of *d*-spacing (λ, E) also important.....

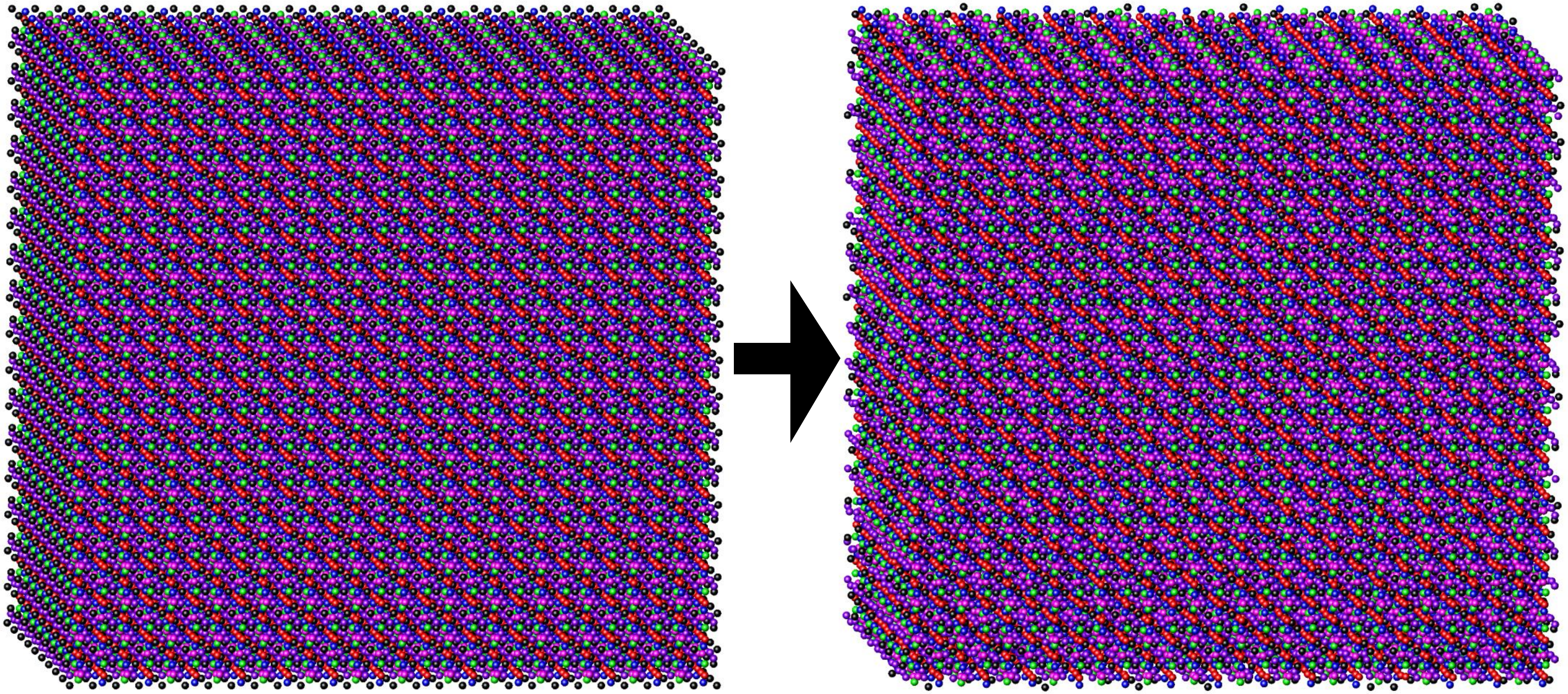
TOTAL SCATTERING



⇒ Diffuse scattering weak and covers a wider *d*-range than Bragg scatt.

REVERSE MONTE CARLO MODELLING

Build an atomic configuration using unit cells from Bragg peak analysis.



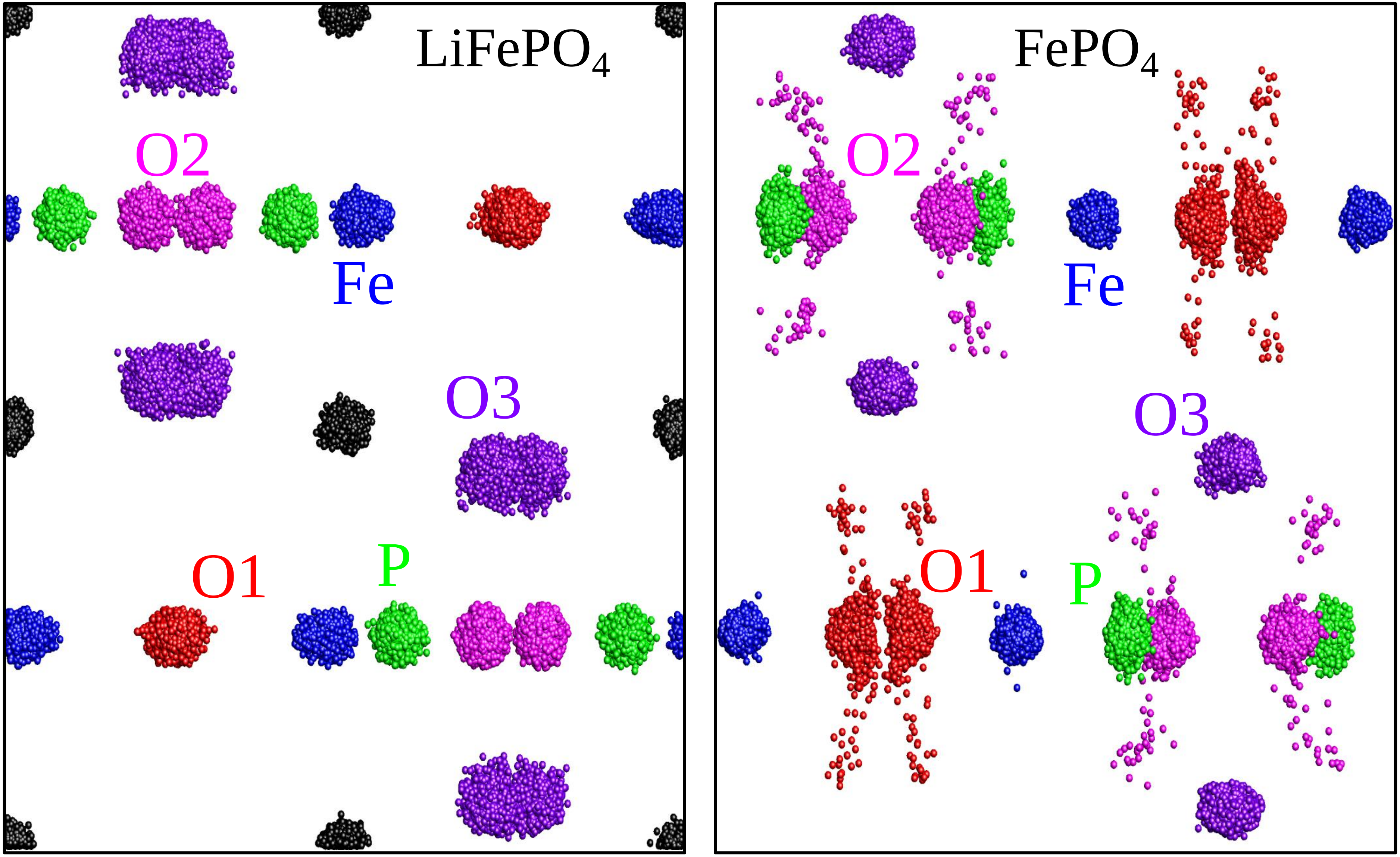
In this case : 9×14×17 unit cells of $LiFePO_4$ (total of 59976 atoms).

Move atoms to fit neutron total scattering data (wide *d*-spacing range).

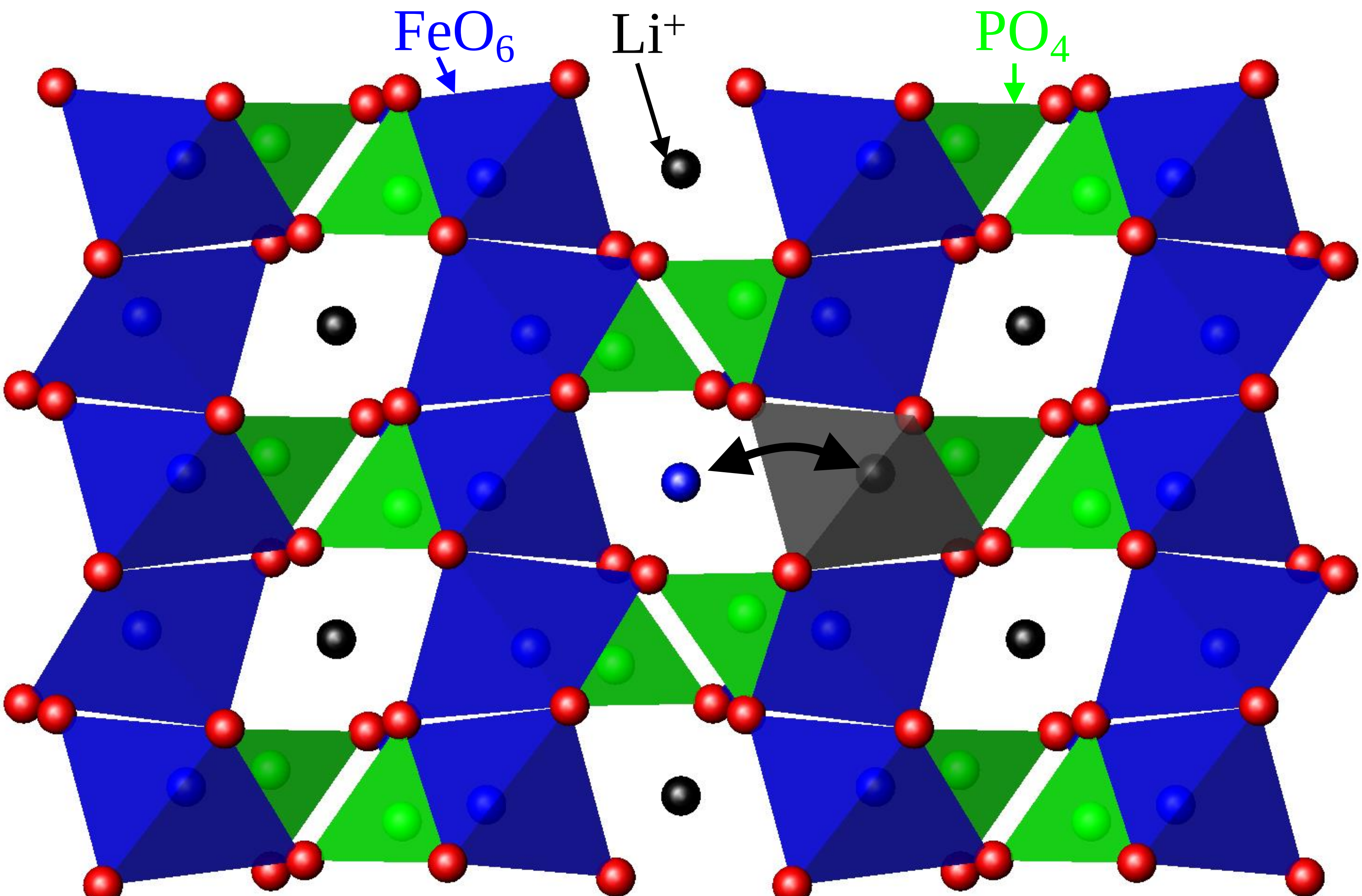
Analyse final configuration to probe local atom-atom correlations, *etc*.

DEFECTS IN $LiFePO_4/FePO_4$

Collapse configurations to a single unit cell.....



DEFECTS IN $LiFePO_4/FePO_4$



Concentration of anti-site defects is low (few %) ⇒ at limit of method.
But they are a factor in capacity fade on repeated charge/discharge.

BATTERIES : FUTURE RESEARCH

There is still considerable research effort devoted to understanding the behaviour of current materials such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$.

However, future challenges include.....

- Identify new cathode and anode materials - higher capacities, lower cost, *etc*.
- Cation valence changes greater than one ($V_2O_5 \rightarrow Li_3V_2O_5$?).
- Faster charge times using nanostructured materials. Smaller particle size $\Rightarrow$ more rapid insertion/removal of lithium ions.
- New materials based on mobile sodium-ions (Na^+).
- Higher valence mobile cations (Mg^{2+}?).
- New liquid electrolytes - non-flammable ionic liquids to allow use of higher voltage cathodes.
- Solid electrolytes to allow use of lithium metal anodes.

CLOSING REMARKS

- Neutron diffraction is a powerful tool to probe the relationship between crystal structure and electrochemical performance in battery materials.

- Essential to understand both the properties of current materials and to direct future research in new candidate systems.

- In-situ neutron diffraction investigations of ‘real’ batteries and ‘total scattering’ studies of the defects within battery materials will be key methods - but not easy!

- Such experiments provide a challenge to future neutron sources and instrumentation, in terms of high flux, good resolution, low backgrounds and ability to collect data over a wide energy range.

ACKNOWLEDGEMENTS

In-situ electrochemical cell development and $LiCoO_2$ work.....

- Tony West (Sheffield Univ.).
- Bo Dong (joint Sheffield-ISIS PhD student).
- Jordi Jacas Biendicho (IREC, Barcelona).
- Dag Noréus (Stockholm Univ.).
- Ron Smith, Colin Offer (ISIS).

Total scattering study of $LiFePO_4$ and $FePO_4$.....

- Sten Eriksson, Stefan Norberg (Chalmers Univ.).
- Helen Playford, Wojciech Sławiński (ISIS).
- Torbjörn Gustafsson, Kristina Edström (Uppsala Univ.).

HRPD data on hexamethylenetetramine.....

- Silvia Capelli, Dominic Fortes (ISIS).

THANK YOU!

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