Developing better energy storage materials and devices with XAS

Never Stand Still | Science

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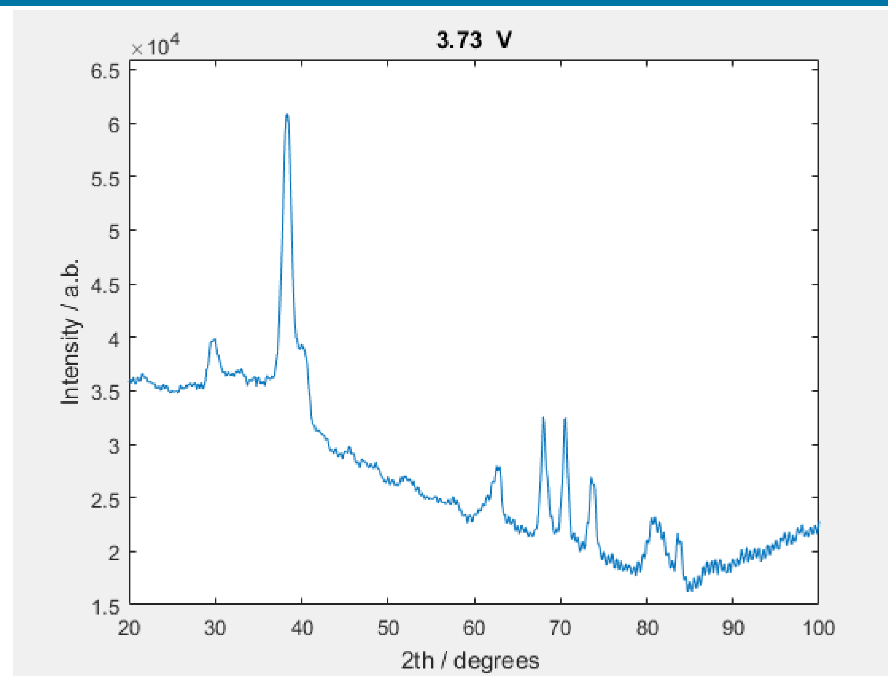
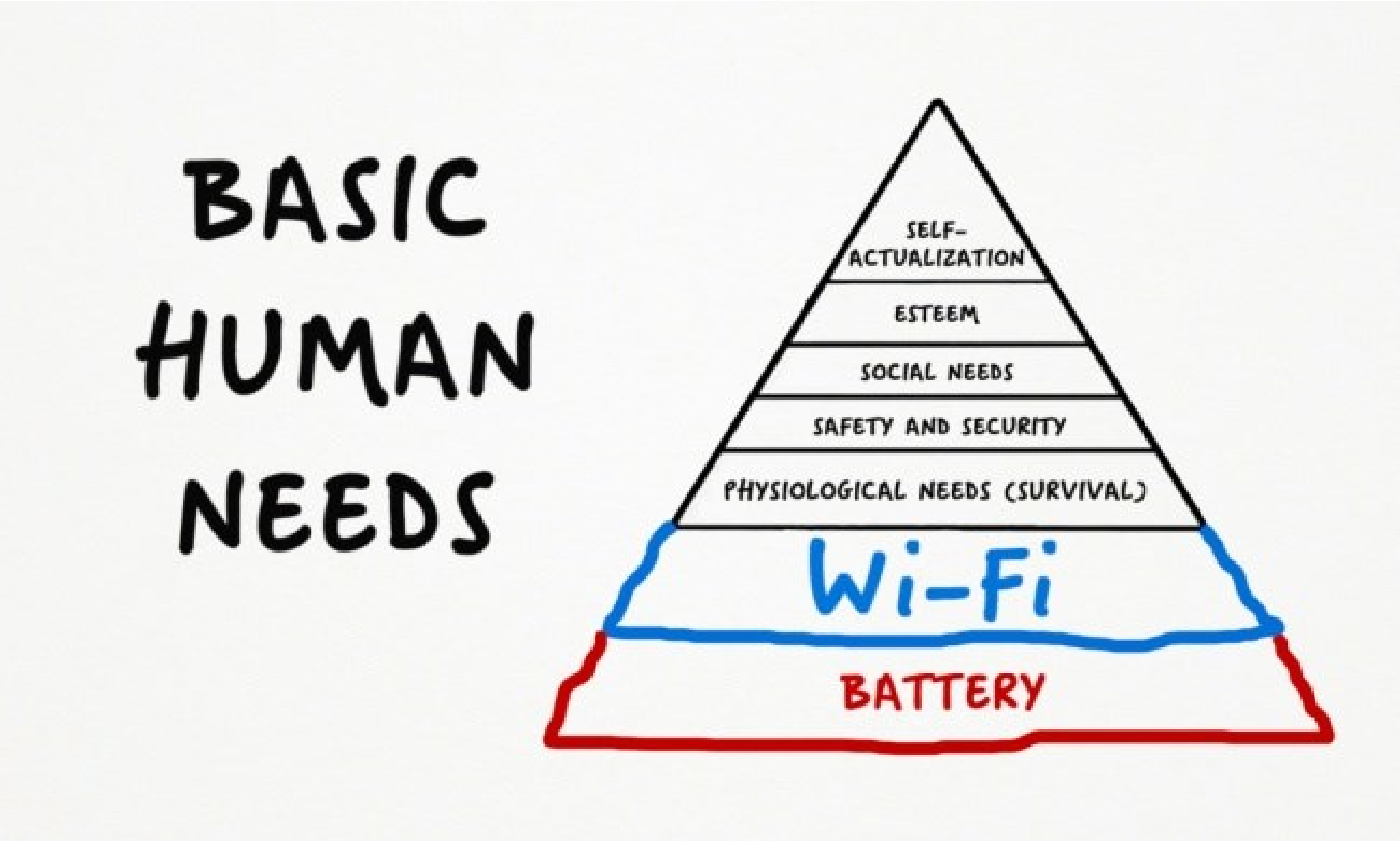


Outline

- An overview of my research field
  - Battery materials research and development
- Examples of how we have used XAS
- What we have learnt
- Cutting edge experiments (*operando* and *in situ* XAS)
  - Thermal expansion materials (ceramics)
- Examples of how we are using XAS

- Multiscale information – critical for future development



The Nobel Prize in Chemistry 2019 was awarded jointly to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries."

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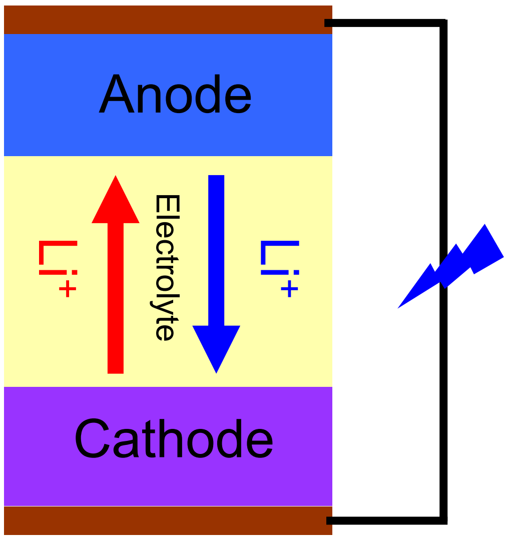
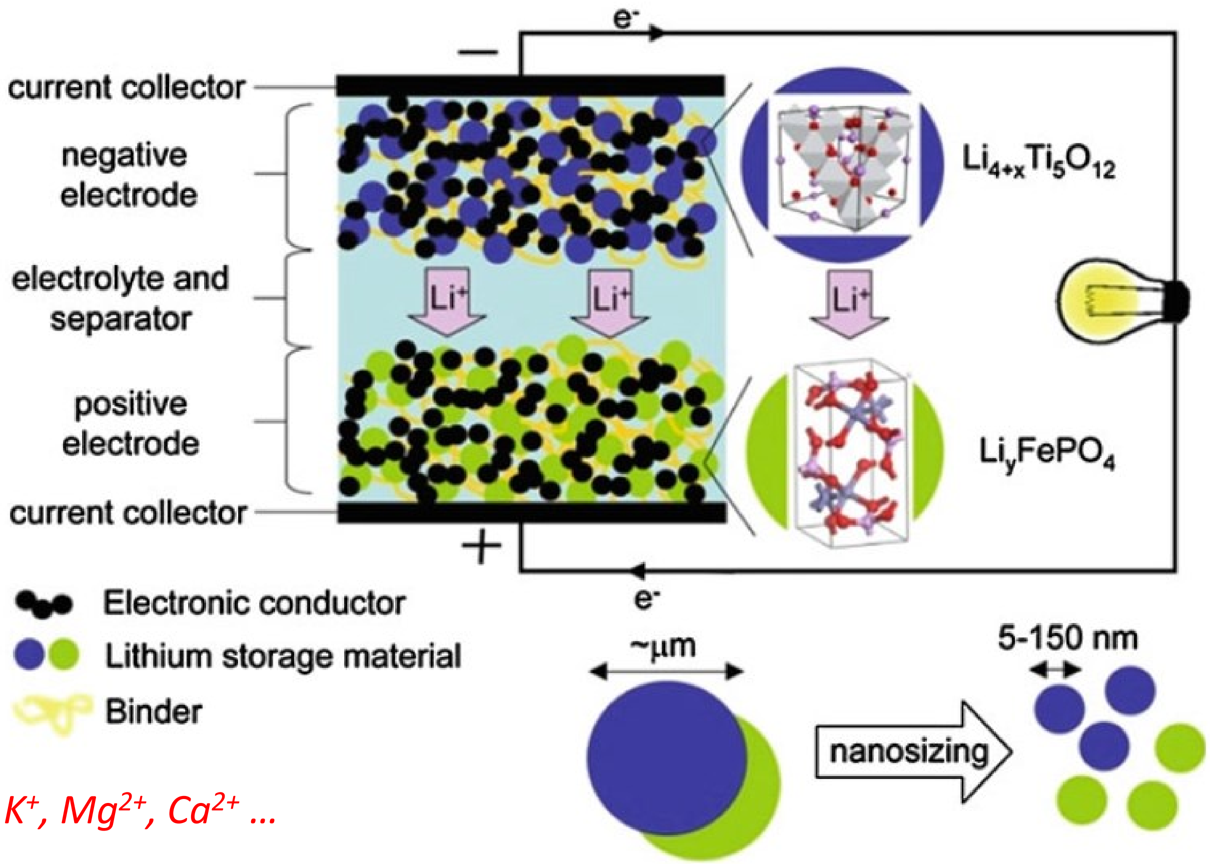
What does a lithium-ion battery really look like inside?





One can replace Li^+ with Na^+, K^+, Mg^{2+}, Ca^{2+} …

Changes that occur (pertinent to XAS) – crystal structure, oxidation state, local environment

XAS is an awesome tool to use!

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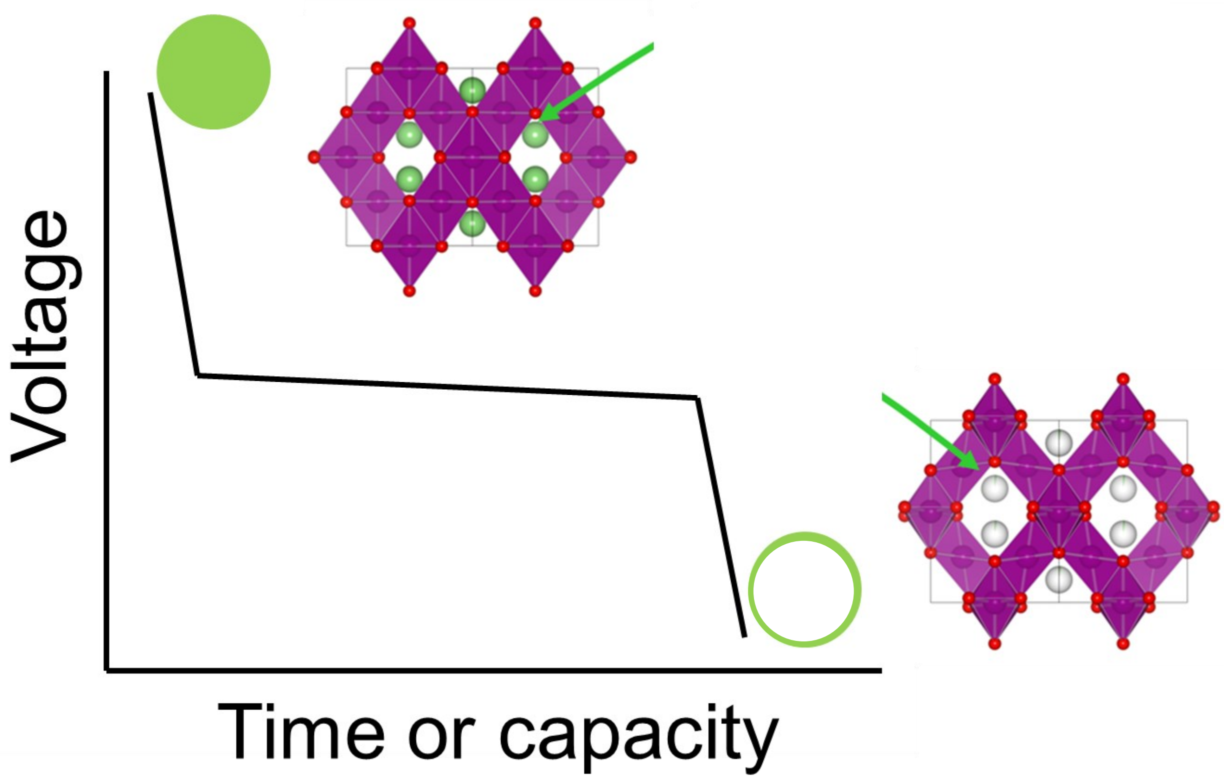
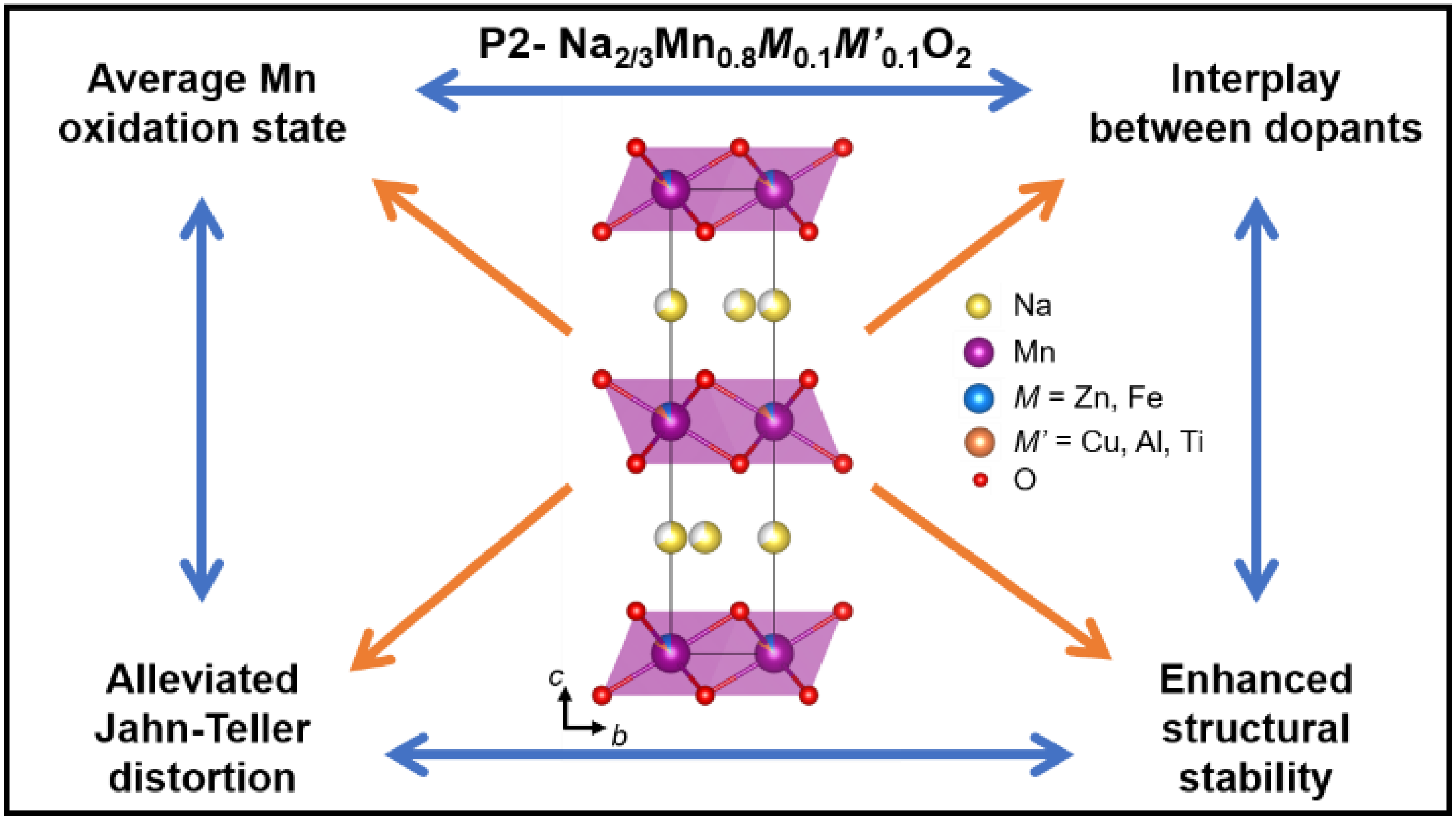
Crystal structure
Evolution
Oxidation state
Local structure
Reaction mechanisms

↔ **Properties**



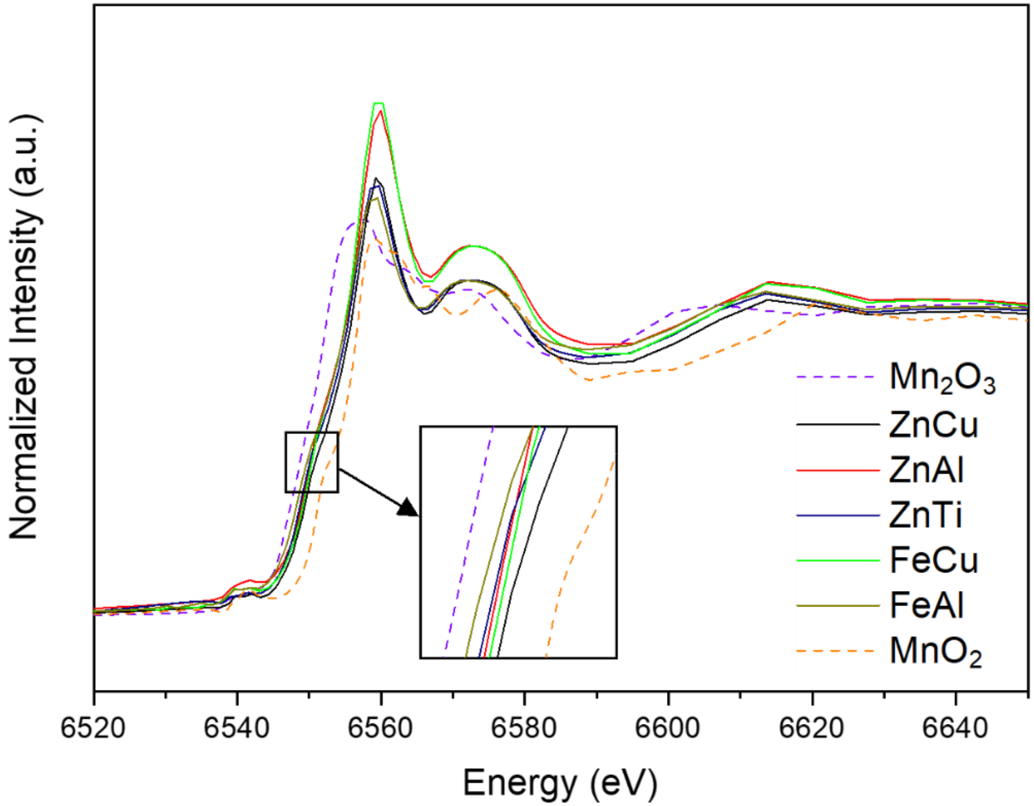
An example: $Na_xMn_{0.8}TM_{0.2}O_2$



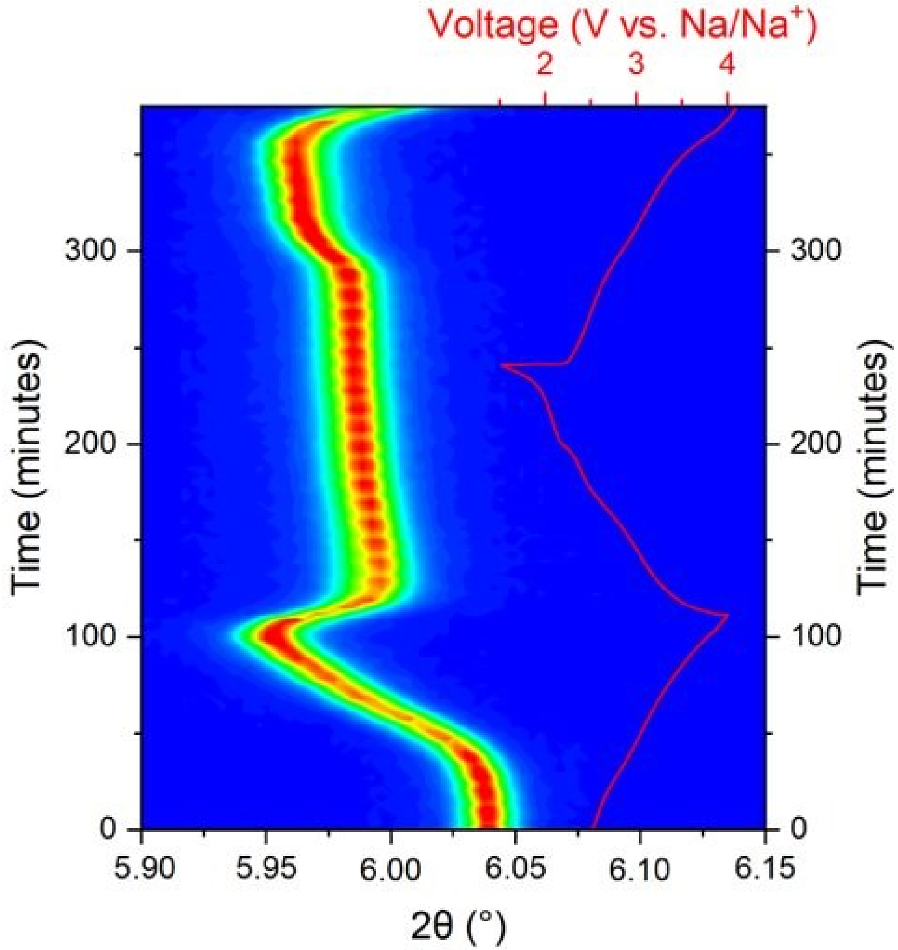
Chemistry of Materials 2021, 33, 11, 3905-3914

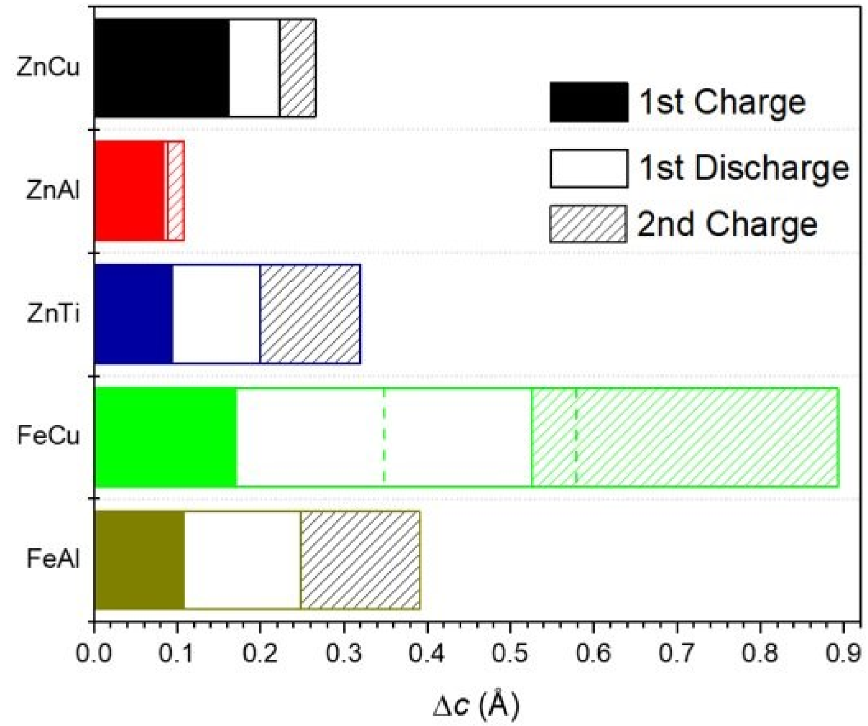
XAS to confirm Mn oxidation state trend

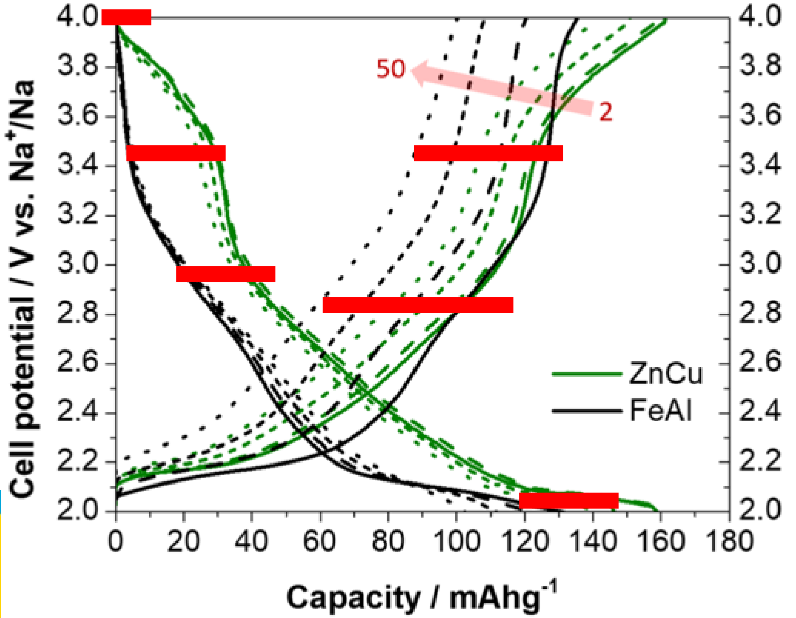
Chemical formula	Abbre-viation	Theoretical Mn oxidation state
$Na_{2/3}Mn_{0.8}Zn_{0.1}Cu_{0.1}O_2$	ZnCu	3.66
$Na_{2/3}Mn_{0.8}Zn_{0.1}Al_{0.1}O_2$	ZnAl	3.54
$Na_{2/3}Mn_{0.8}Zn_{0.1}Ti_{0.1}O_2$	ZnTi	3.41
$Na_{2/3}Mn_{0.8}Fe_{0.1}Cu_{0.1}O_2$	FeCu	3.54
$Na_{2/3}Mn_{0.8}Fe_{0.1}Al_{0.1}O_2$	FeAl	3.41



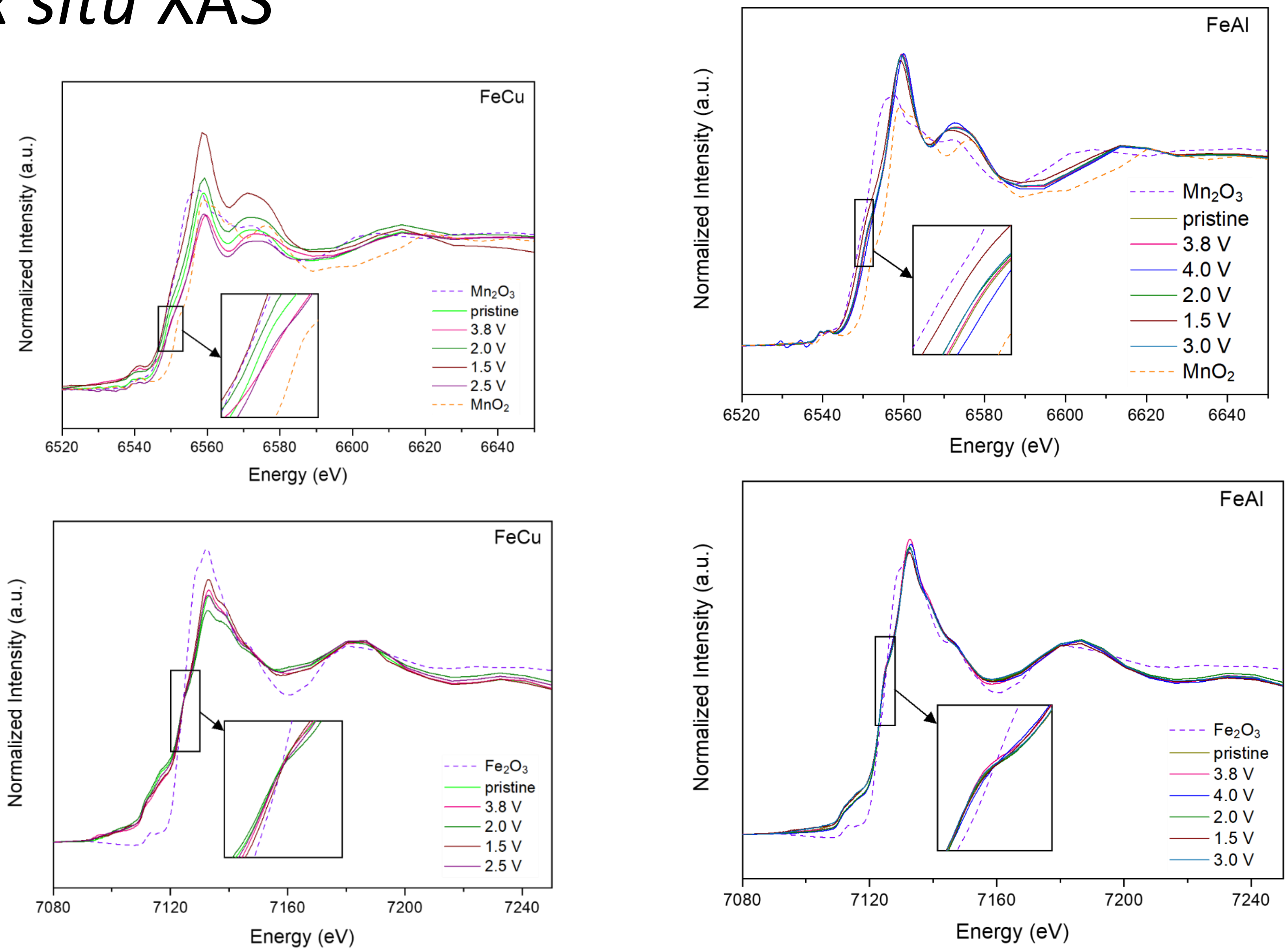
Structural Evolution





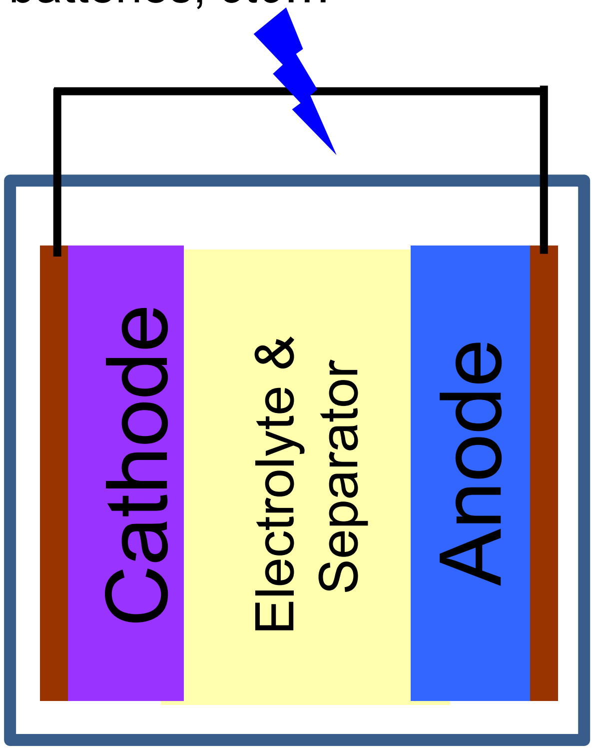


Ex situ XAS


FeCu
Normalized Intensity (a.u.)
Energy (eV)
6520
6540
6560
6580
6600
6620
6640
Mn2O3
pristine
3.8 V
2.0 V
1.5 V
2.5 V
MnO2
FeAl
Normalized Intensity (a.u.)
Energy (eV)
6520
6540
6560
6580
6600
6620
6640
Mn2O3
pristine
3.8 V
4.0 V
2.0 V
1.5 V
3.0 V
MnO2
FeCu
Normalized Intensity (a.u.)
Energy (eV)
7080
7120
7160
7200
7240
Fe2O3
pristine
3.8 V
2.0 V
1.5 V
2.5 V
FeAl
Normalized Intensity (a.u.)
Energy (eV)
7080
7120
7160
7200
7240
Fe2O3
pristine
3.8 V
4.0 V
2.0 V
1.5 V
3.0 V

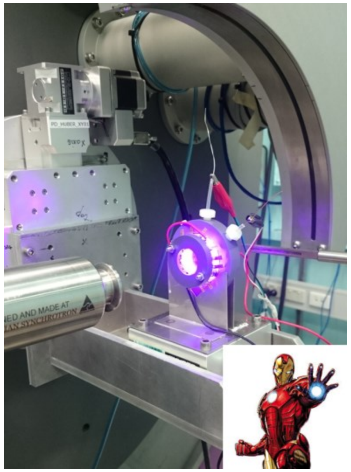
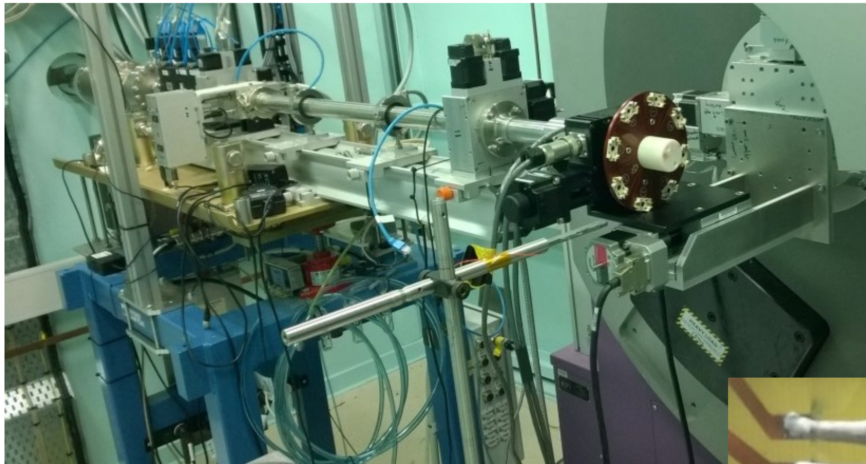
"*In situ* experiments" in devices....

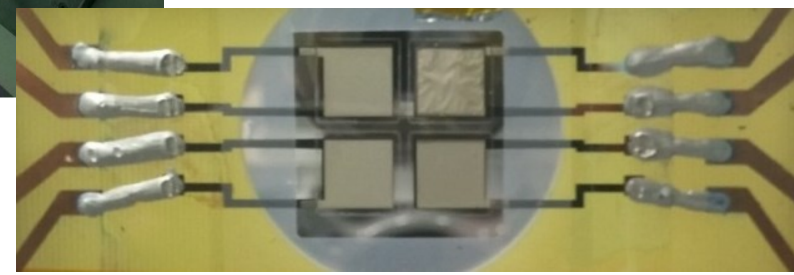
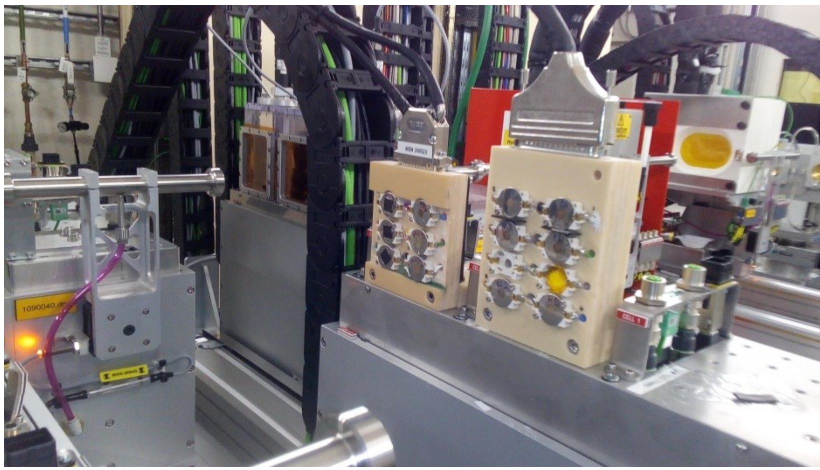
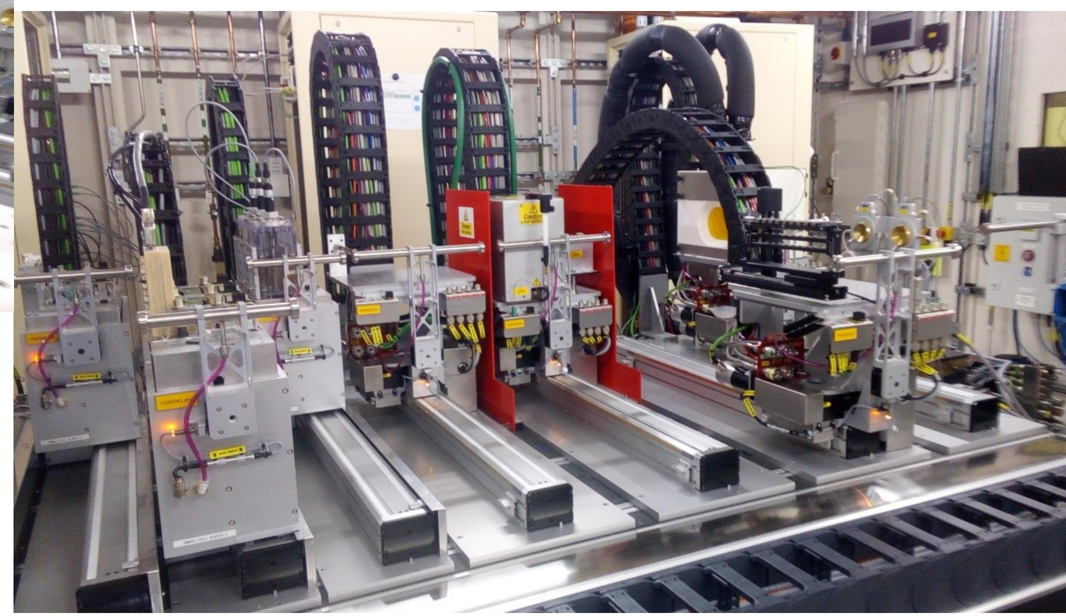
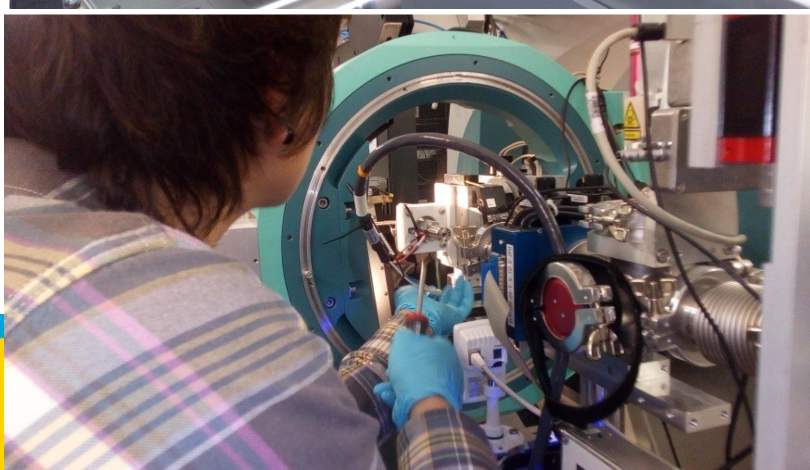
Fuel cells, batteries, *etc*…



Electrode mix = **active material**, carbon, PVDF/PFTE
Current collectors (Al, Cu), stainless steel casing
Electrolyte = salt in carbonate solution
Separator = glass fibre, polyethylene

- Structure as a function of device performance (e.g. electrochemistry)
- Device performance at different temperatures (e.g. electrochemistry at LT, RT, HT)

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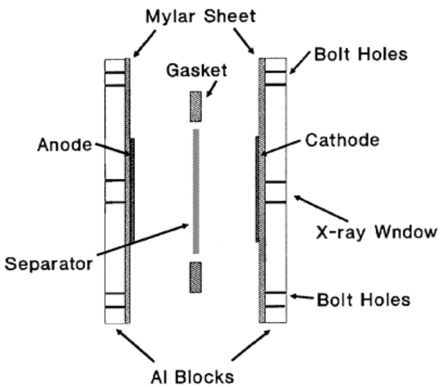
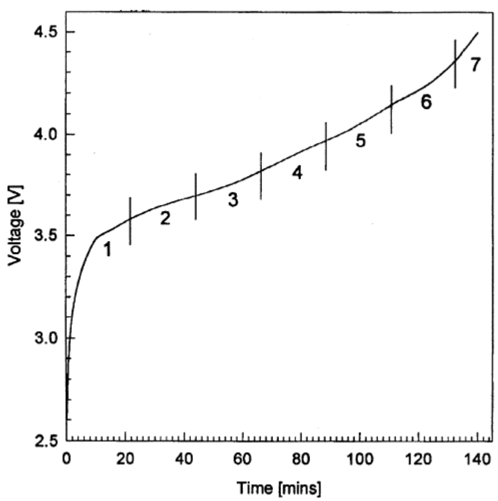
It would be so cool to do *in situ* XAS

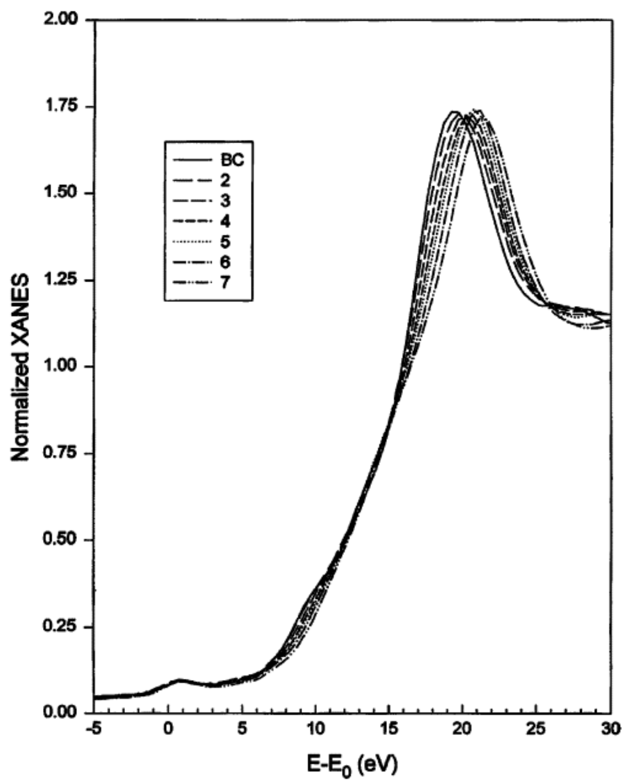
Current Australian Synchrotron beamlines – not so good at this*
(beam-based phenomena)

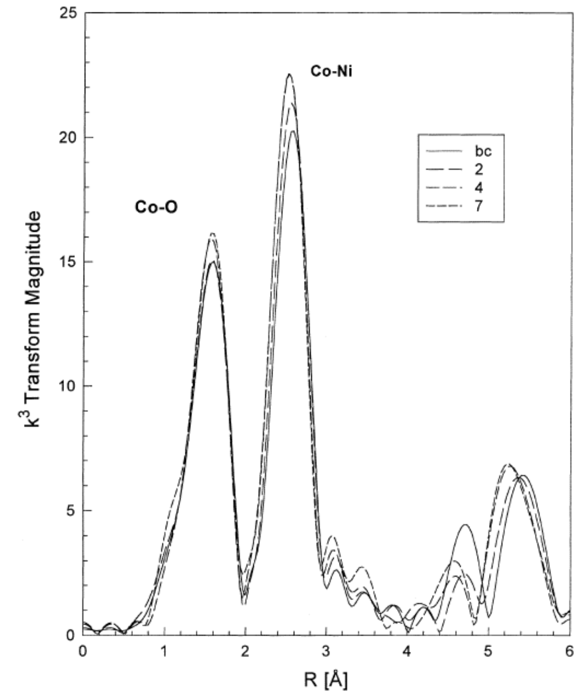
- International synchrotrons

- MEX









Co K edge

Journal of Power Sources 92 (2001) p1-8

Some recent work – so called conversion electrode **BiSb**

- Very difficult to probe with diffraction
- Upon (de)lithiation nanomaterials are formed

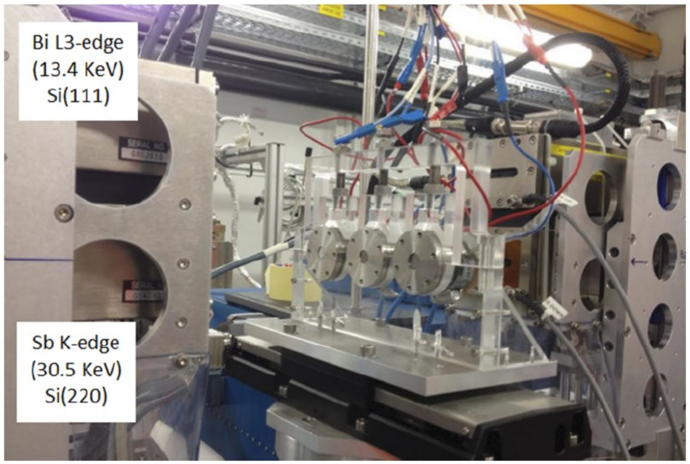
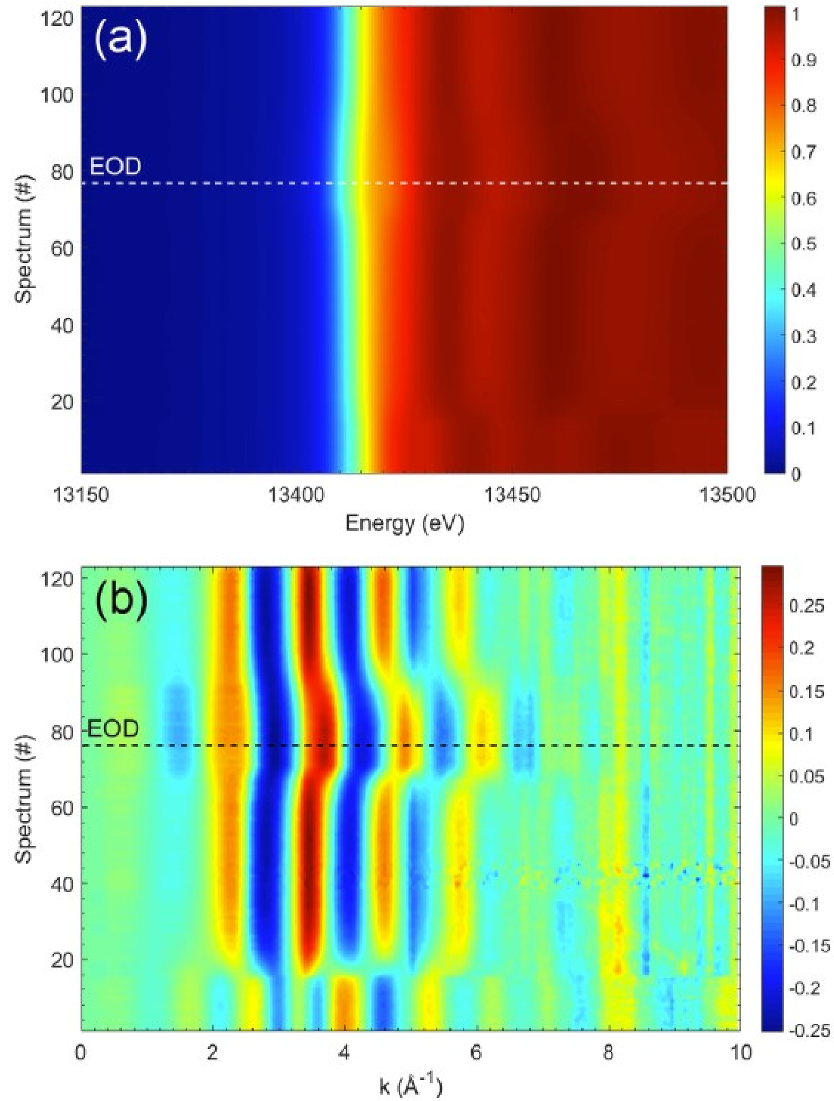


Figure 1: Experimental sample stage used for the simultaneous study of three electrochemical cells by *operando* Sb K-edge and Bi L_3-edge XAS.



Principal component analysis

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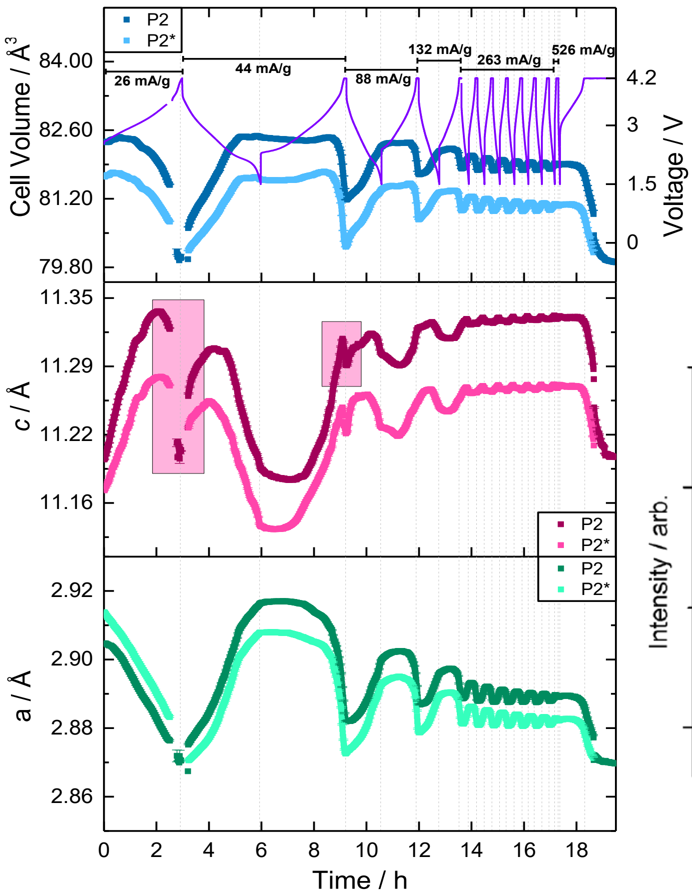
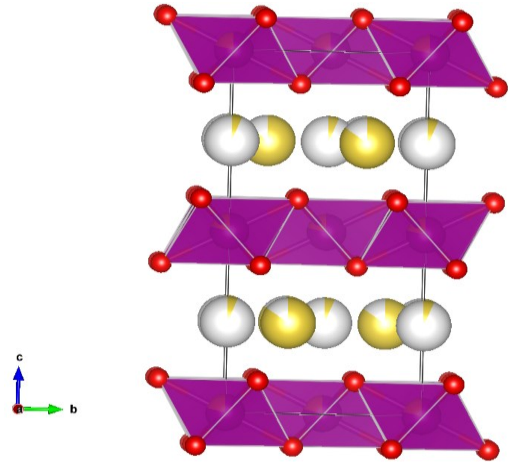
Long term and fast cycling experiments

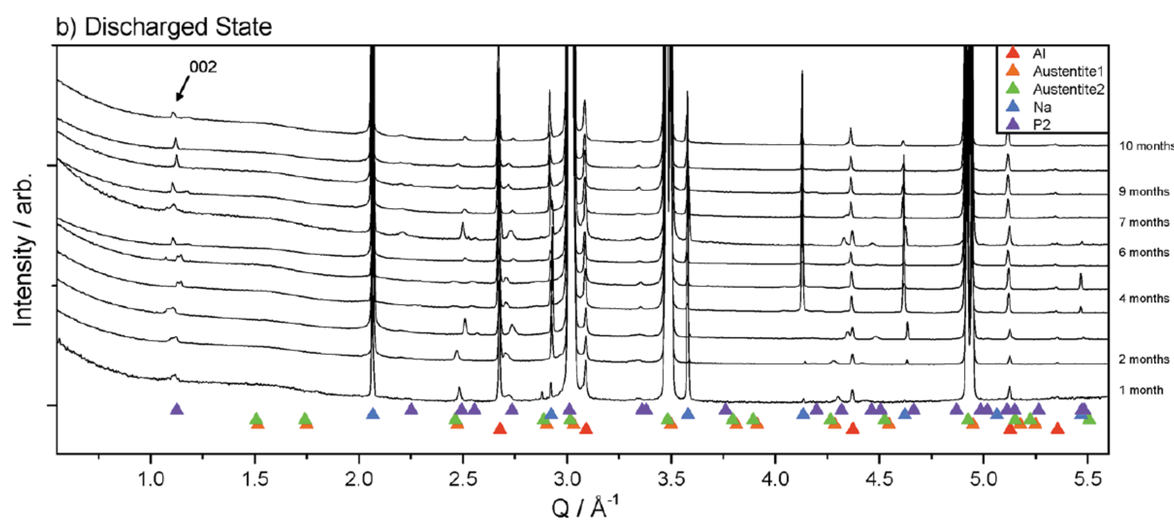
P2- $Na_{0.67}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$

Fast experiments 45 s/dataset @ALBA





Long duration ~ 2 years @ Diamond



2019 "*Exploring the rate dependence of phase evolution in P2-type $Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$*" **D. Goonetilleke, S. Wang**, E. Gonzalo, M. Galcerán, D. Saurel, S. J. Day, F. Fauth, T. Rojo, **N. Sharma**, Journal of Materials Chemistry A, **7**, 12115-12125

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Looking at beyond lithium-ion batteries

E.g. Li-S batteries

Conventional Li-ion

155 mAh g^{-1}

$Li_{1-x} + Li_xCoO_2 \rightleftharpoons LiCoO_2$

0.5-0.7 Li

Li-S

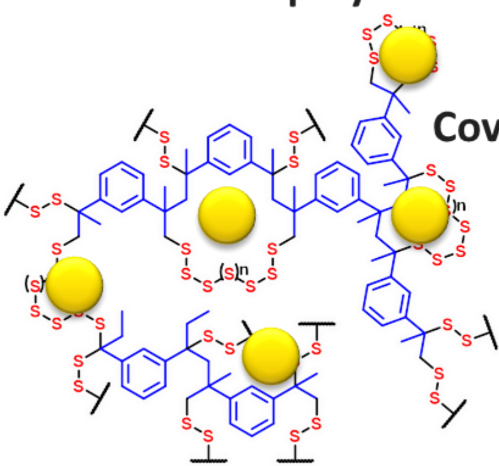
1672 mAh g^{-1}

≈ 10x greater

$16Li + S_8 \rightleftharpoons 8Li_2S$

16 Li

Sulfur-rich copolymers

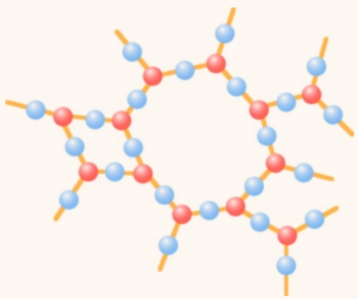


Covalently-bonded sulfur

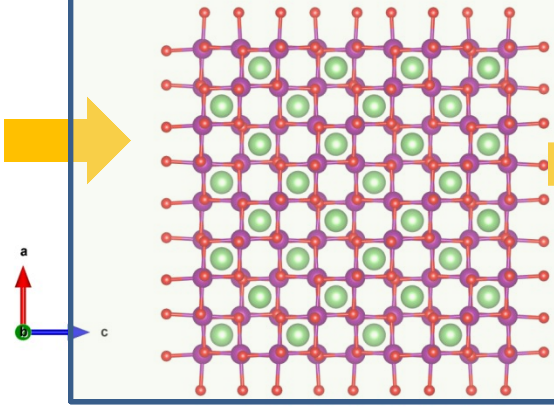
Scale is critical...

Length

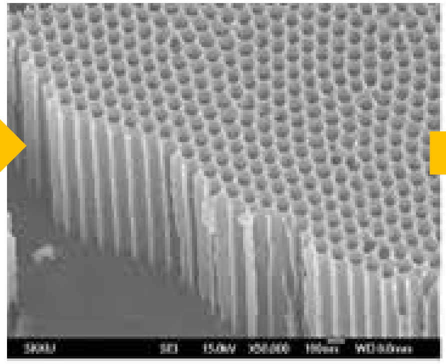
Local information



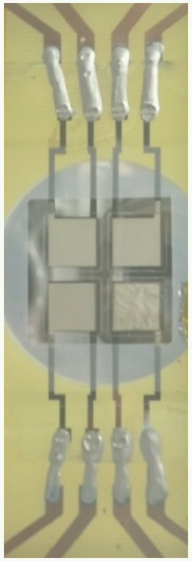
Long-range order



Nanoscale ordering



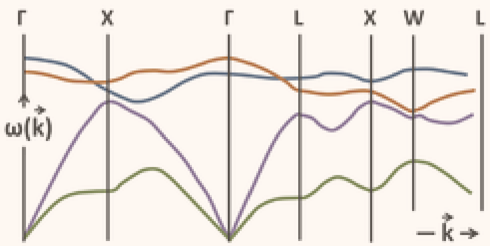
Fabrication



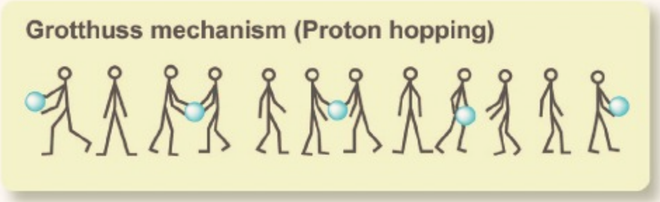
Surface considerations

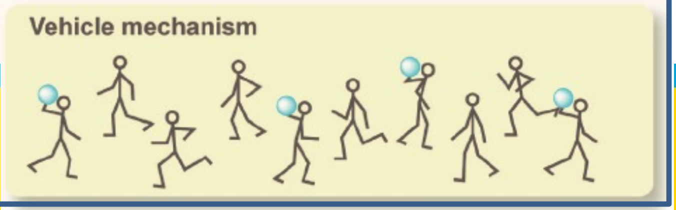
Dynamics

Lattice vibrations



Ion hopping and concerted motion





Bulk conductivity (grain boundaries)

σ_{e-} σ_{ion}

Post-Docs

Henrik Andersen

Uttam Mittal

PhD

Michael Fenech
Lisa Djuandhi
Matthew Teusner

Honours

Liam McKinlay
Rajko Romic

Previous students

PhD

James Christian (Cap-XX - UNSW)
Divya Sehrawat (Croda)
Damian Goonetilleke (KIT/BASF)
Junnan Liu (Harbin Engineering U)
Emily Cheung (Teaching)
Conrad Gillard
Jennifer Stansby (UNSW)
Jimmy Wu

Science Honours

Othman Al Bahri (Cambridge)
Luke Stellar (Coffey)
Mackenzie Hagan (Poker Player)
Hieu Nguyen (Building)
Sunny Wang (Stanford)
Kathleen Djohari (NMI -> radiology)
Eleanor Parker (Inventia biosciences)
Maxwell Ong (Asphalt Services)
Ivan Johan (Memjet)

Engineering Honours

Charith Perera (Tesla-> Amazon)
Ken Zheng (Siemens)
James Bott (Ecoult)
Bernd Schulz (PhD Mats Sci UNSW)

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