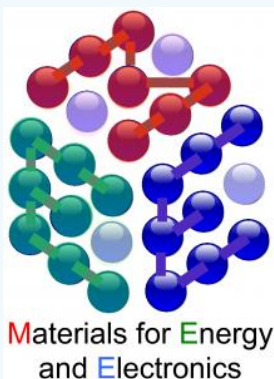


Can computational modelling reveal what experiments can't?

R. Attard-Trevisan, C. Vijeun, M. Fehse, R. Parmenter, P. Thompson, A. Longo, G. Cibin, E.M. Kelder, A.V. Chadwick and M. Alfredsson



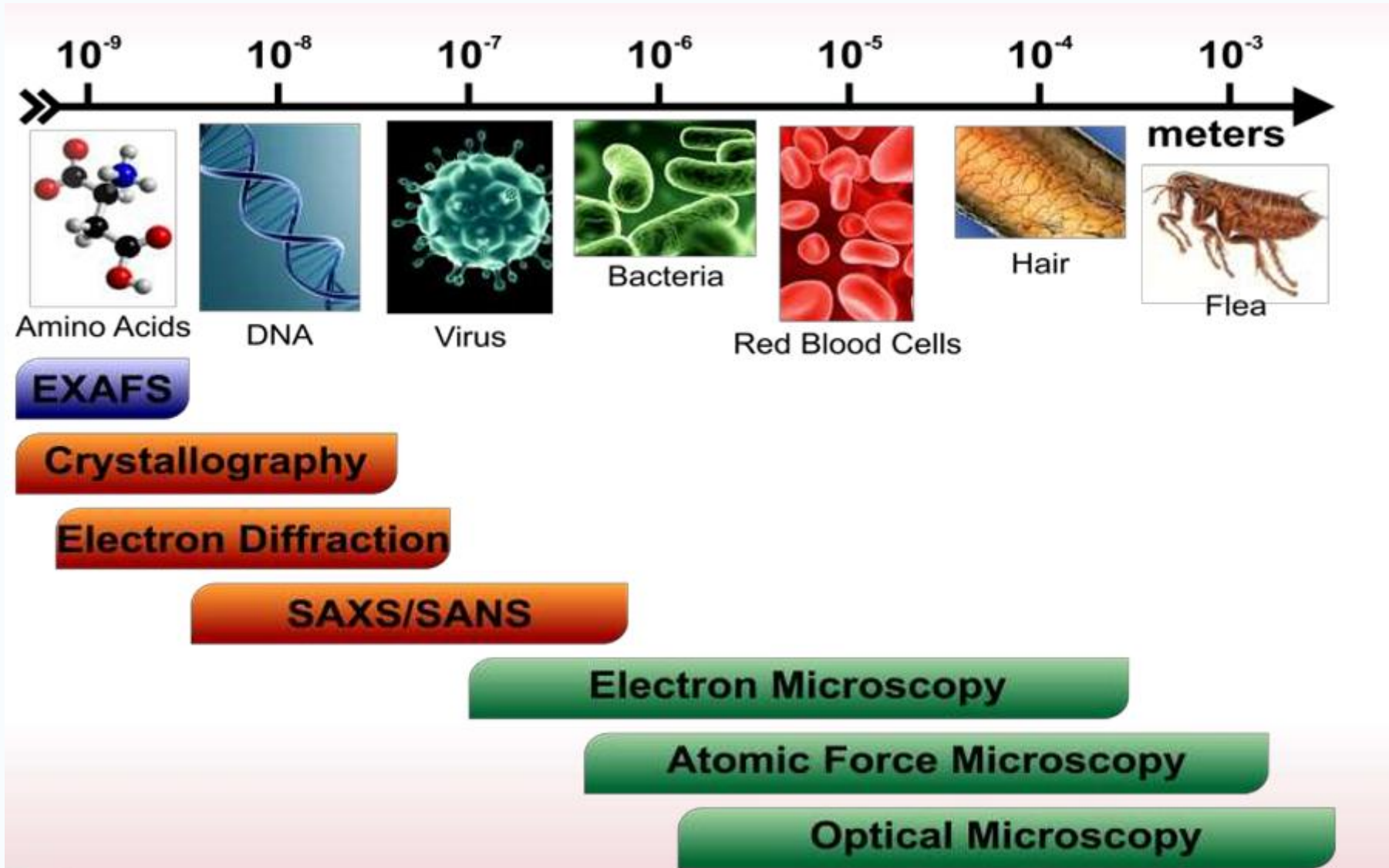
School of Natural Sciences,
University of Kent, Canterbury, UK
m.l.alfredsson@kent.ac.uk

Stand for ambition.
kent.ac.uk

26/03/2026
Zoom-meeting

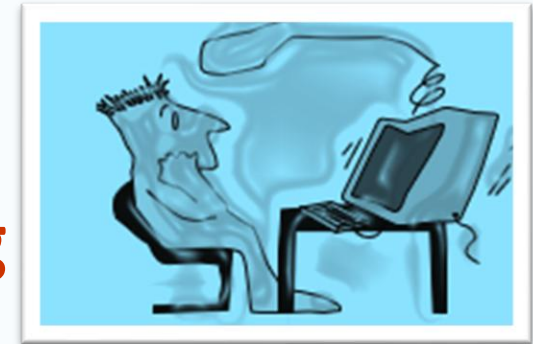


Size and Scale



Layout

- TUTORIAL: Use of Atomistic simulations to interpret experimental X-ray data
 1. What information can we extract?
 2. How to set up your calculation
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 4. How to use the information to understand our scientific conandrum
- RESEARCH talk: Can computational modelling reveal what experiments can't?



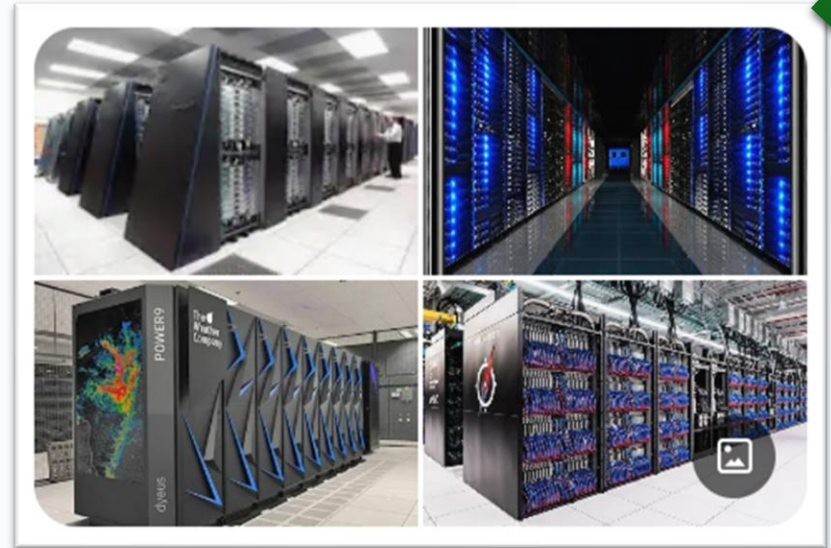
Synchrotron v. HPC

They all look the same?



Synchrotrons

High Performance
computing (HPC)

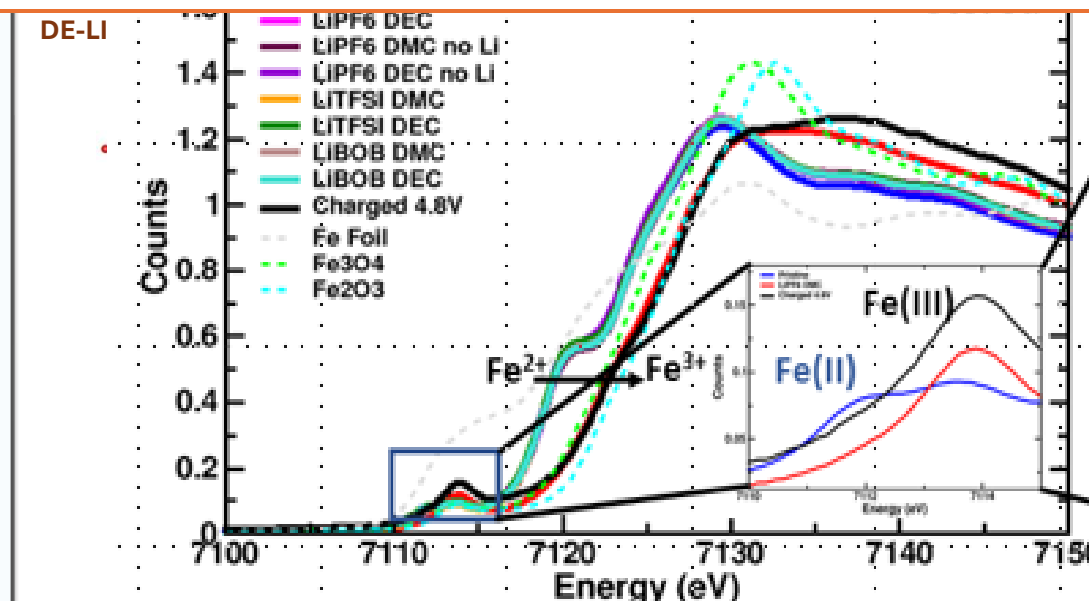


- Application process (S,H)
- Energy consuming (S,H)
- Computing fast results (H)
- Limitations – over subscription (H,(S))
- Less data but higher intensity faster data collection (S)
- Automatic/robots faster data collections (S)

How does a battery work?

$\text{Li}_2\text{FeSiO}_4$ (Operando XAS)

Can we use computer simulations to support the interpretation of the data?



Brownrigg et al., *J. Mat. Chem. A*, 3, 7314-7322 (2015)

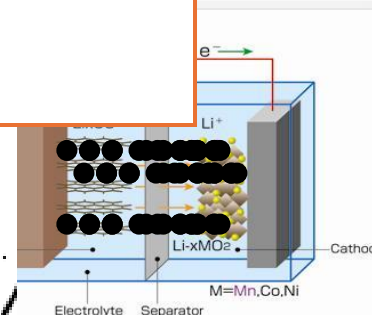


site electrode:

Electronic conductivity
Binder

Electrolyte:

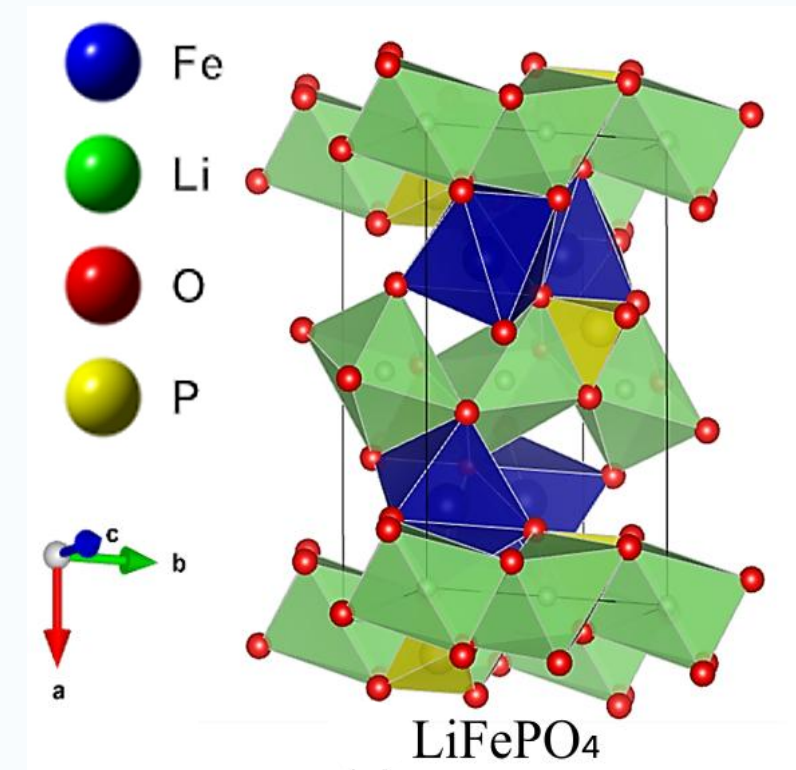
Organic solvent
Salt (e.g. LiPF₆)



Why Polyanionic compounds?

Fe-based compounds as they are:

- Low cost
- Environmentally benign
- Non-toxic
- Biodegradable
- Can be synthesised following aqueous based routes.
- Aqueous-based binders
- Reduce energy consumption during manufacturing and processing



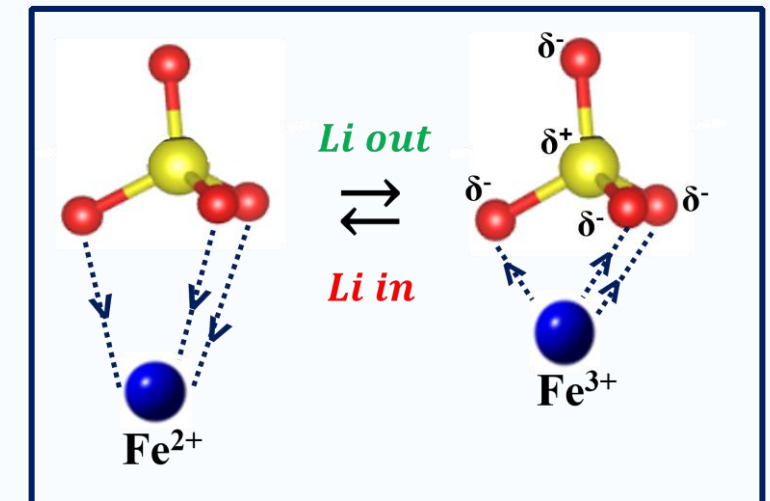
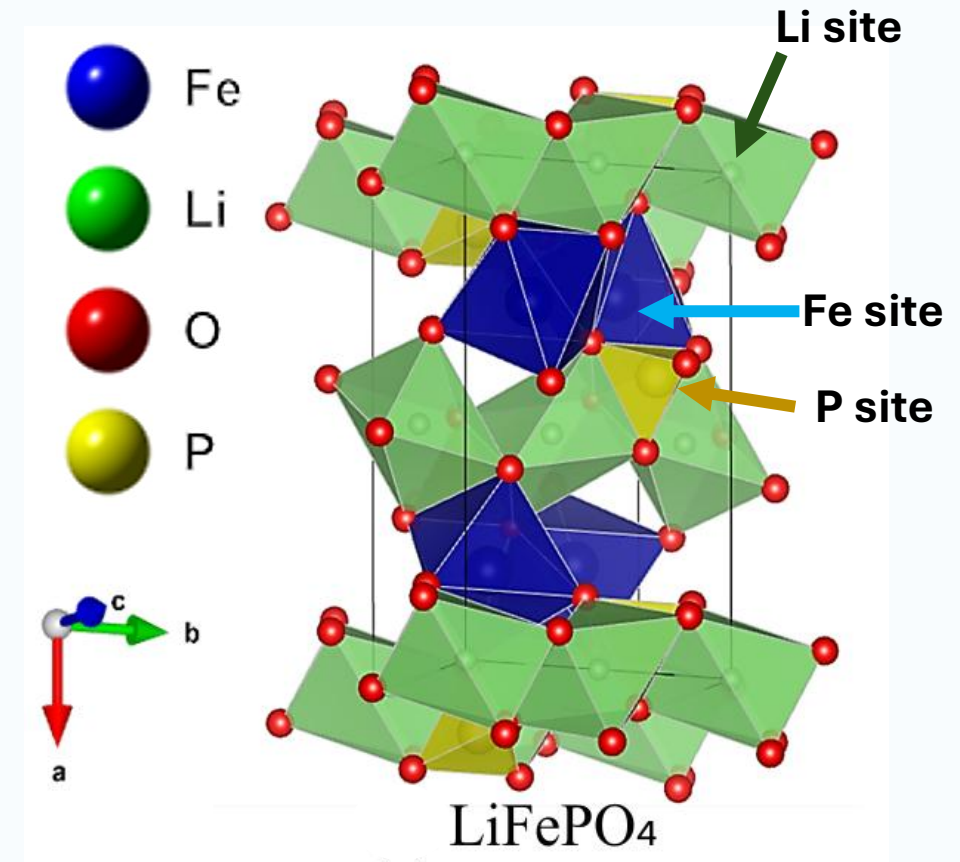
LiFePO₄ (LFP) Crystal Structure

- **LFP structure:**
 - Olivine-type structure (*Pnma*)
 - PO₄ tetrahedra; FeO₆ octahedra
 - Layers are stacked – 3D framework
- **Li-ion diffusion occurs through a 1D pathway across the *b*-axis**



Capacity Retention in LFP:

- **Strong P-O covalency** stabilises the Fe²⁺/Fe³⁺ state through the **Fe-O-P back-bonding**
- High theoretical specific capacity (170 mAh/g)
- Good thermal & structural stability



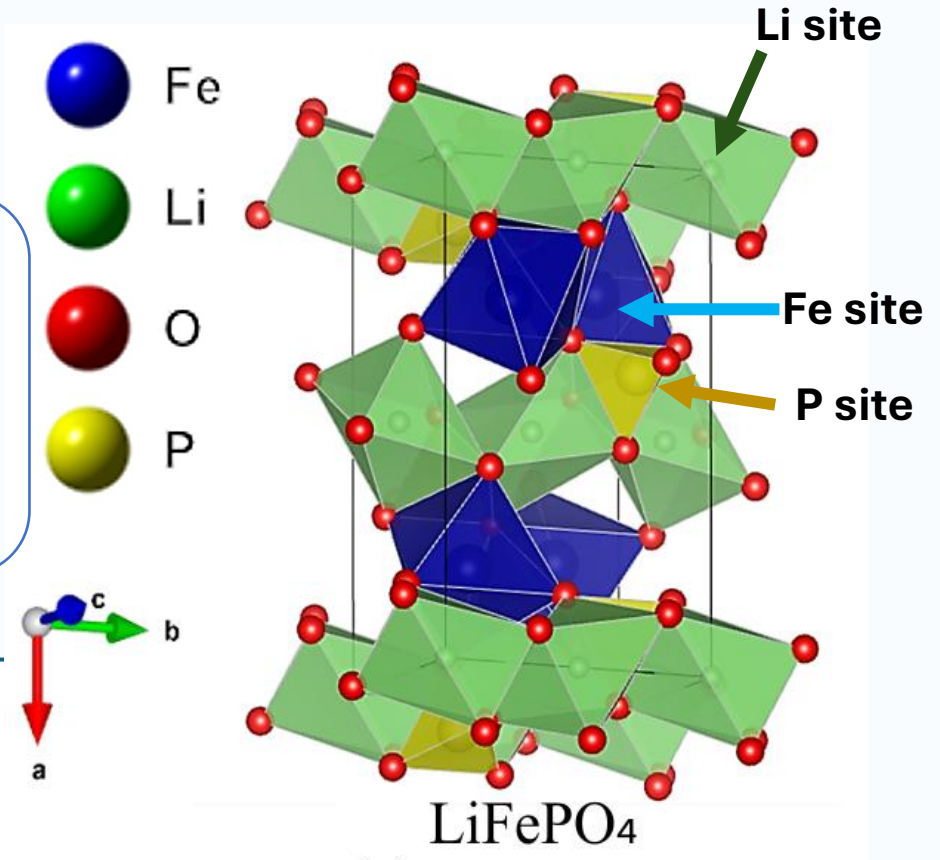
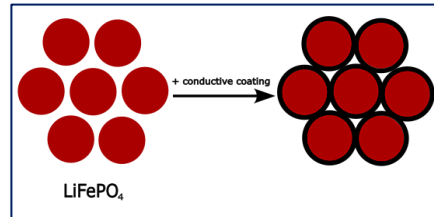
LiFePO₄ (LFP) Crystal Structure

Cons:

- LFP has poor electronic and ionic conductivity ($\sim 10^{-9}$ S cm⁻¹); Impedes Li-ion diffusivity
- Voltage 3.5 V

Solutions:

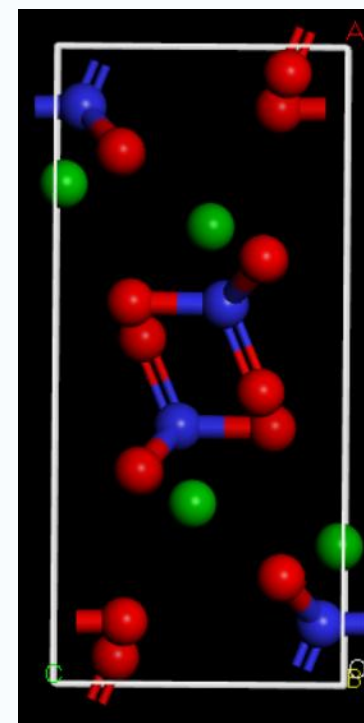
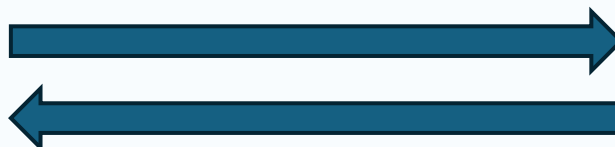
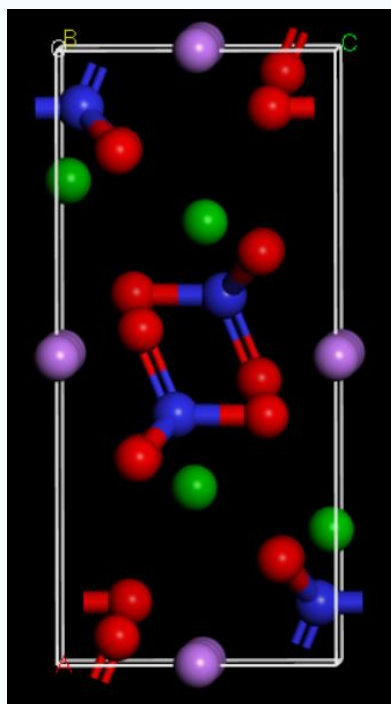
- Conductive coating
- Different binders in electrodes
- Nanoparticle morphology and size
- Cation doping
 - Aliovalent (Mn²⁺)
 - Supervalent (Al³⁺, Sc³⁺, V³⁺, Ho³⁺, Y³⁺)



For this tutorial we will use Materials studio (D'Assult package) to model LiFePO_4 (LFP) and FePO_4 (FP)

Steps:

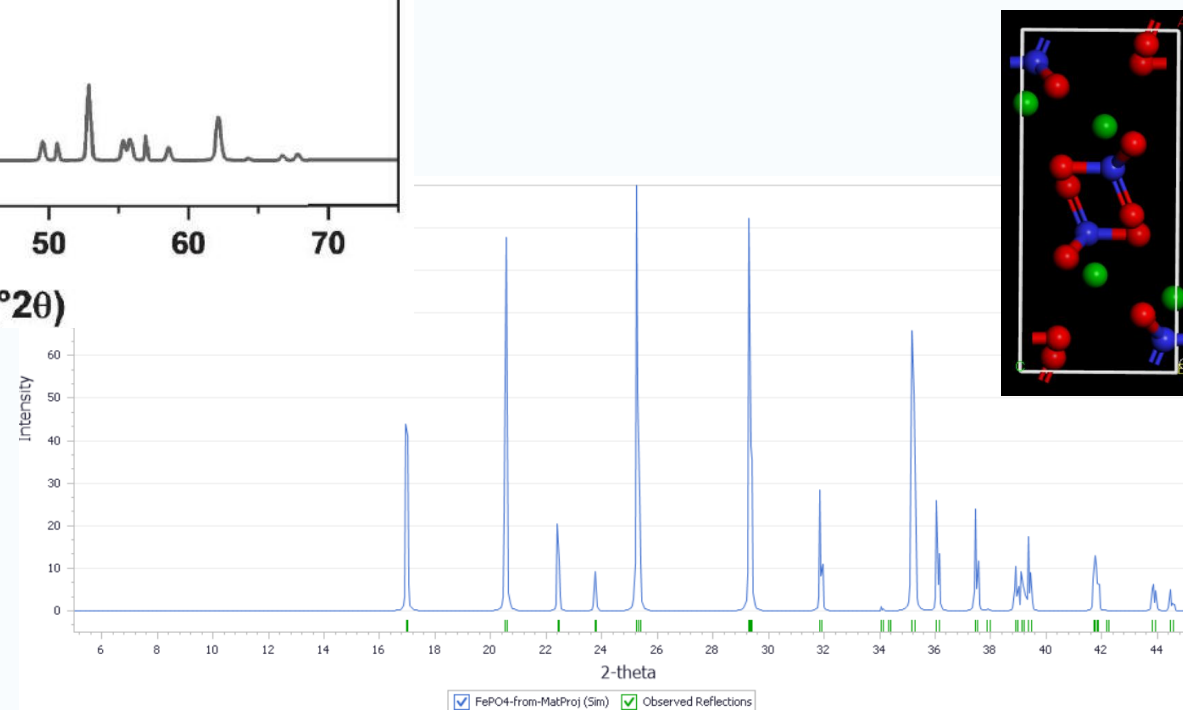
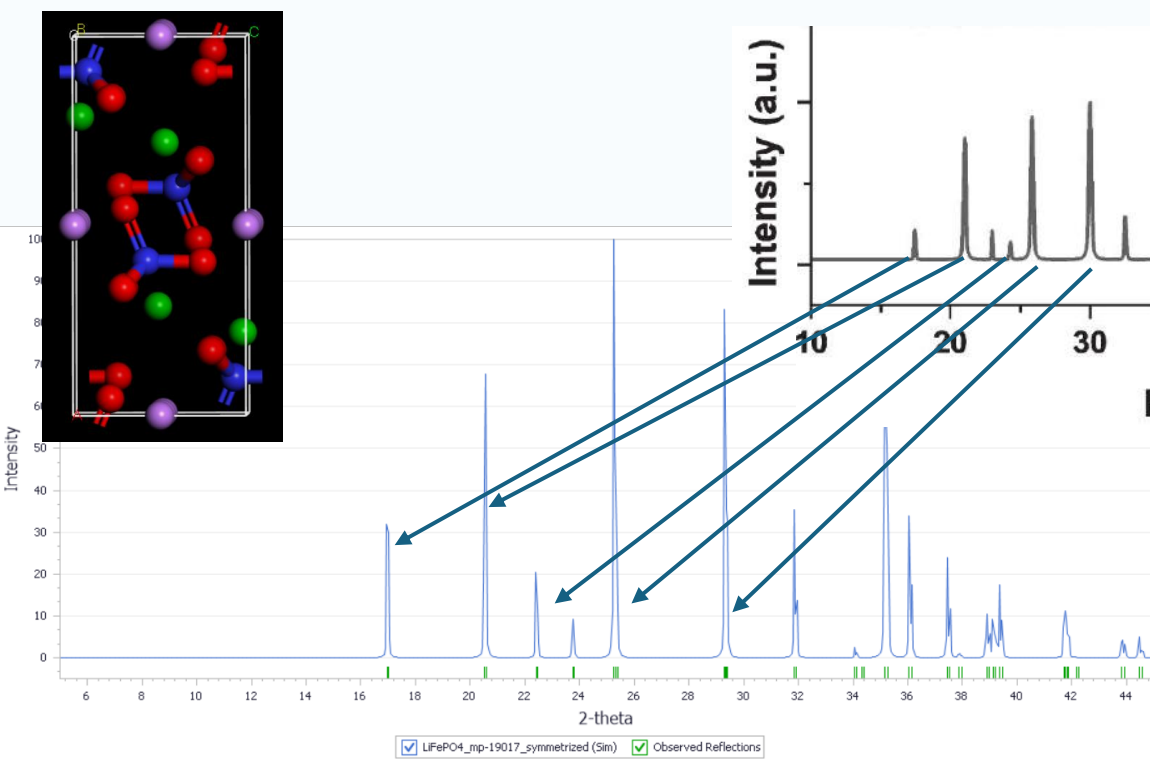
1. Download the LiFePO_4 .cif file from Materials Project
2. Import the **.cif file in Materials studio GUI** and confirm it is the correct structure
3. Create the FePO_4 structure – note same space group



For this tutorial we will use Materials studio (D'Assult package) to model LiFePO_4 (LFP) and FePO_4 (FP)

Steps:

1. Run a geometry optimisation
2. Calculate the XRD-pattern using the Module **Reflex**



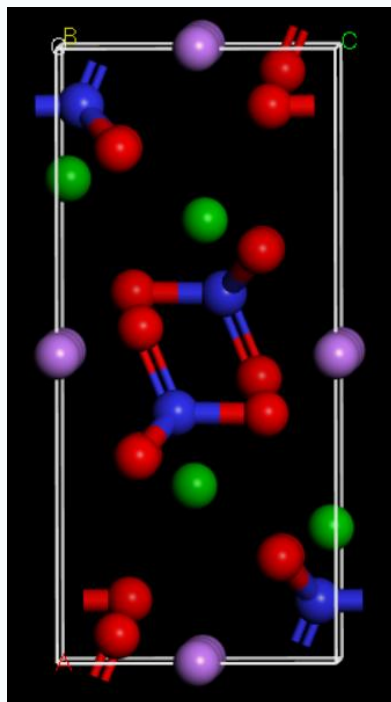
For this tutorial we will use Materials studio (D'Assult package) to model LiFePO_4 (LFP) and FePO_4 (FP)

Steps:

1. Calculate the X-ray Absorption Near Edge Spectra (XANES)
2. Properly represent the ELECTRONIC STRUCTURE

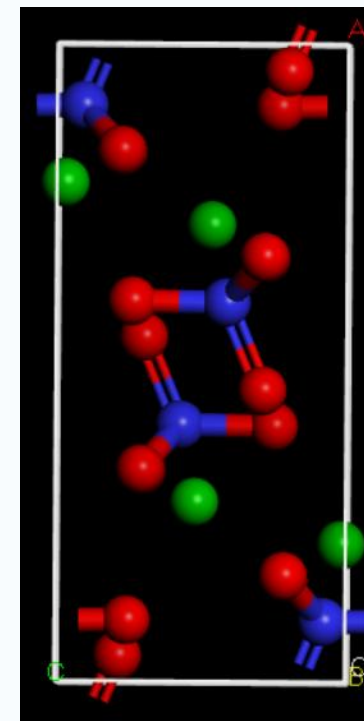
High Spin (HS) or Low Spin (LS)
AFM or FM or PM?

LiFePO_4

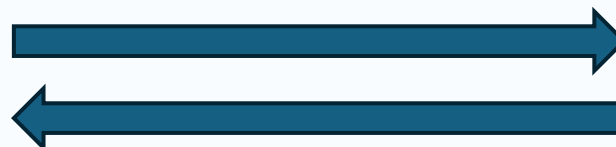


High Spin (HS) or Low Spin (LS)
AFM or FM or PM?

FePO_4



Li_xFePO_4

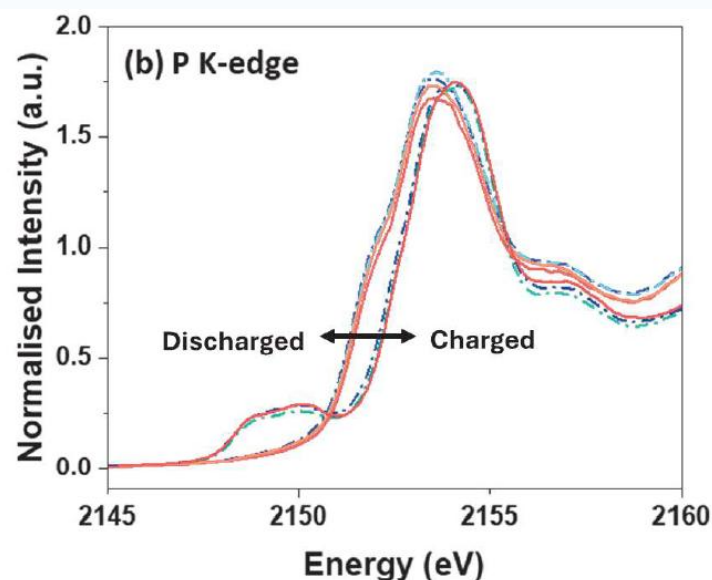
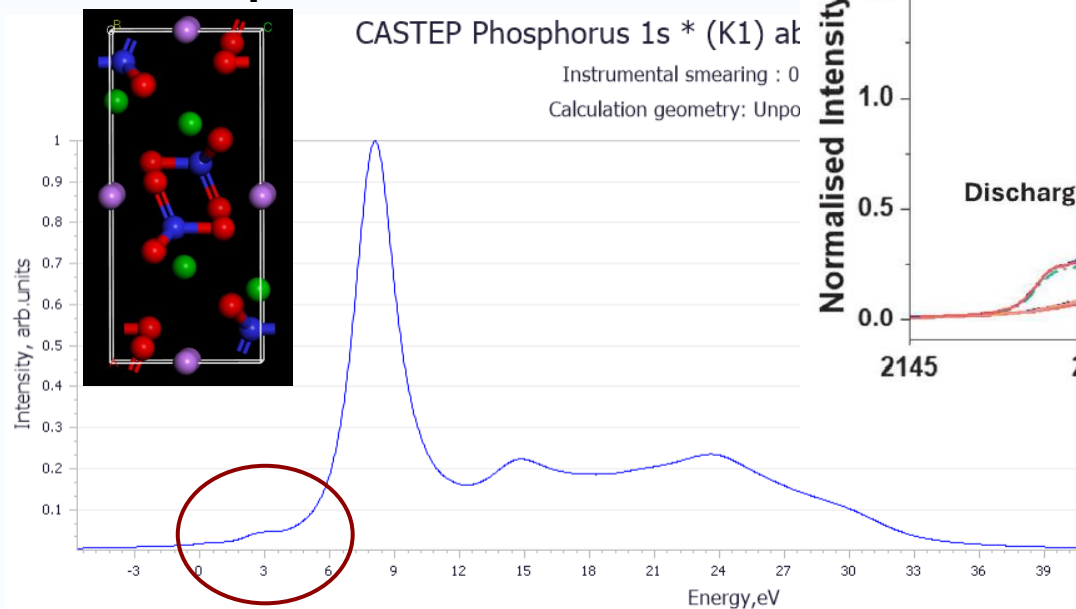


For this tutorial we will use Materials studio (D'Assult package) to model LiFePO_4 (LFP) and FePO_4 (FP)

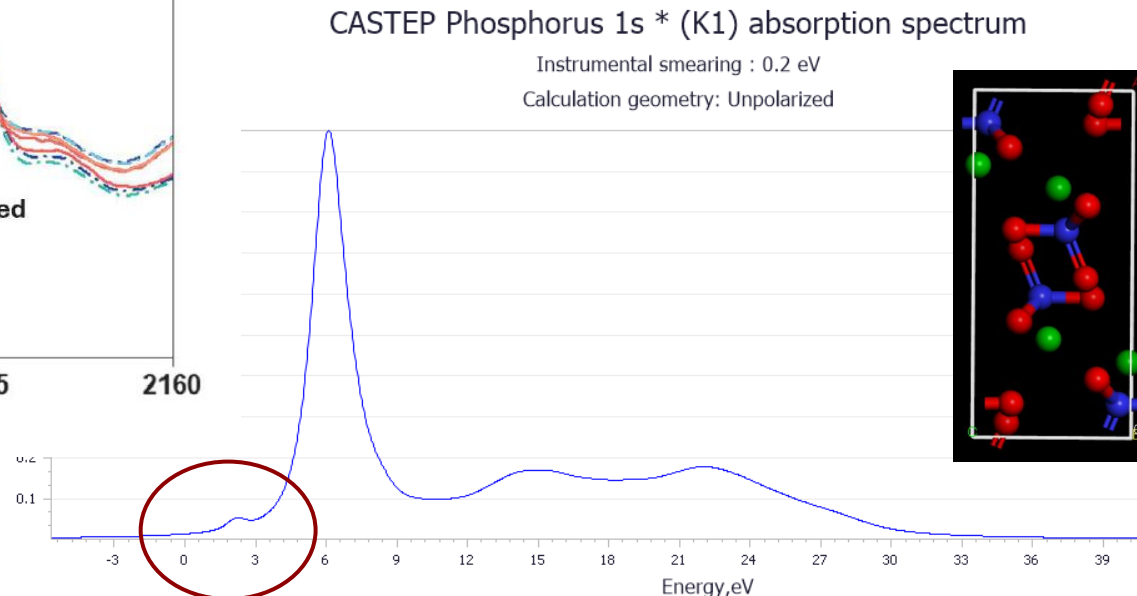
Steps:

1. Calculate the X-ray Absorption Near Edge Spectra (XANES)
2. Properly represent the ELECTRONIC STRUCTURE
3. Calculate PDOS to interpret your features

LiFePO_4



FePO_4

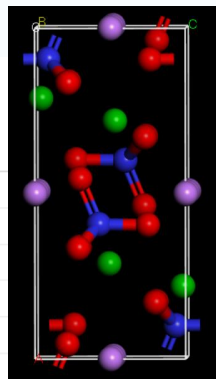


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Steps:

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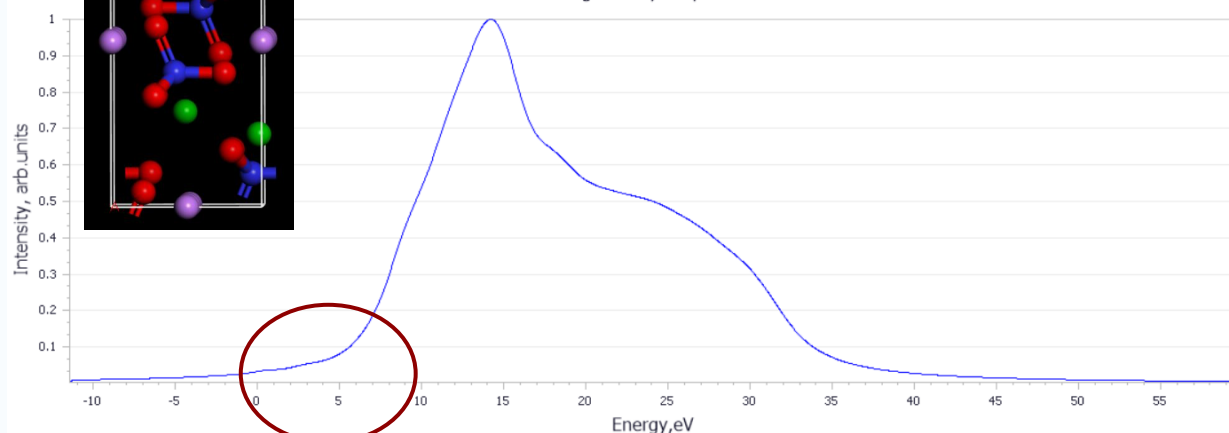
LiFePO_4



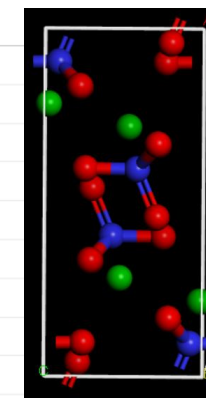
CASTEP Iron 1s * (K1) absorption spectrum

Instrumental smearing : 0.2 eV

Calculation geometry: Unpolarized



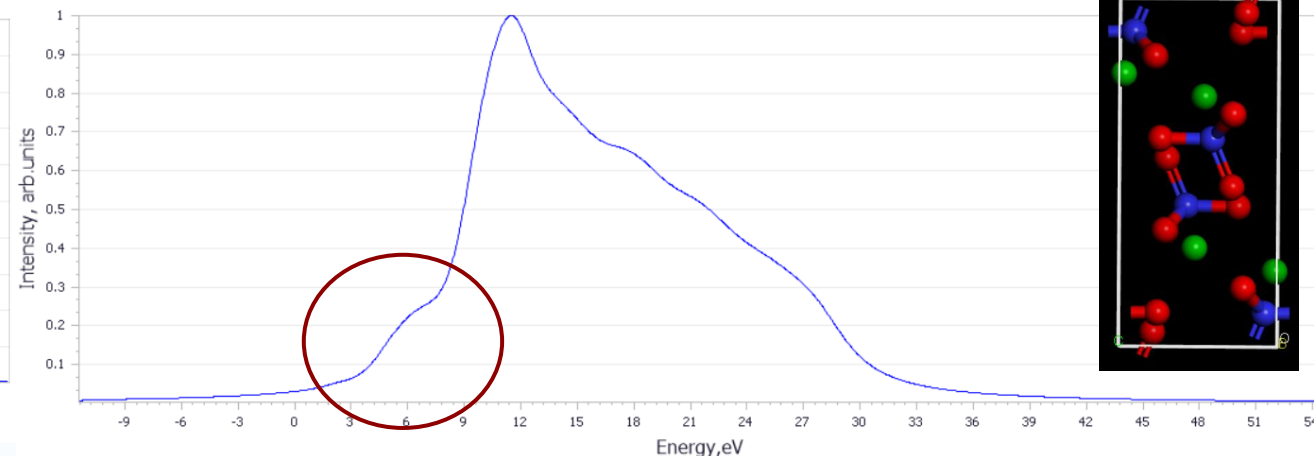
FePO_4



CASTEP Iron 1s * (K1) absorption spectrum

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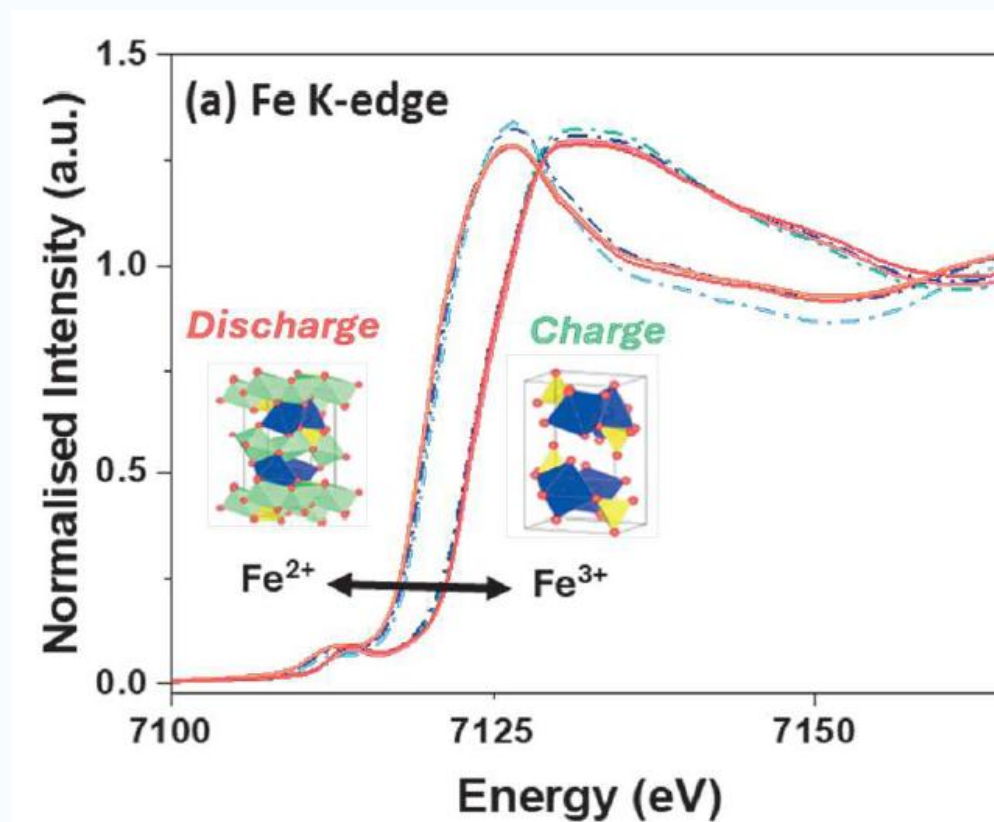
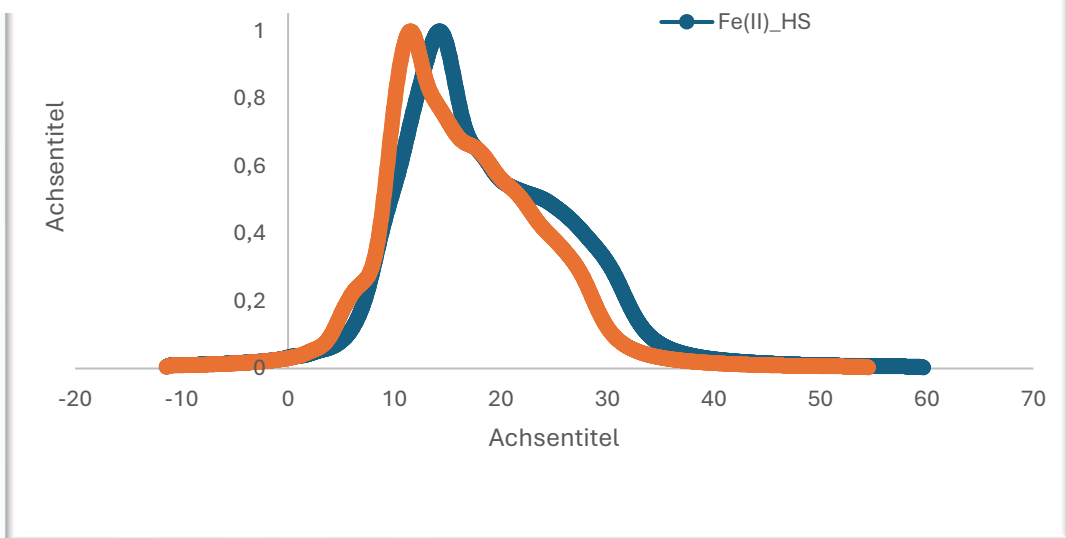
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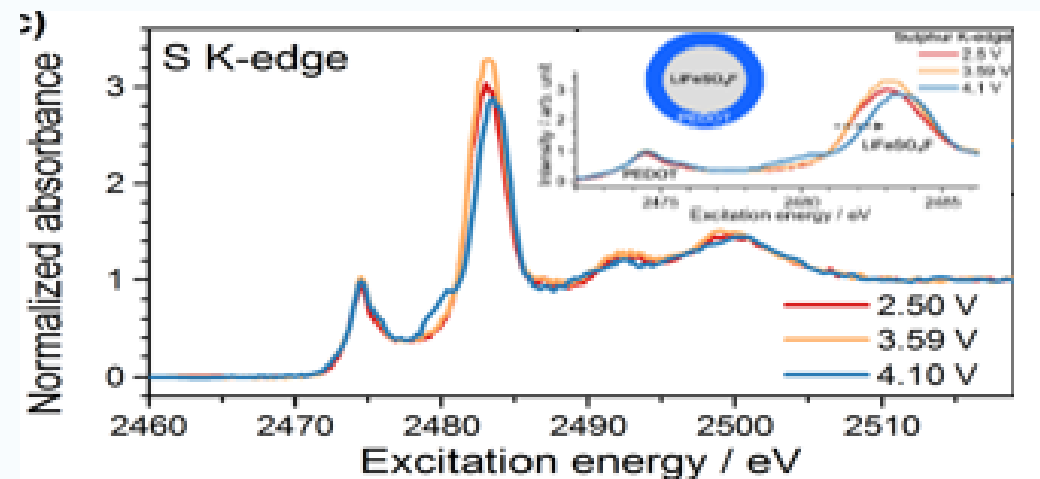
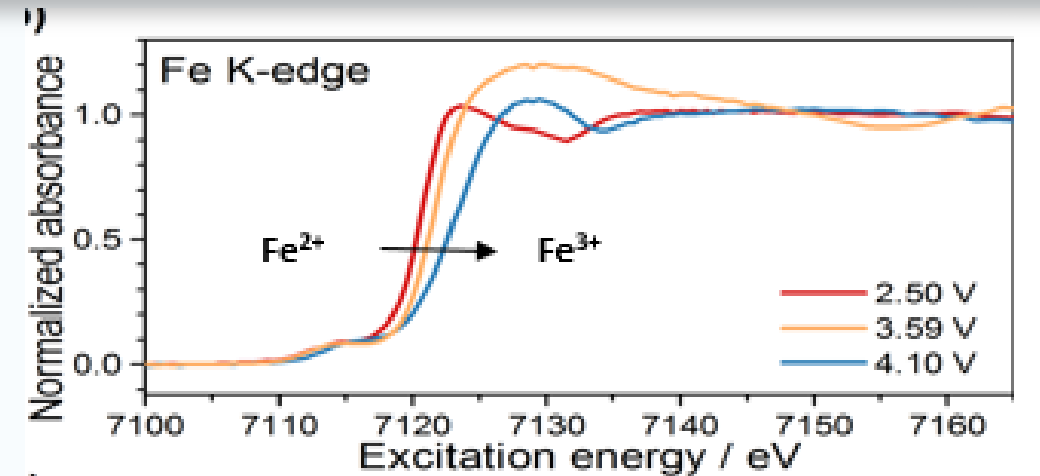
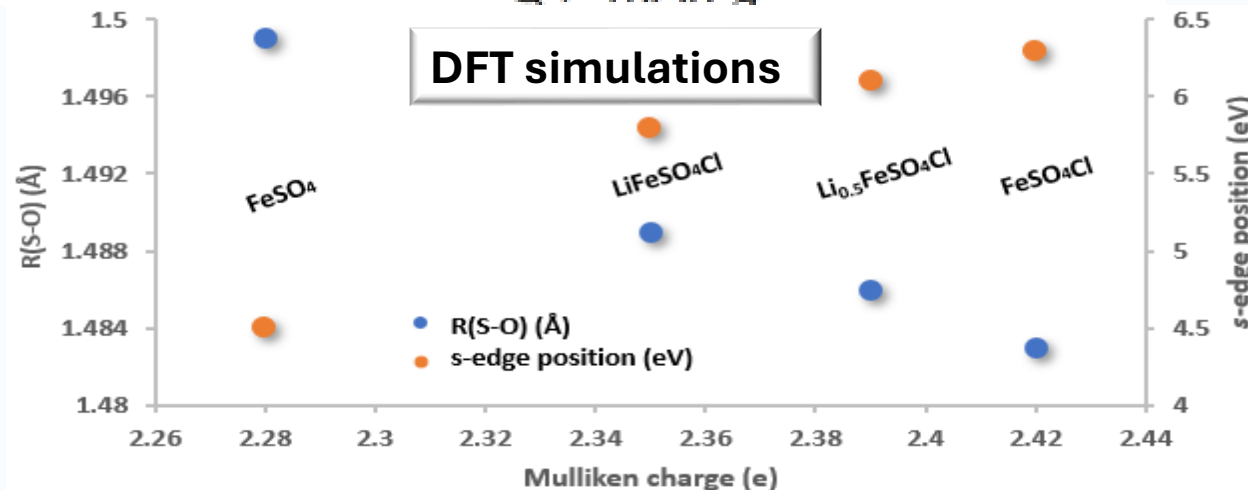
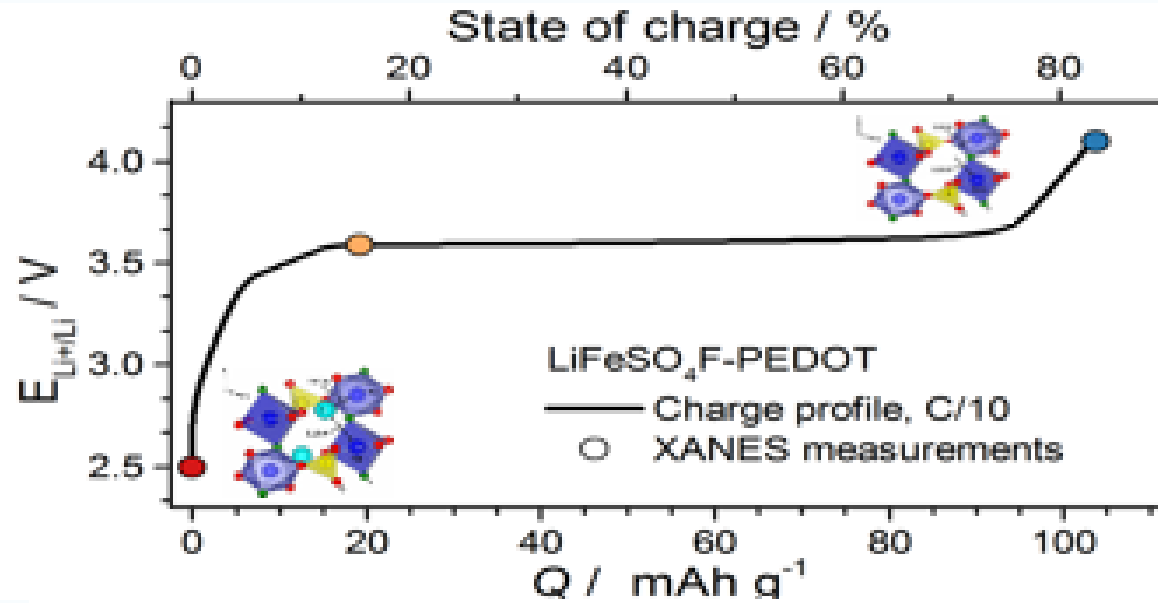
Two Issues:

1. Fe K-edge not shifted in calculation
2. Pre-edge features not correctly reproduced

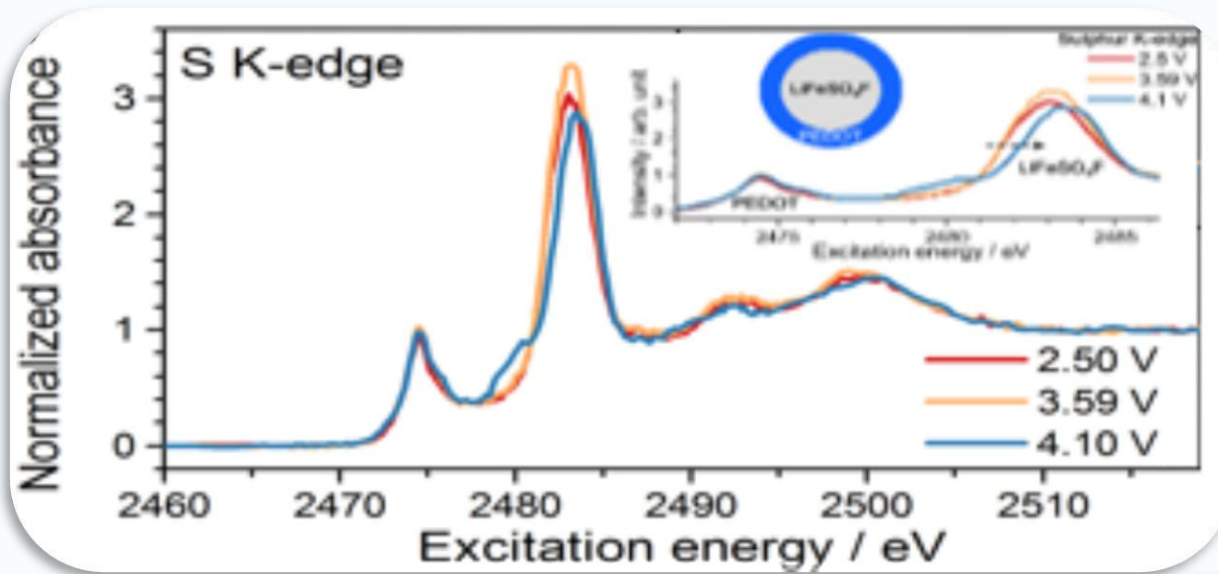


Addressing 1st Issue LiFeSO₄F - PEDOT (XAS)

- **S K-edge** in the SO₄²⁻ anion is sensitive to **changes** in electron distribution
- **Electron distribution changes with battery cycling**

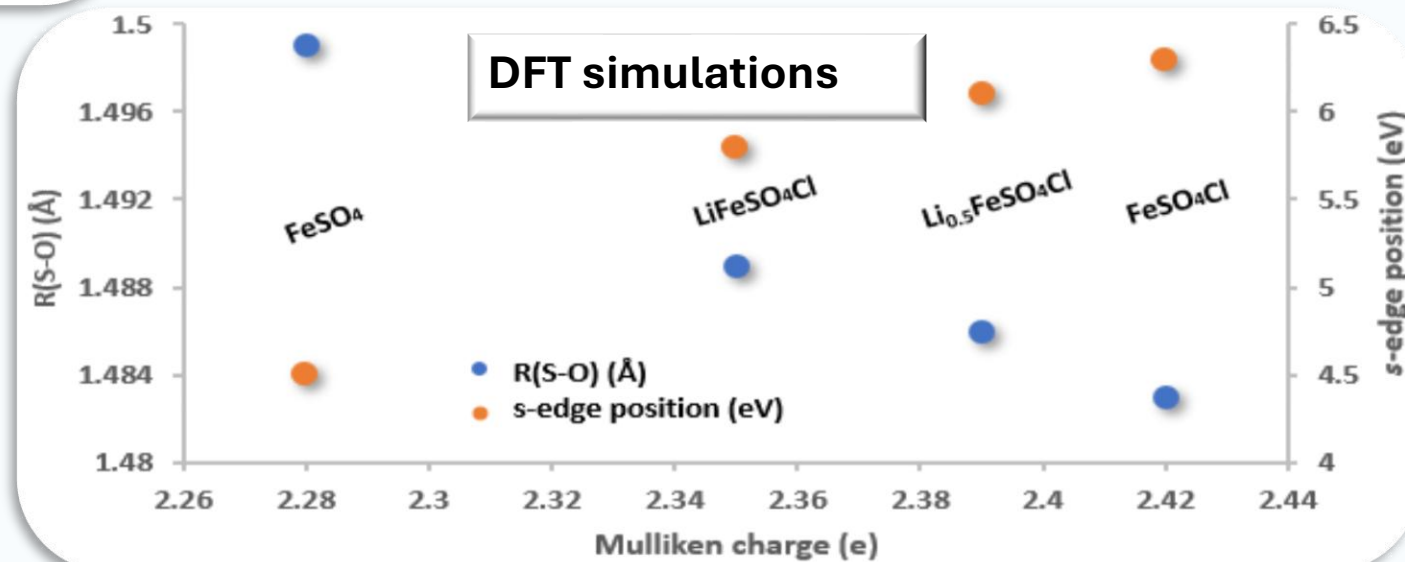


LiFeSO₄F - PEDOT (XAS)



- **S K-edge** in the SO₄²⁻ anion is sensitive to **changes** in electron distribution
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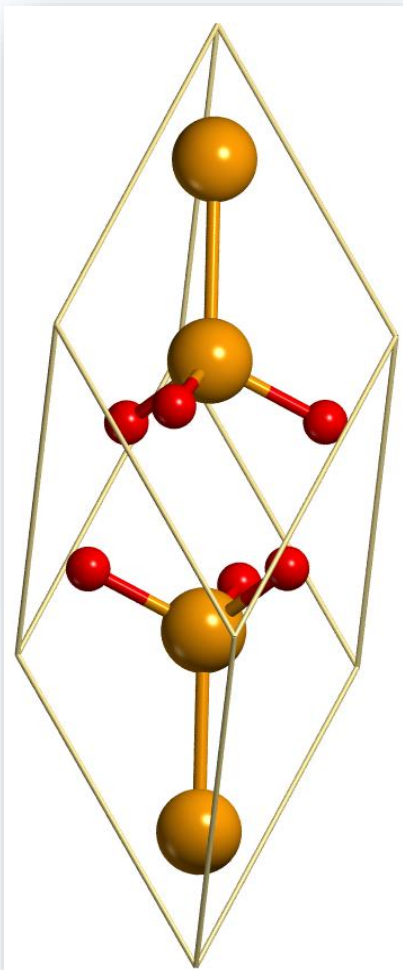
- **S K-edge** increases with oxidation of Fe²⁺ to Fe³⁺
- **R(S-O) bond distance** decreases as Fe²⁺ is oxidised to Fe³⁺
- **Mulliken charges on S** increases as Fe²⁺ is oxidised to Fe³⁺



Addressing 2nd issue

Density of States

$\alpha\text{-Fe}_2\text{O}_3$

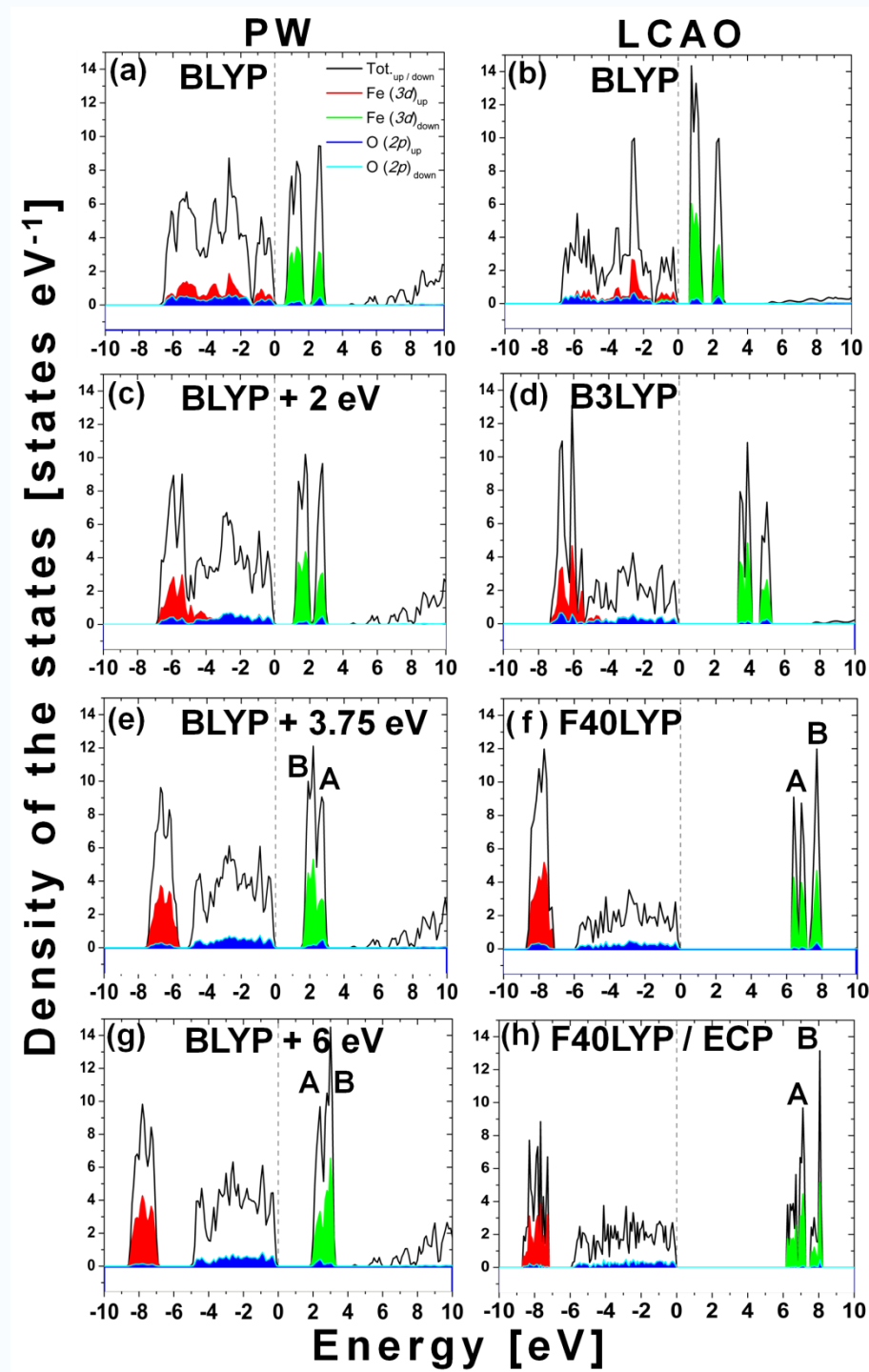


➤ Experimentally $\alpha\text{-Fe}_2\text{O}_3$:
charge transfer (CT)
insulator; O 2sp $\rightarrow$ 3d

➤ BLYP $\Rightarrow$ Mott Insulator
O 2sp/Fe 3d $\rightarrow$ Fe 3d

➤ B3LYP $\Rightarrow$ Mott Insulator
O 2sp/Fe 3d $\rightarrow$ Fe 3d

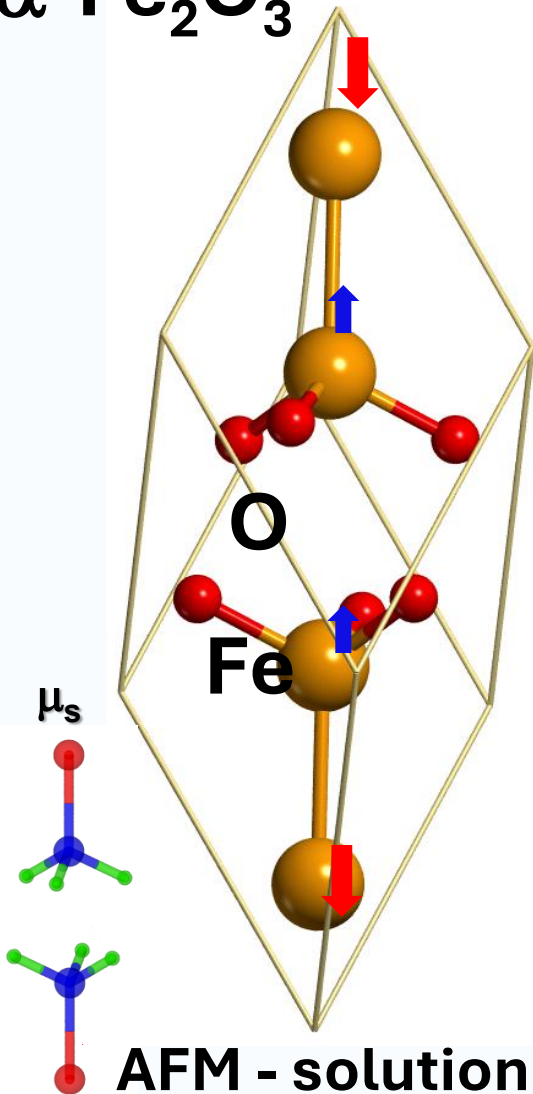
➤ BLYP+3.75 and F40LYP
 $\Rightarrow$ CT Insulator;
O 2sp $\rightarrow$ Fe 3d



Modelling of XANES spectra

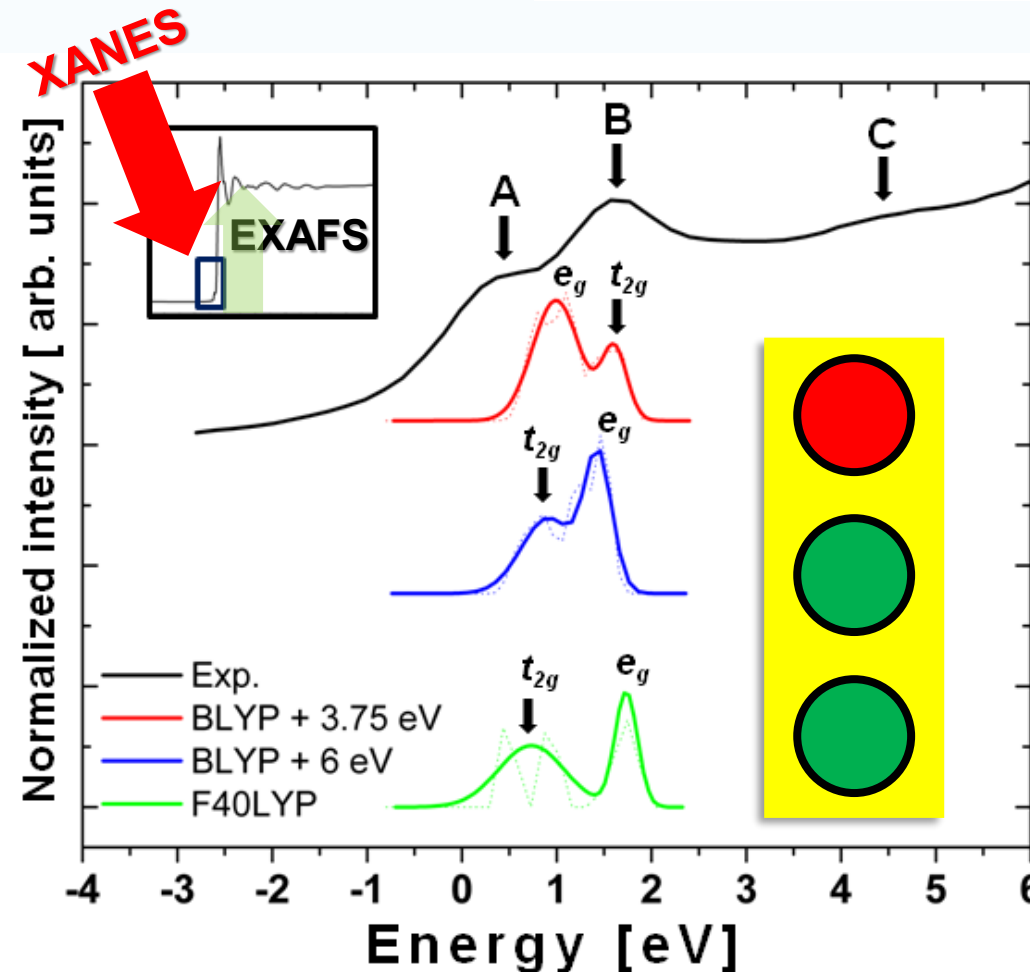
Which of the interpretations is correct?

$\alpha\text{-Fe}_2\text{O}_3$



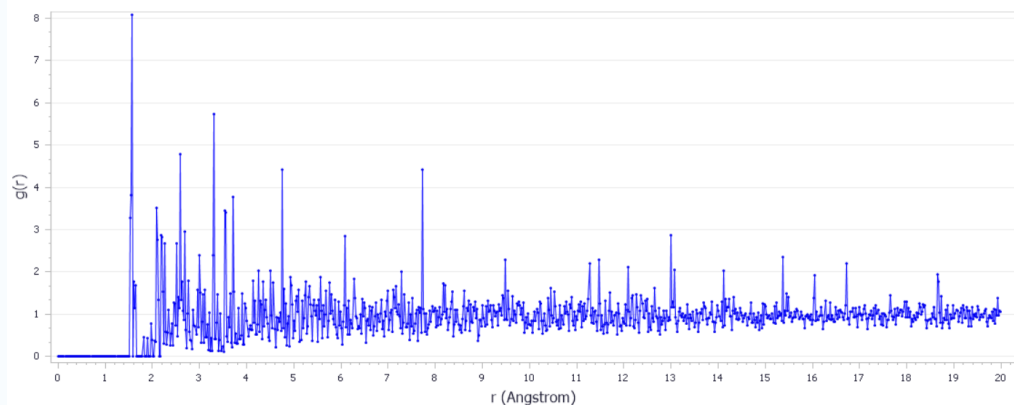
AFM - solution

What is the solution?
Hybrid DFT methods
applied to model XANES

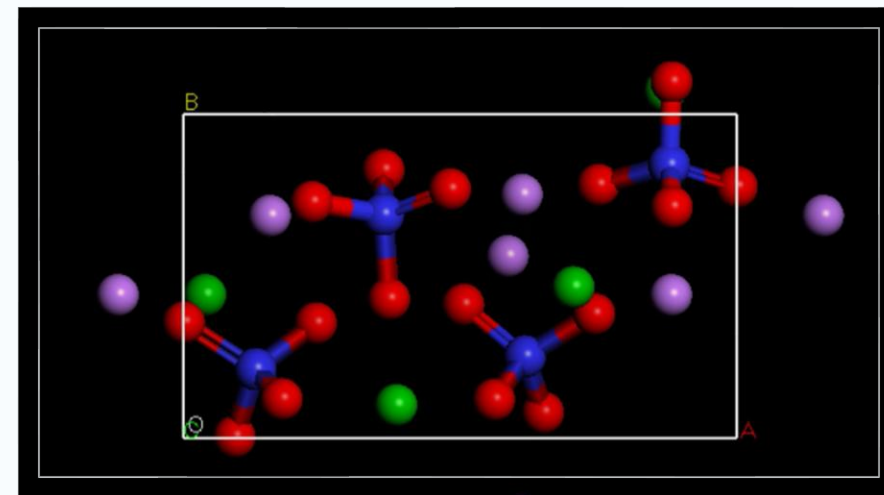
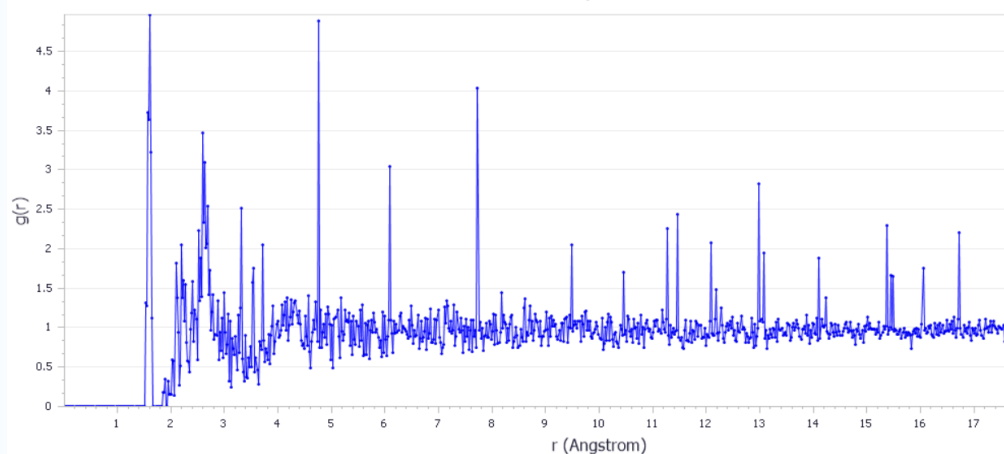


Modelling of EXAFS spectra

Forcite Analysis - RDF

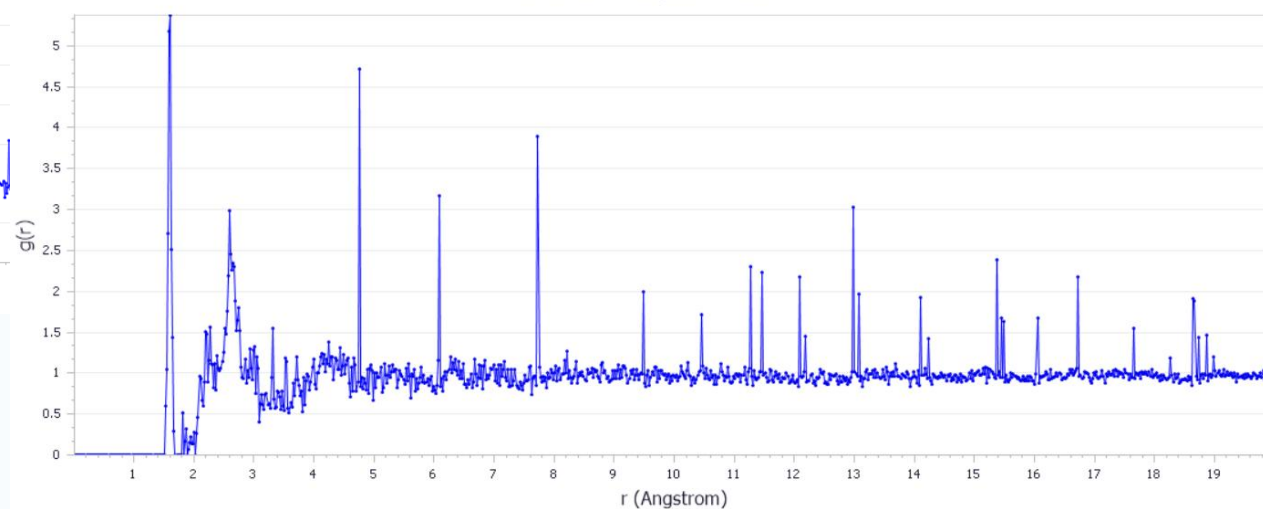


Forcite Analysis - RDF



Time

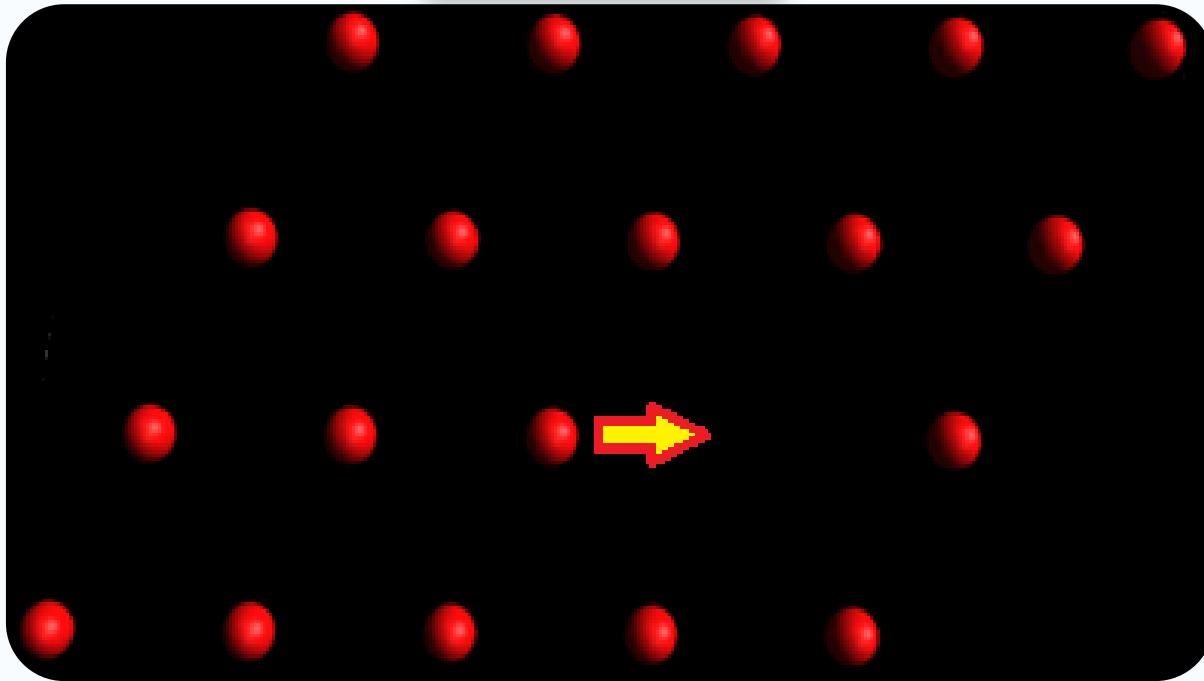
Forcite Analysis - RDF



Modelling of EXAFS spectra

Solid oxide fuel cells – Conduction mechanisms

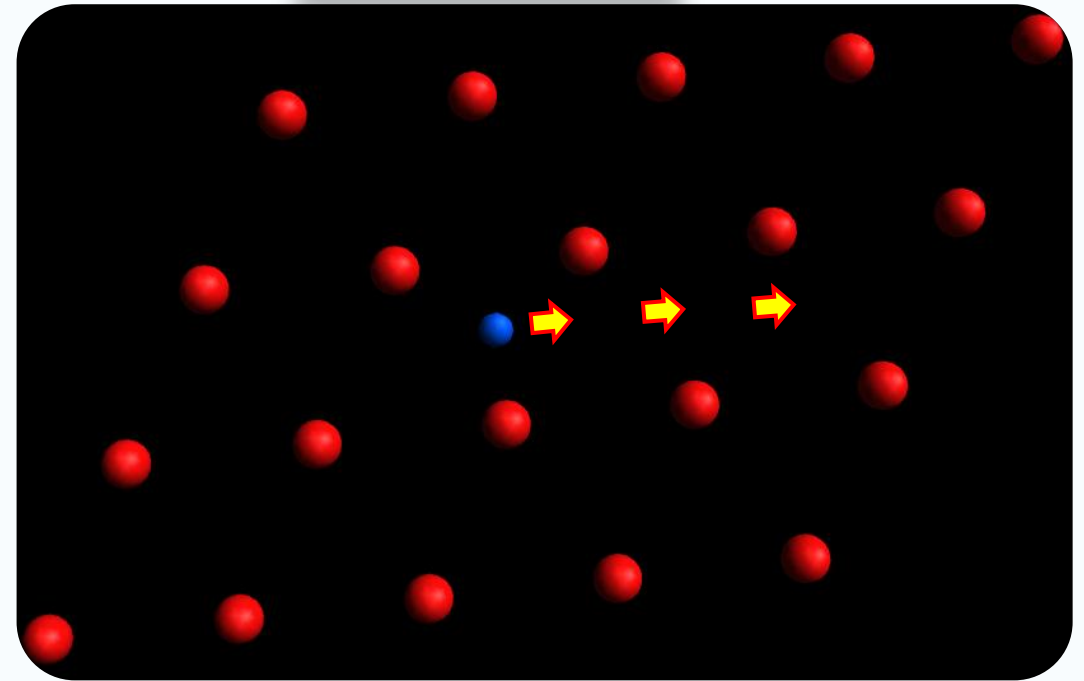
Vacancy



Working temp ~900°C

Marcus Bertuzzo

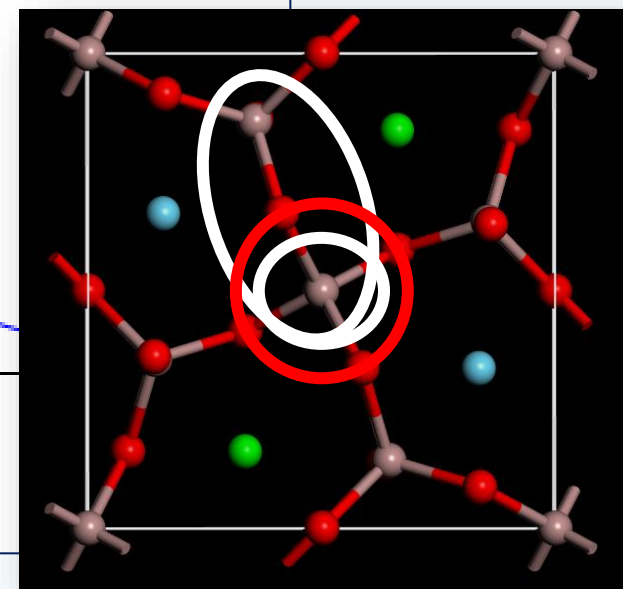
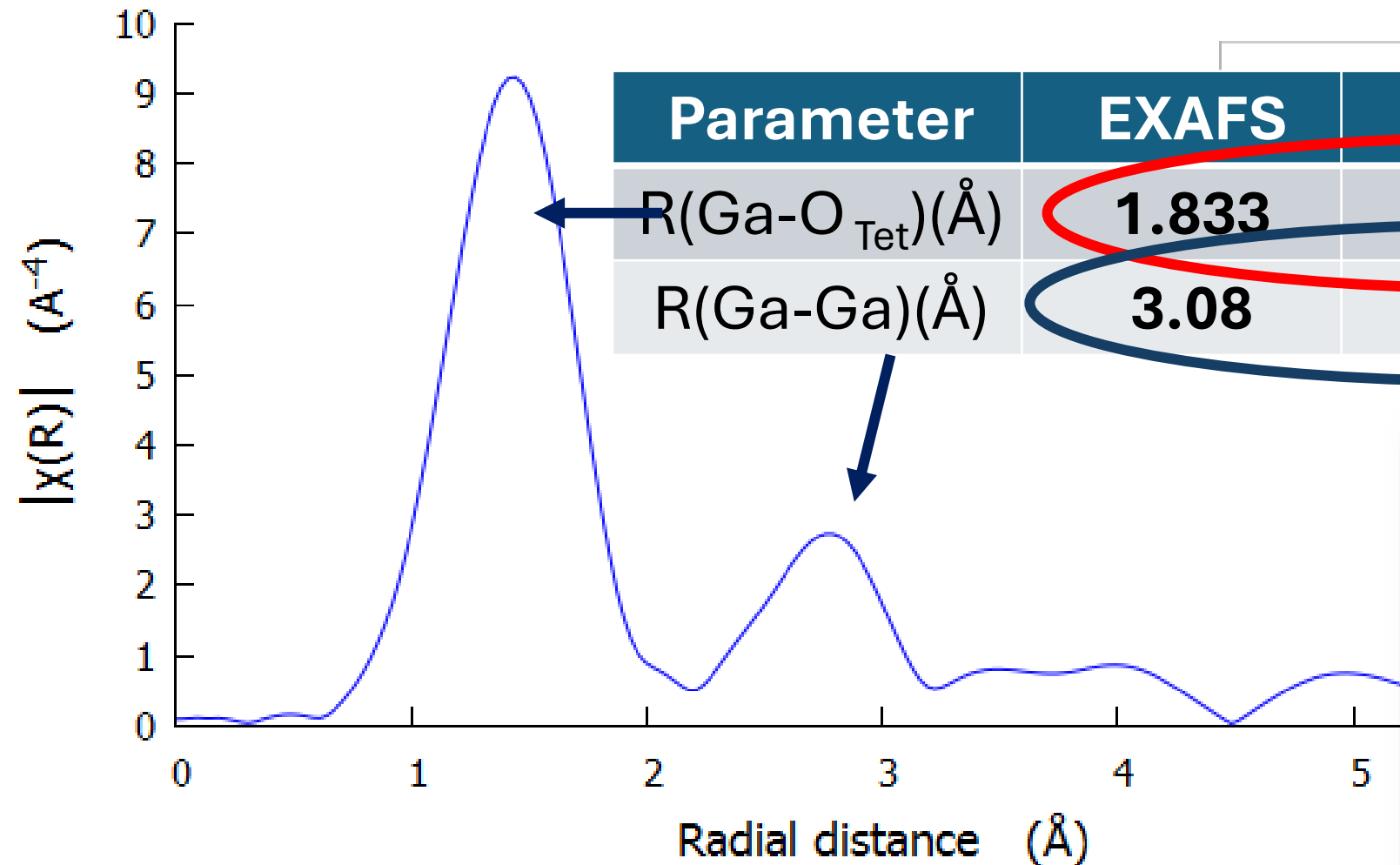
Interstitial



Working temp ~600°C

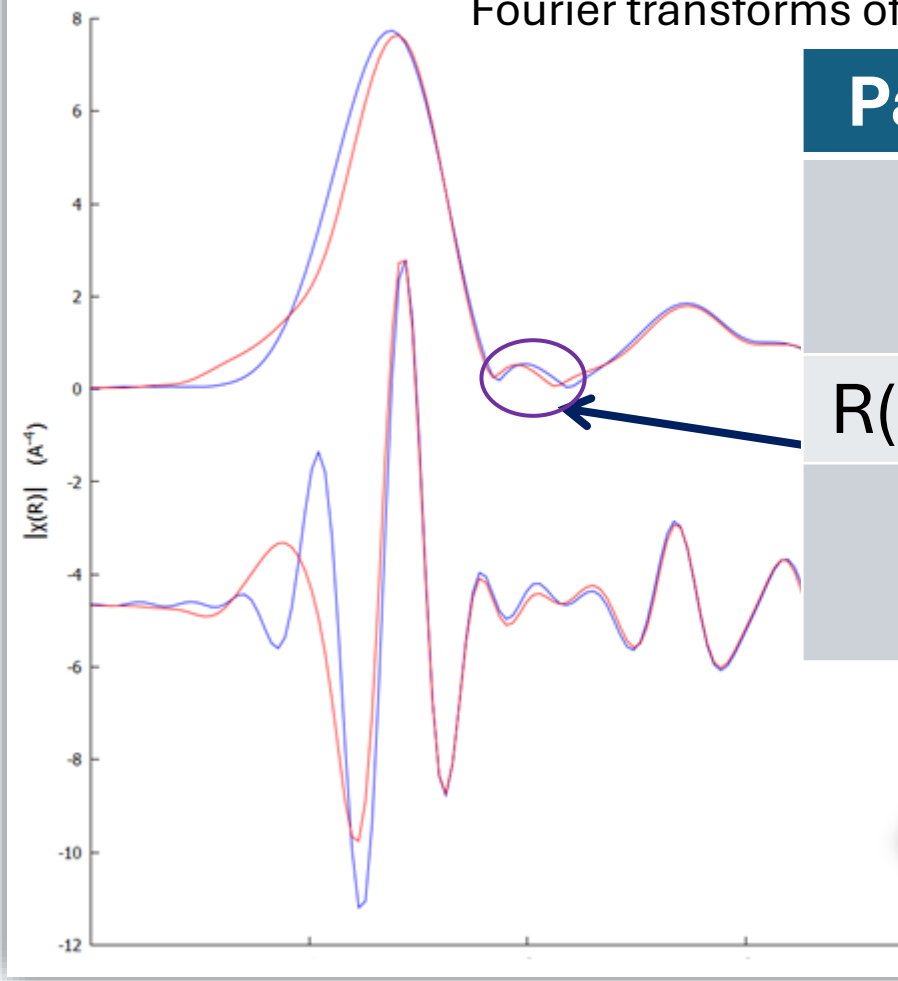
Results – LaSrGa₃O₇

LaSrGa₃O₇ in R space

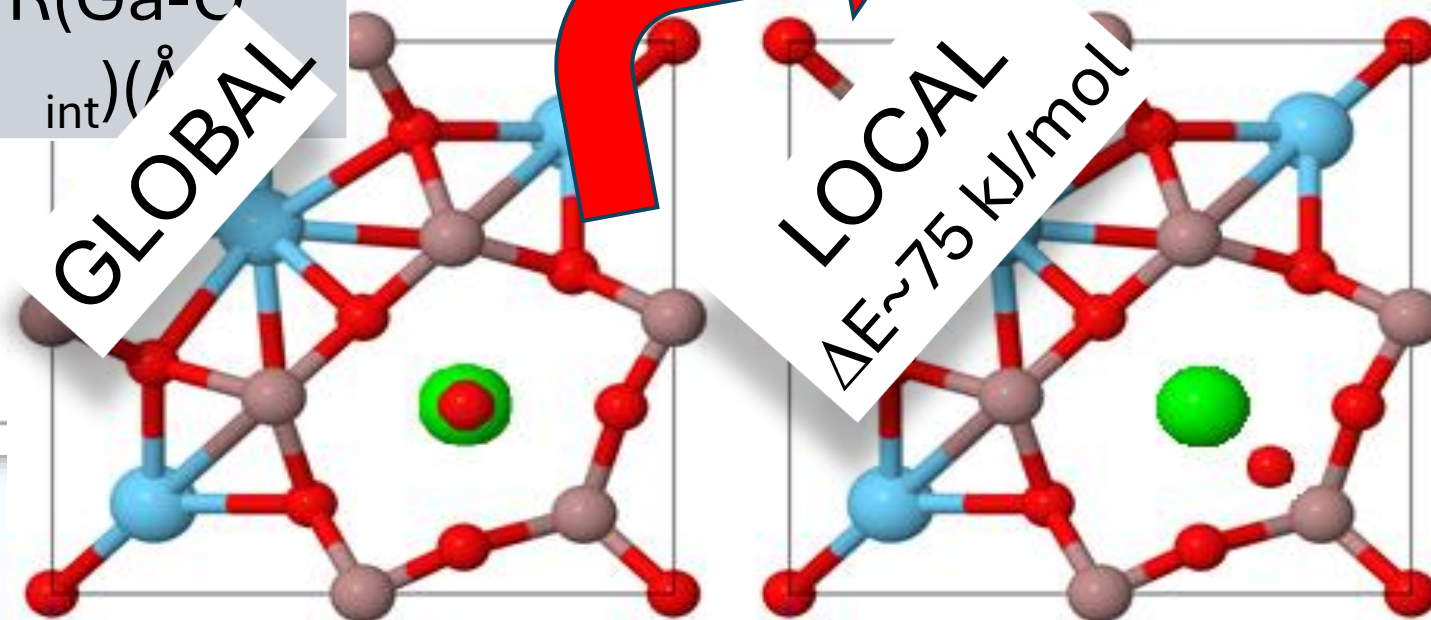


La_{1.5}Sr_{0.5}Ga₃O_{7.25}

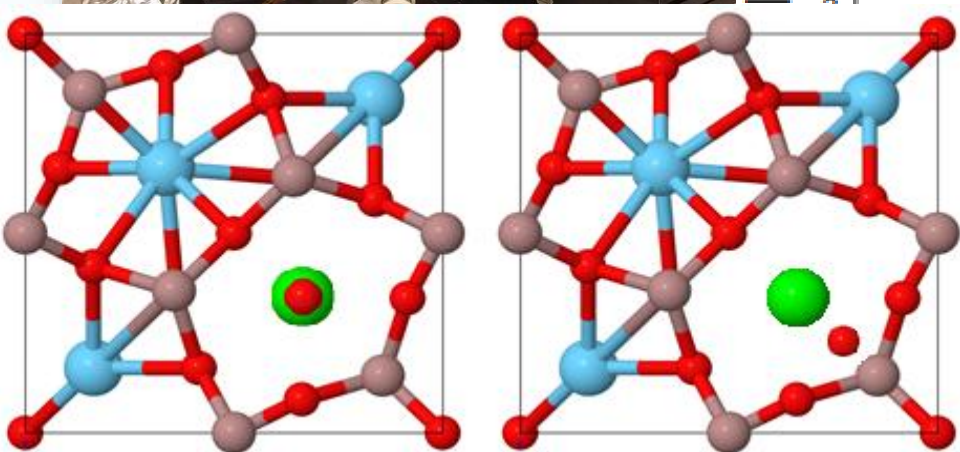
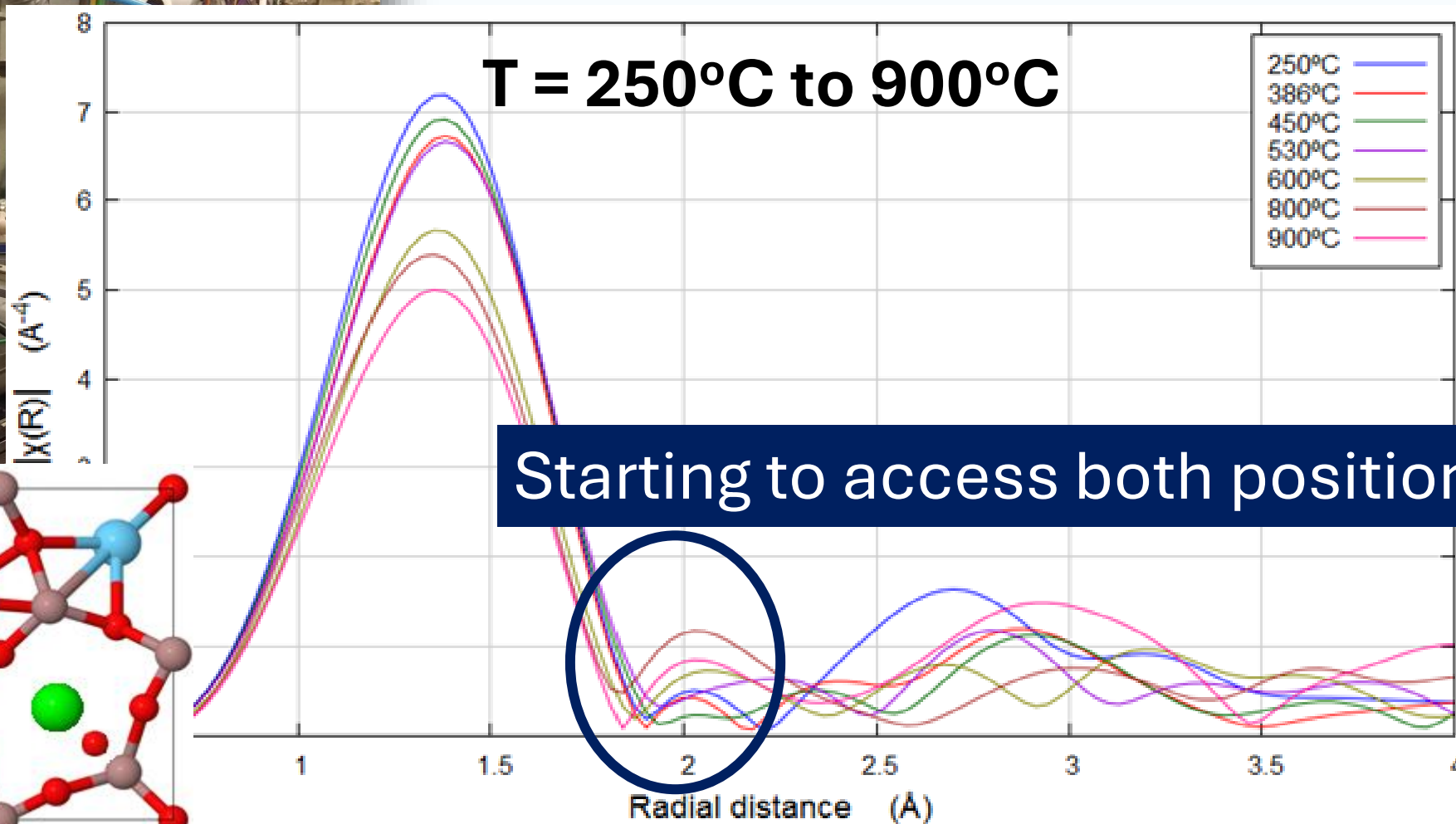
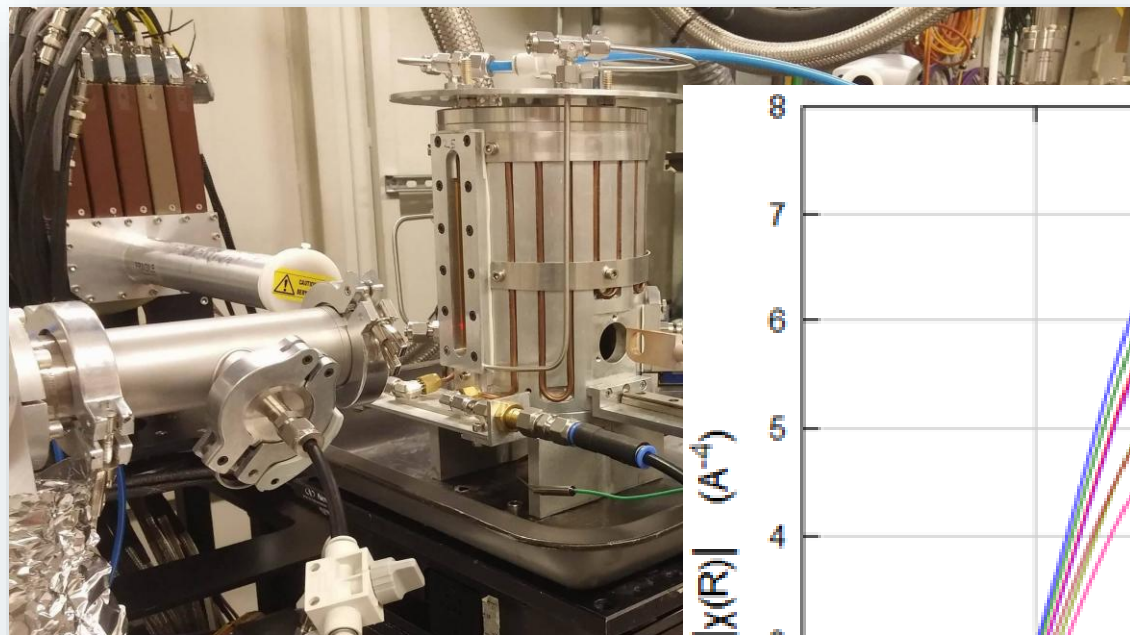
Ga K-edge EXAFS spectra (k^3 -weighted) and corresponding Fourier transforms of the parent



Parameter	EXAFS	DFT
R(Ga-O _{Tet})(Å)	1.833	1.84
R(Ga-Ga)(Å)	3.08	3.11
R(Ga-O _{int})(Å)	2.036	2.07

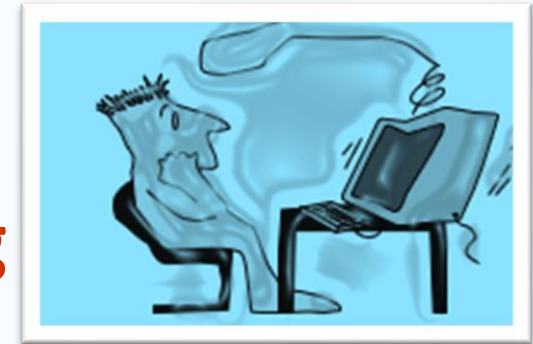


Getting hotter.....



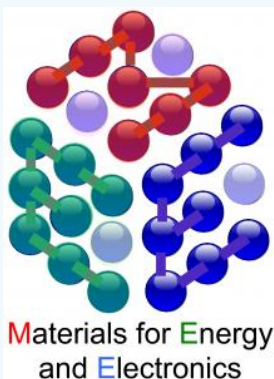
Layout

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- RESEARCH talk: Can computational modelling reveal what experiments can't?



Can computational modelling reveal what experiments can't?

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School of Natural Sciences,
University of Kent, Canterbury, UK
m.l.alfredsson@kent.ac.uk

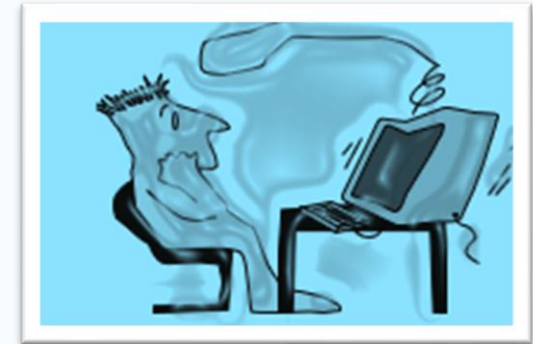
Stand for ambition.
kent.ac.uk

26/03/2026
Zoom-meeting



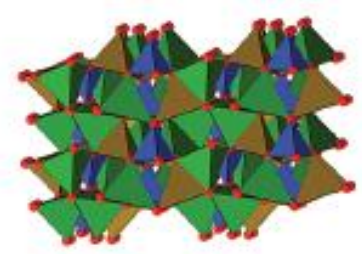
Layout

- Oxygen redox in $\text{Li}_2\text{FeSiO}_4$: Insights from X-ray Raman Spectroscopy (XRS)
- How manage Oxygen redox in LiNiMnCoO_2 (NMC): Insights from DFT simulations

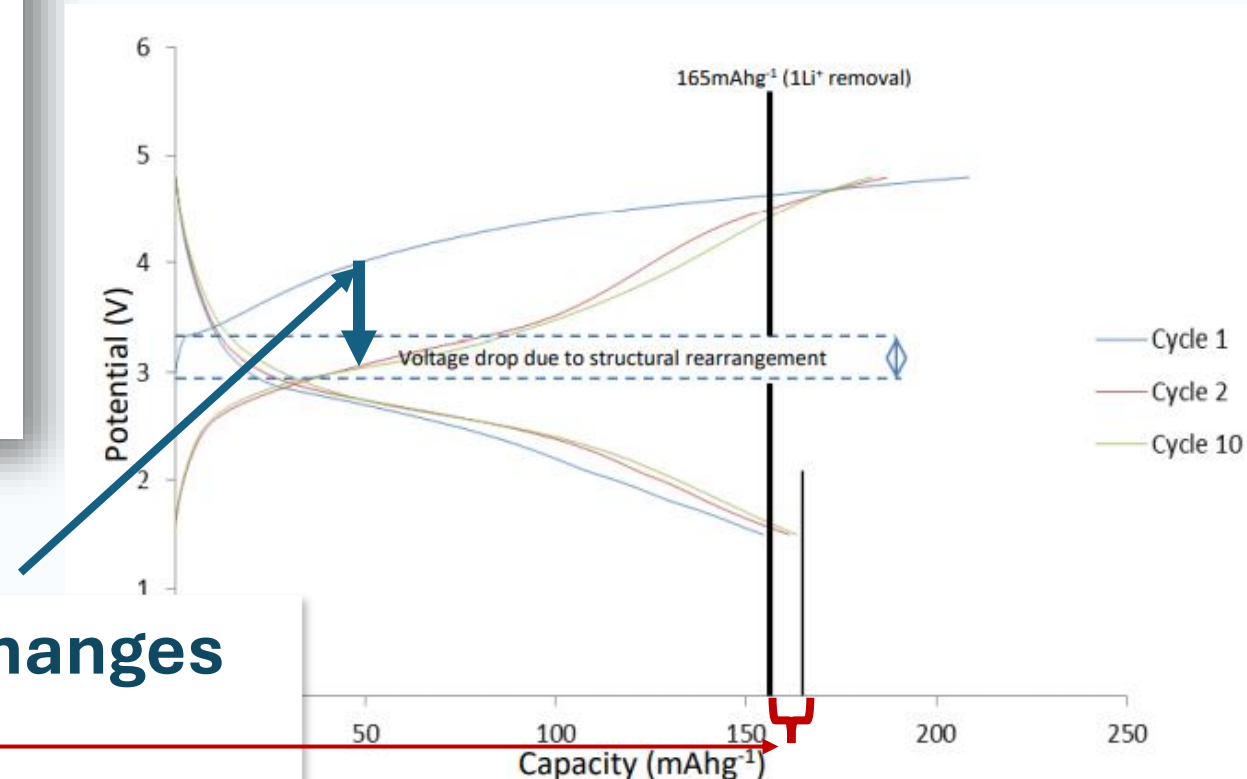
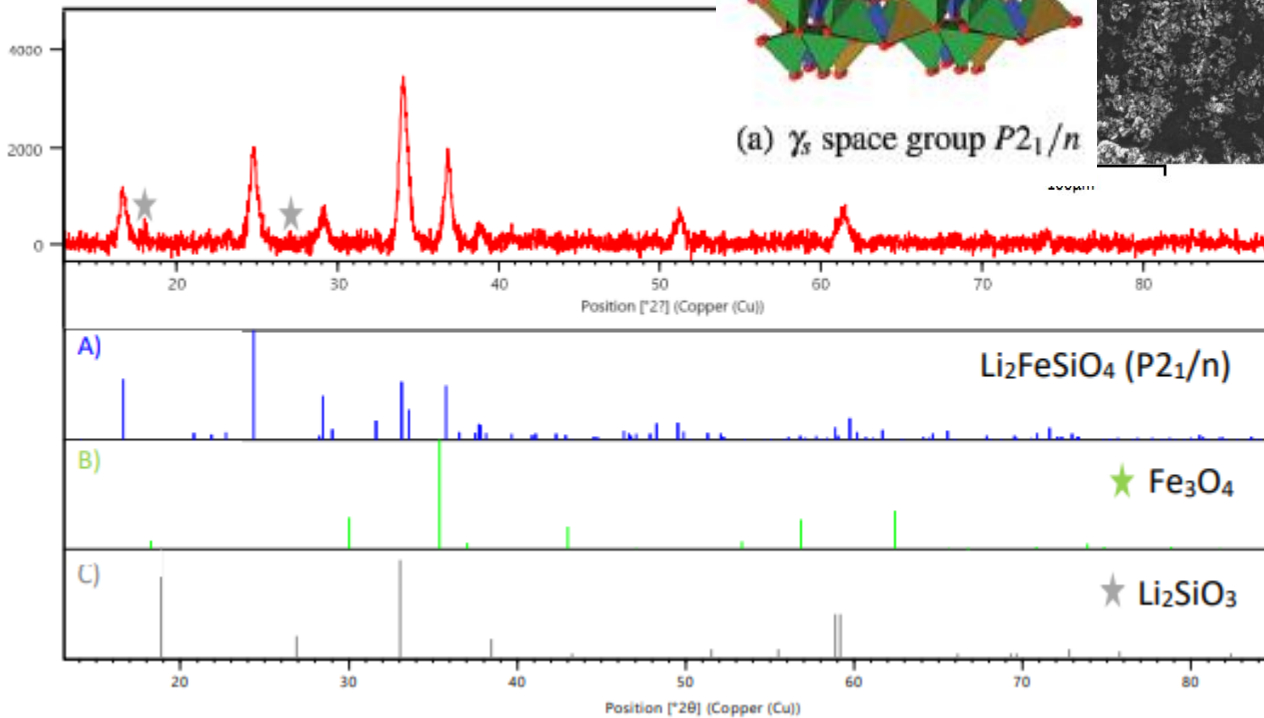
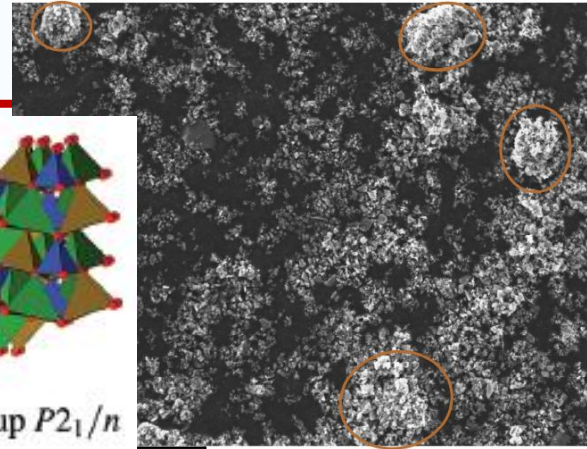


$\text{Li}_2\text{FeSiO}_4$ (XRD)

Sol-Gel



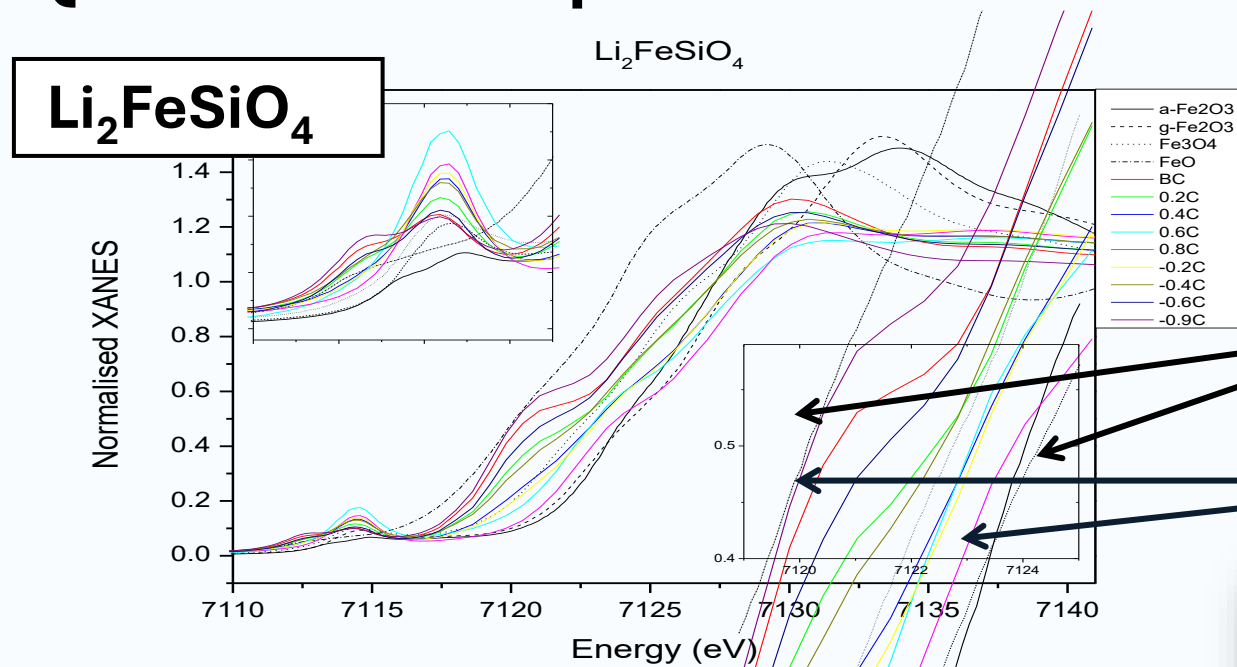
(a) γ_s space group $P2_1/n$



1. Voltage drop because structural changes
2. Extra capacity?

Li₂FeSiO₄ (In operando XAS)

Question 1: Is it possible to access the $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{4+}$ redox pair?



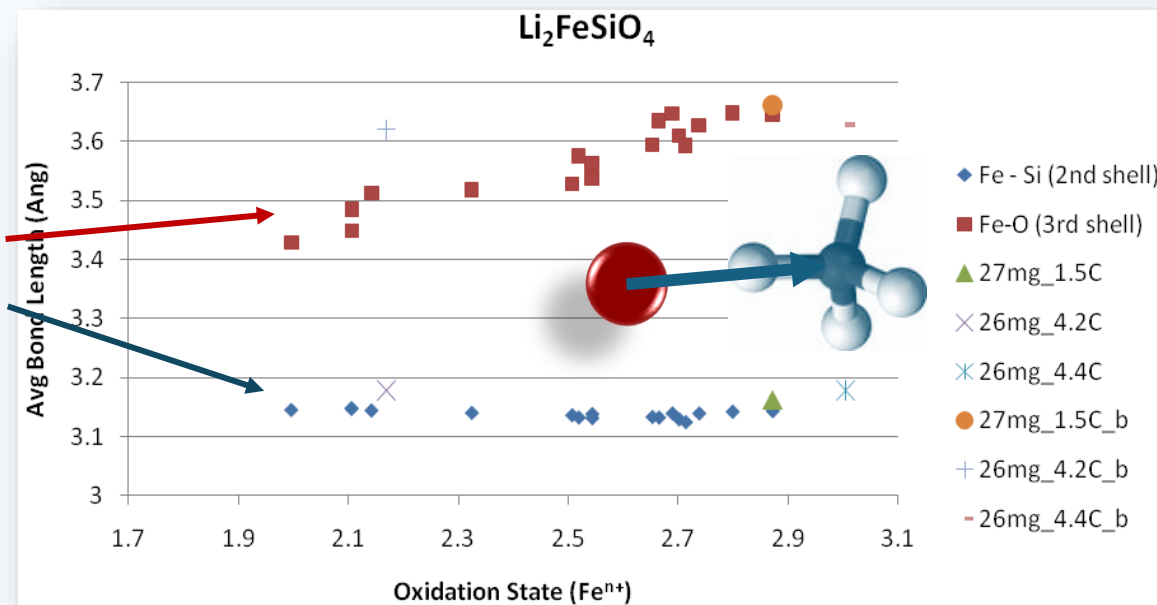
No evidence Fe⁴⁺

Fe(II)O and
Fe₂(III)O₃

**Cycled samples
Between (2+) and (3+)**

- **Fe – O distance increase with oxidation state**
- **Si – Fe constant as oxidation state change**

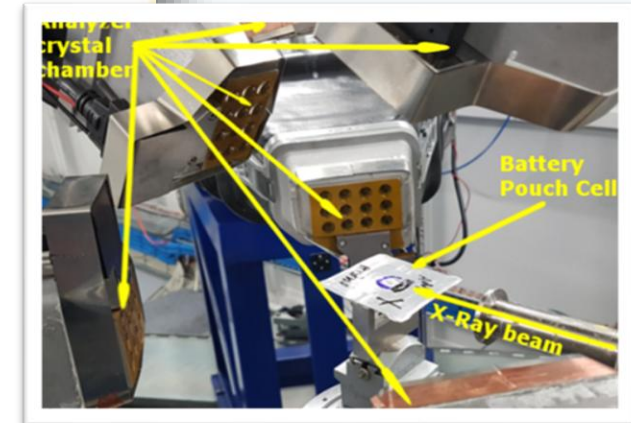
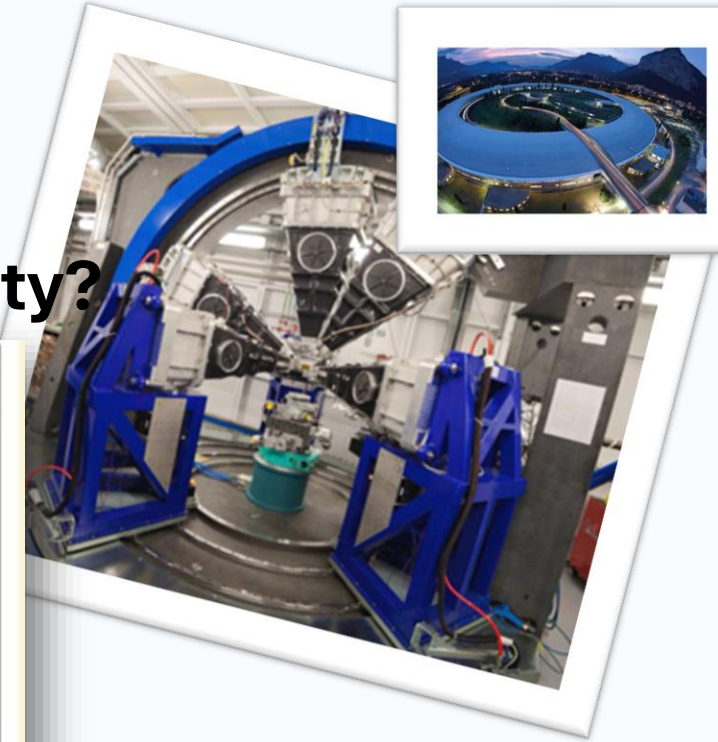
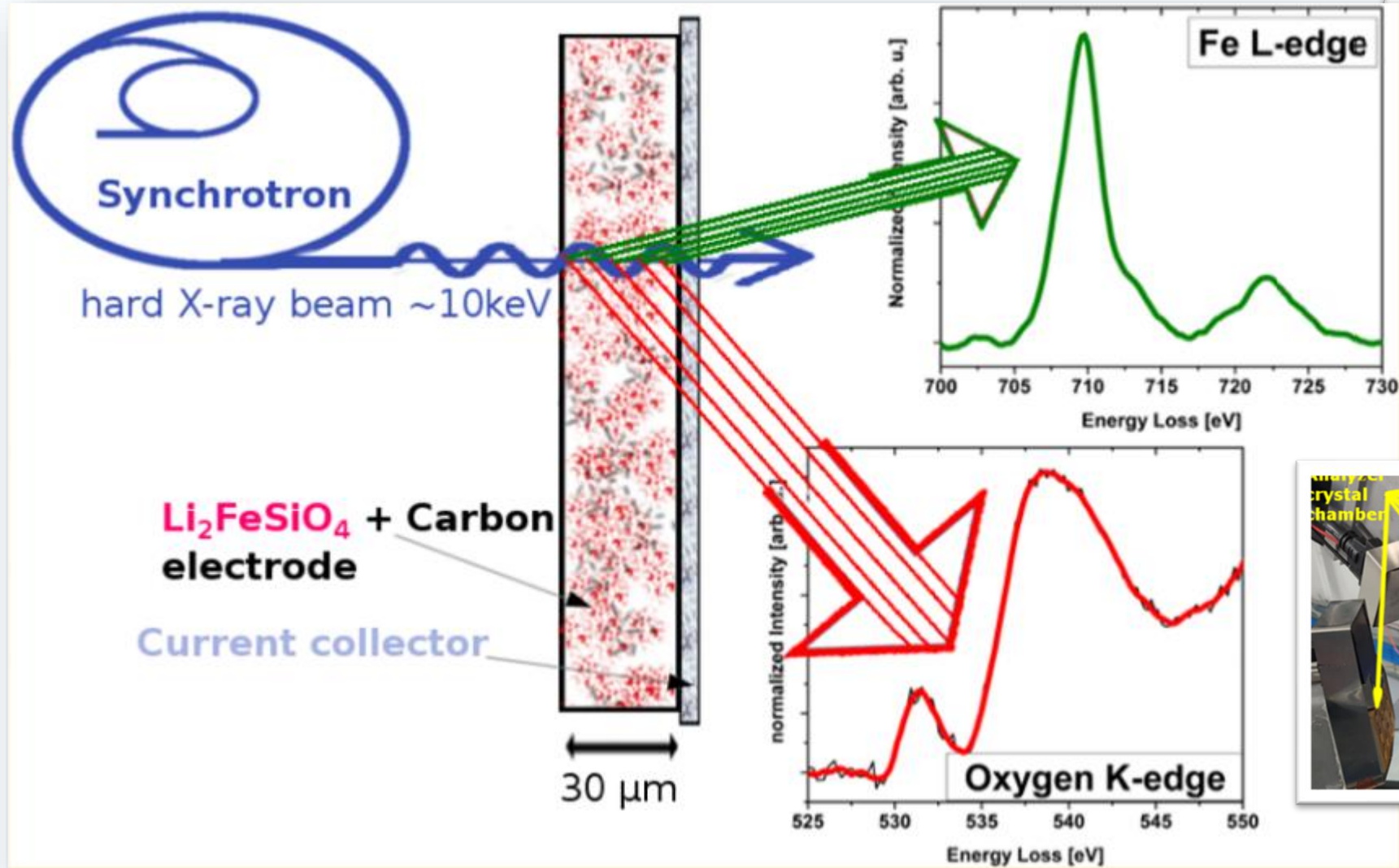
Question 2: Is O redox active?



$\text{Li}_2\text{FeSiO}_4$ (XRS) – Oxygen edge

Question 2:

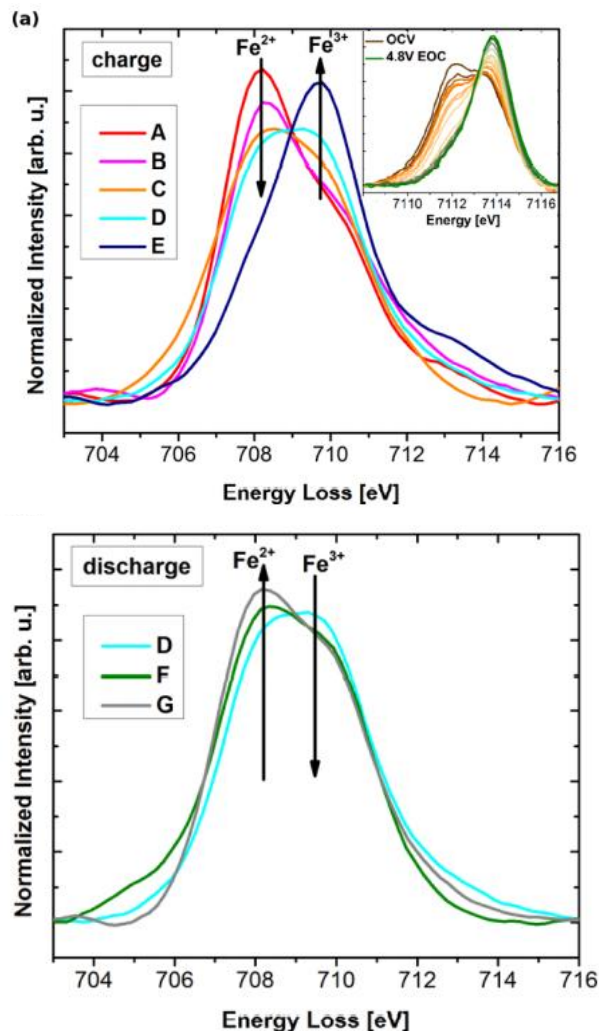
Is it possible to oxygen contributes to extra capacity?



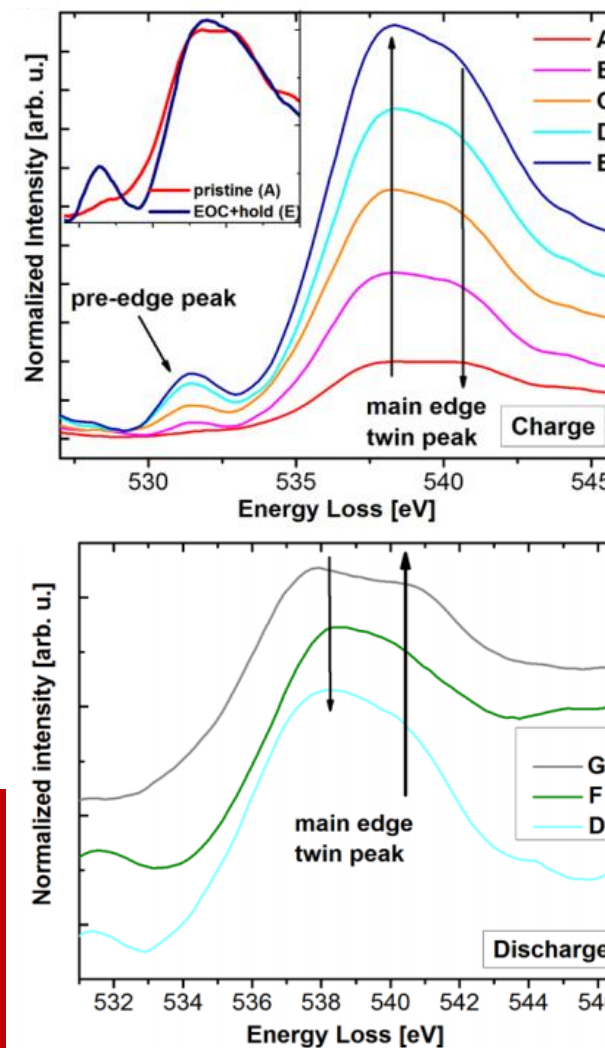
$\text{Li}_2\text{FeSiO}_4$ (XRS) – Oxygen edge

Question 2: Is O redox active?

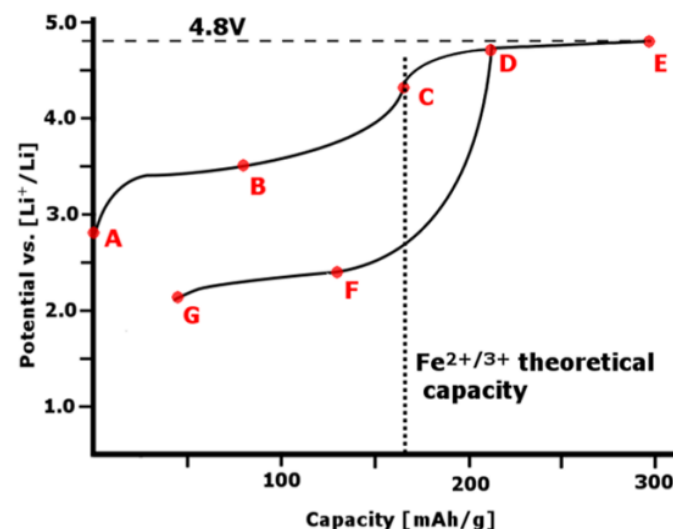
Fe L-edge



O K-edge



**Oxygen contributes
to the extra
capacity**

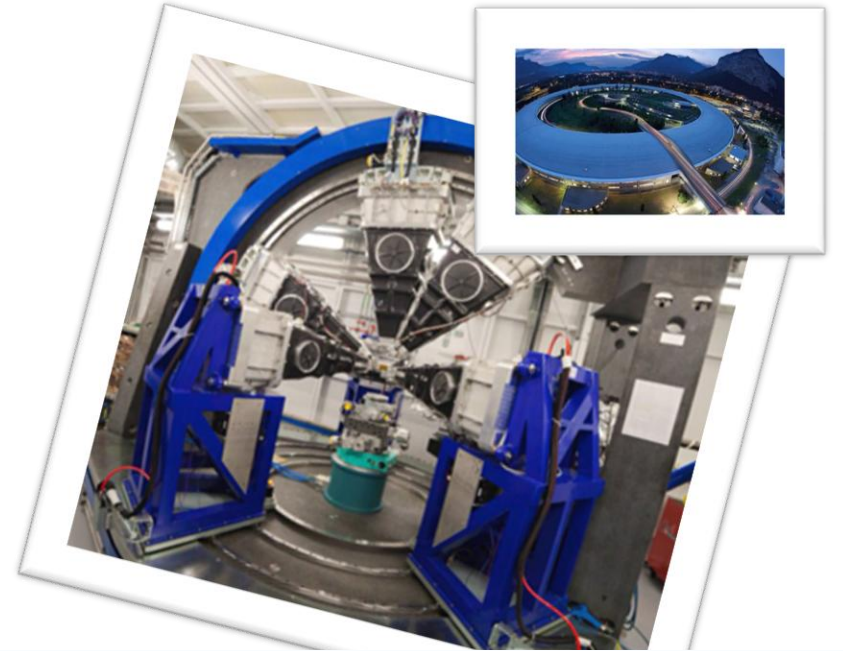


Take away message

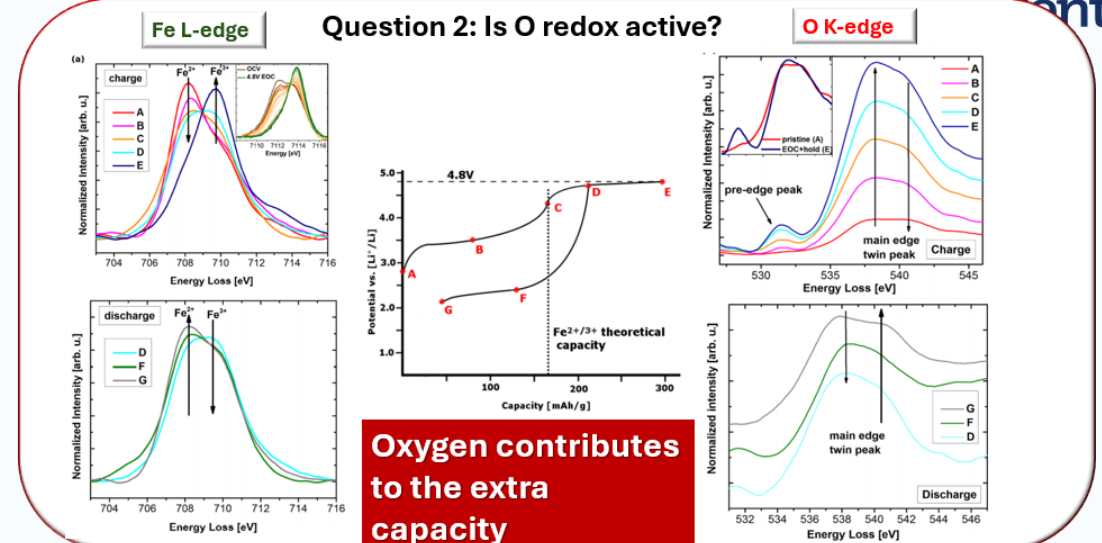
- No evidence of Fe^{4+}
- Electrolyte degradation above 4.2 eV
- Modify electrolyte hold cell at 4.5 eV
- O K-edge is redox active
- **Oxygen contributes to extra capacity**

What does the calculations tell us:

- $\text{Fe}^{3+}/\text{Fe}^{4+}$ reached about $>5.6 \text{ V}$
- Oxygen contributes to the DOS
- Modelling is **CRUCIAL** for the interpretation of the XRS simulations
- Your chances to get beamtime INCREASES if you predicted the XRS spectra



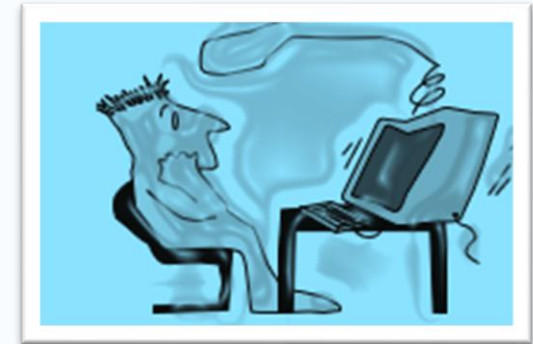
$\text{Li}_2\text{FeSiO}_4$ (XRS) – Oxygen edge



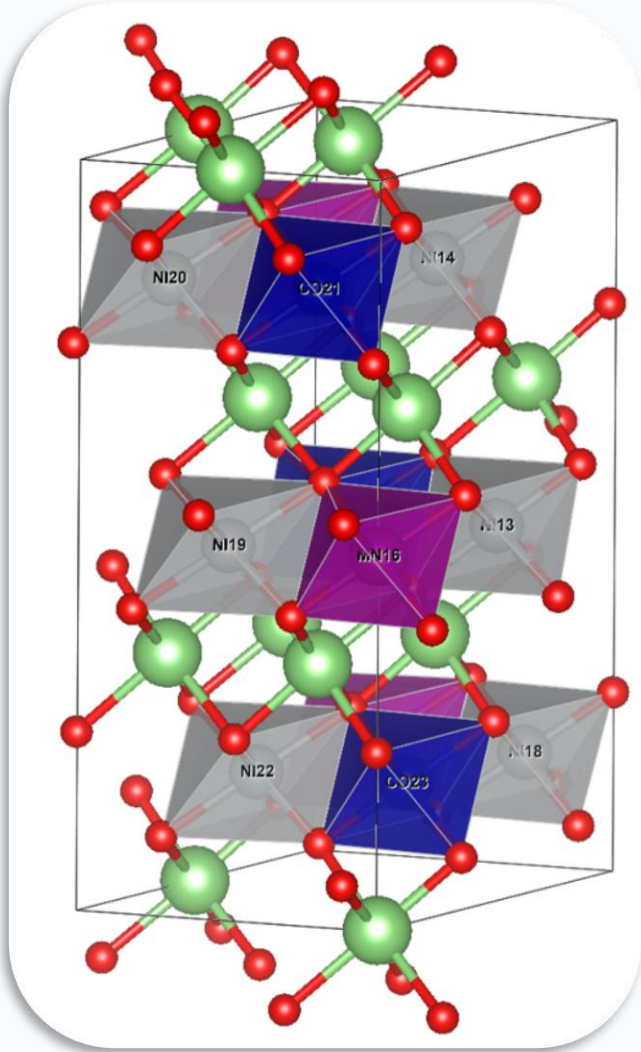
Bulk-Sensitive Soft X-ray Edge Probing for Elucidation of Charge Compensation in Battery Electrodes, Fehse M, Sahle CJ, Hogan MP, Cavallari C, Kelder EM, Alfredsson M, Longo A, J. of Physical Chemistry C, 123, p. 24396-24403 (2019)

Layout

- Oxygen redox in $\text{Li}_2\text{FeSiO}_4$: Insights from X-ray Raman Spectroscopy (XRS)
- How manage Oxygen redox in LiNiMnCoO_2 (NMC): Insights from DFT simulations



Aims of study



Our aims are:

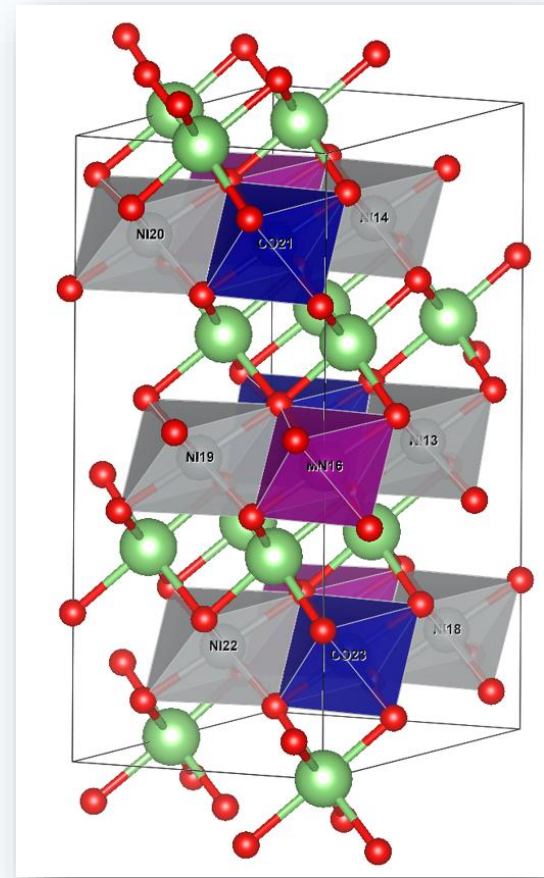
- Understand the activation of oxygen for different stoichiometries of NMC and
- Understand its effects on electrochemical performance



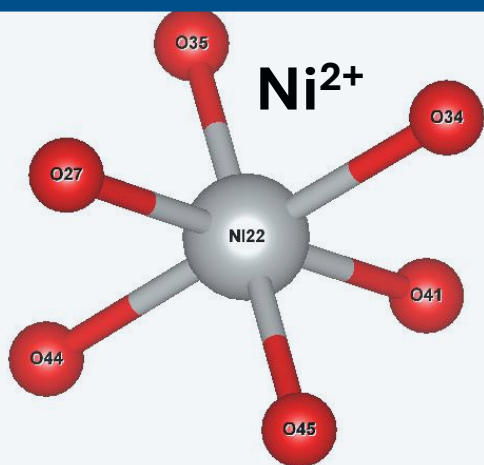
Computational Setup

Computational Set-up

- *CRYSTAL2023¹ – All electron Gaussian basis set*
- **PBE0** – hybrid functional
- 2x2x1 cell contains 12 transition metal (TM) sites.
- We thus refer to it as the *12-formula unit cell*.
 - **NMC633**: Ni-poor NMC phase compare NMC622
 - **NMC1011**: Ni-rich NMC phases compare NMC811



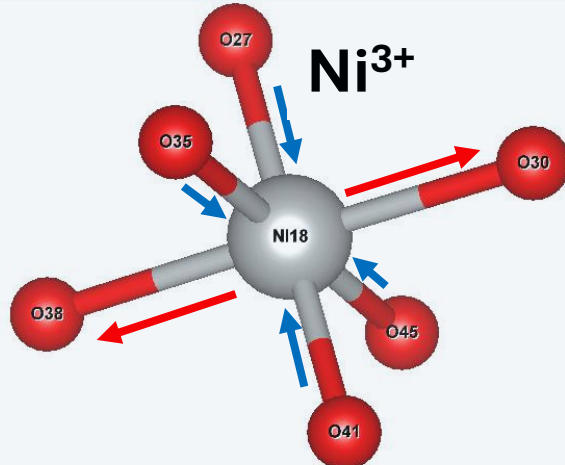
Jahn-Teller Distortion – Validation of method



Ni²⁺ Bond lengths (Å)

Ni-O	2.014
Ni-O	2.018
Ni-O	2.025
Ni-O	2.032
Ni-O	2.051
Ni-O	2.059

**6 x
Similar
Ni-O**



Ni³⁺ Bond lengths (Å)

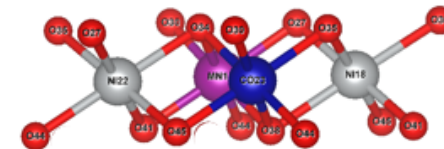
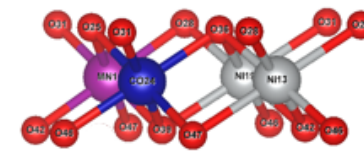
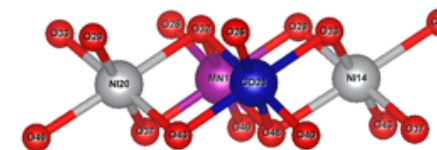
Ni-O	1.879
Ni-O	1.881
Ni-O	1.907
Ni-O	1.914
Ni-O	2.097
Ni-O	2.103

**4 x & 2 x
Similar
Ni-O**

- Local distortion and spin state of the TM ions are **strongly correlated**. Even if composition is the same, **different layers have different local structures**.

- 1st and 3rd layer:
 - **Ni²⁺** **HS**, JT inactive
 - **Ni³⁺** **LS**, **JT active**
 - **Co³⁺** **LS**, JT inactive
 - **Mn⁴⁺** **HS**, JT inactive

- 2nd layer:
 - **Ni²⁺** **HS**, JT inactive
 - **Ni³⁺** **LS**, **JT active**
 - **Co³⁺** **LS**, JT inactive
 - **Mn⁴⁺** **HS**, JT inactive



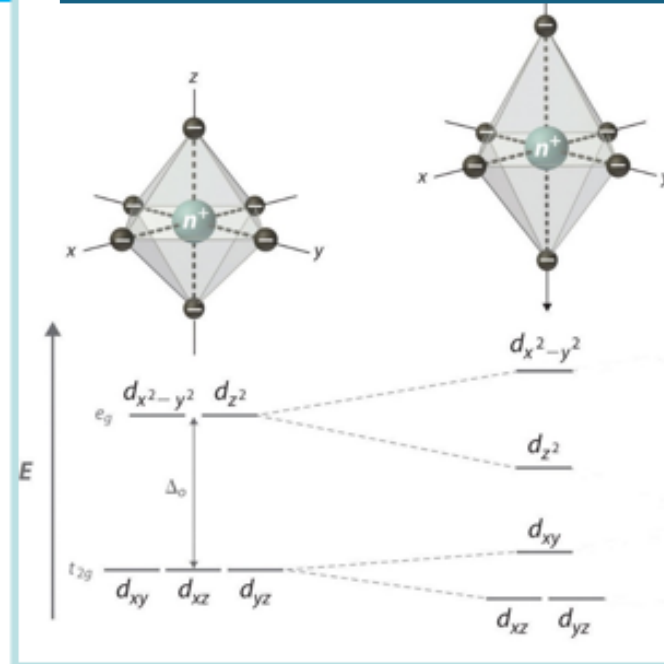
PBE0 using the CRYSTAL23 code correctly identify local geometries

Polarons

NMC633: Observed Metastable State

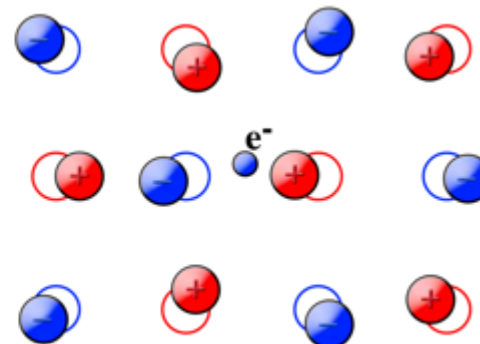
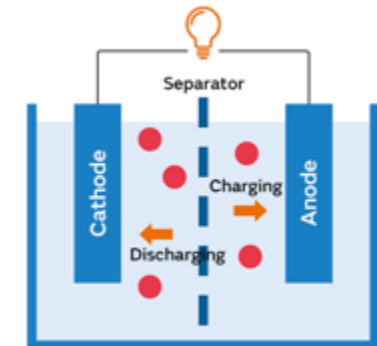
- **Intermediate state (IS)** observed for Co^{3+} (d^6) in NMC633, when Co is located in a distorted environment.
- The structure is **metastable** relative to the low spin (LS) solution, but a local minimum in the energy surface could be formed as transient species during cycling.
- **Importance of polaron-induced distortions.**
- $\Delta E_{LS-IS} \sim 0.5 \text{ eV}$ per Cobalt ion.
- **Oxidation and electronic state of the TMs adapt to the local environment.**
- Local distortions induced by **polarons** can force ions to adopt a different spin-configuration, even if other configurations are energetically more favorable.

$$\Delta E_{LS-IS} \sim 0.56 \text{ eV per Cobalt ion.}$$



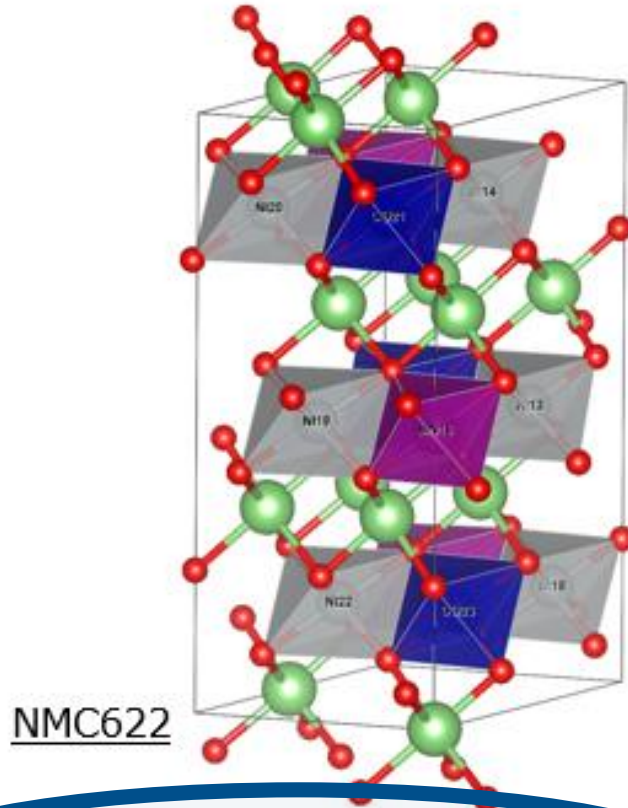
Why is this important?

- e^- are added and removed from the d -orbitals upon battery cycling. If the local environment permits, some e^- may be pulled from and added to TM sites where the JT distortion is not the most stable.
- **Could be important in the degradation of a battery.**



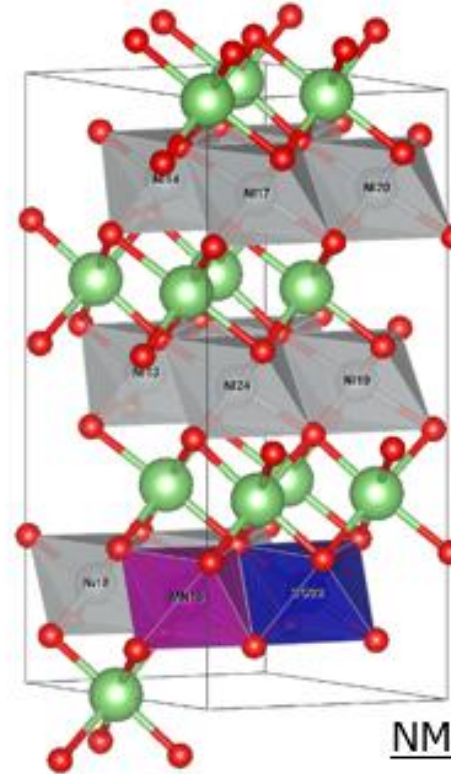
Ion distribution

Our focus is on **Nickel-poor** and **-rich** $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC) cathodes.



NMC622

- Ni/Mn disproportionation is present in each TM layer.
- Each layer occupied evenly by 1Ni^{2+} , 1Ni^{3+} , 1Mn^{4+} and 1Co^{3+} .



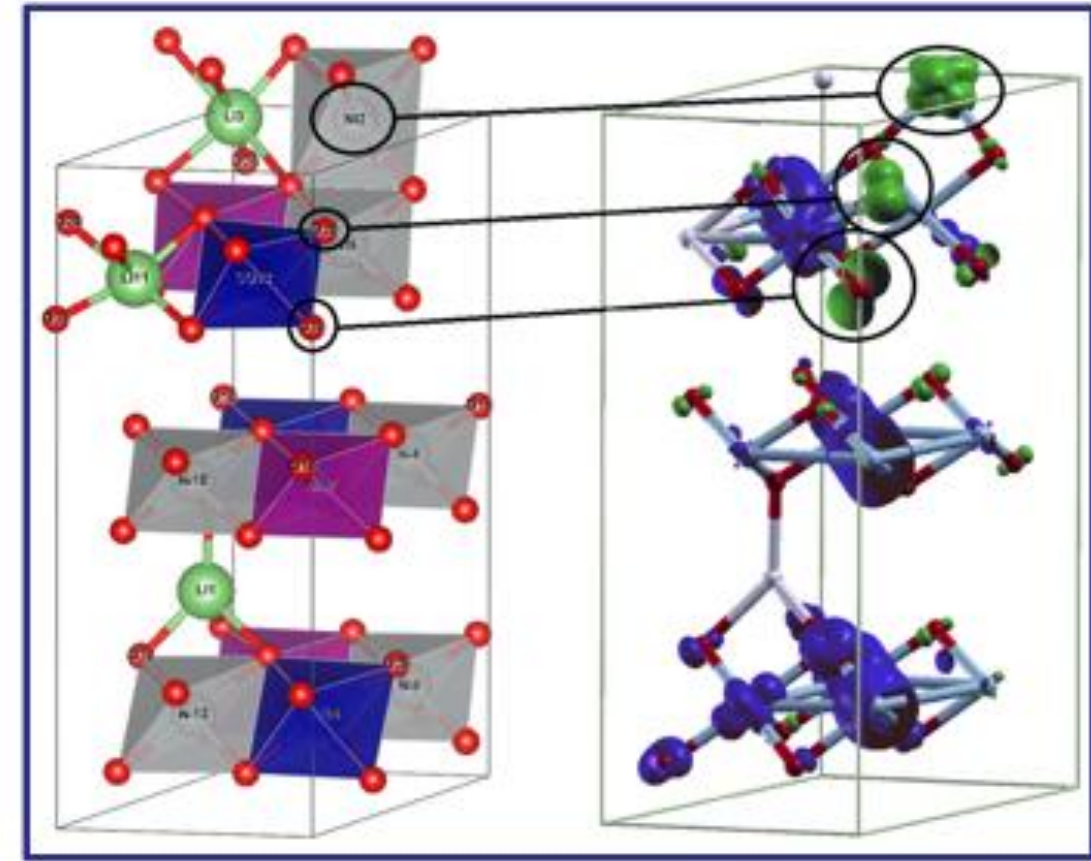
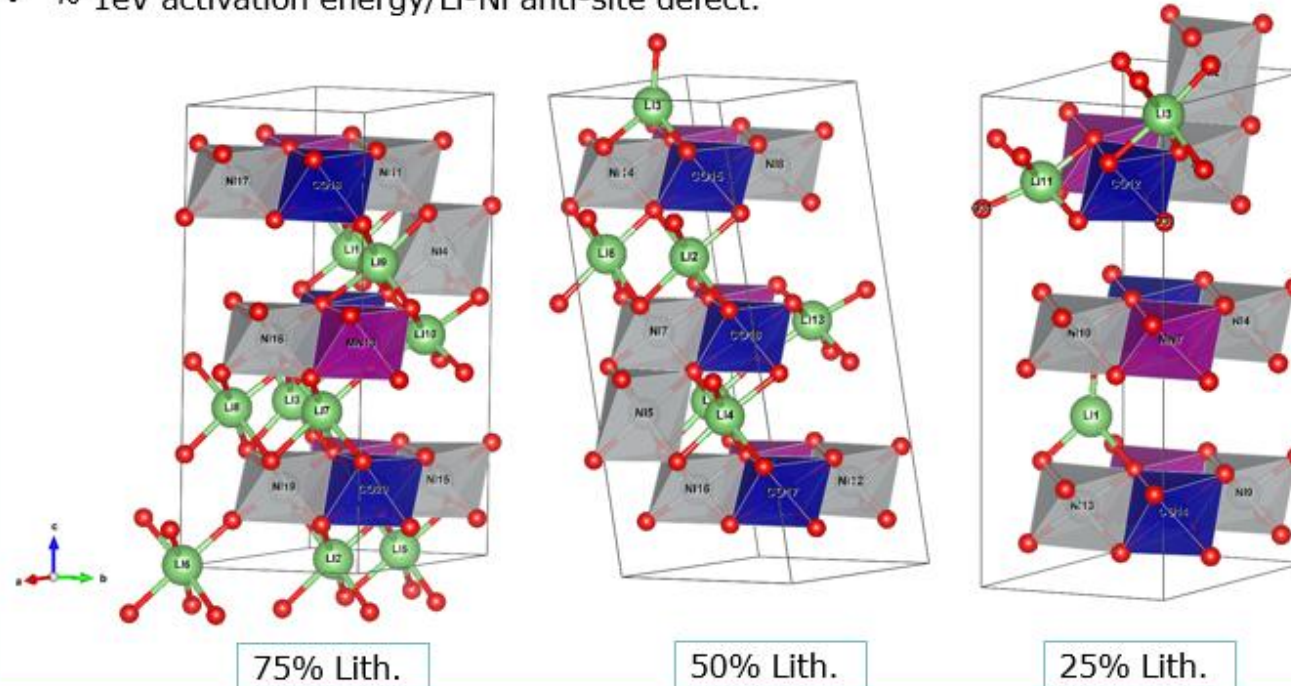
NMC811

- Configuration with Mn and Co in same layer is more favorable.
- A 12-formula unit cell is used in both cases.

De-lithiation – OXYGEN redox

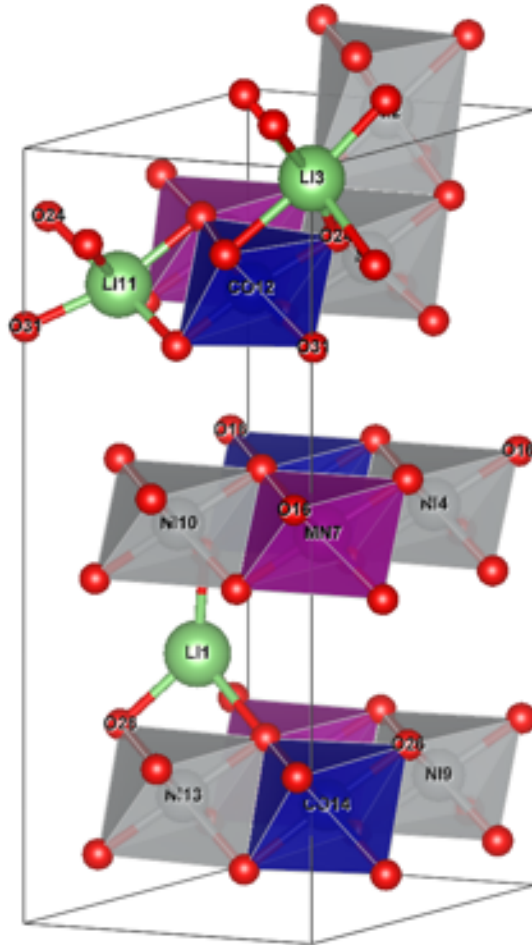
Local threshold for O activation: at 75% and 50% lithiation no O activation.
Once the cell reaches 25% lith. Oxygen will participate in a redox reaction.

- ~ 1eV activation energy/Li-Ni anti-site defect.

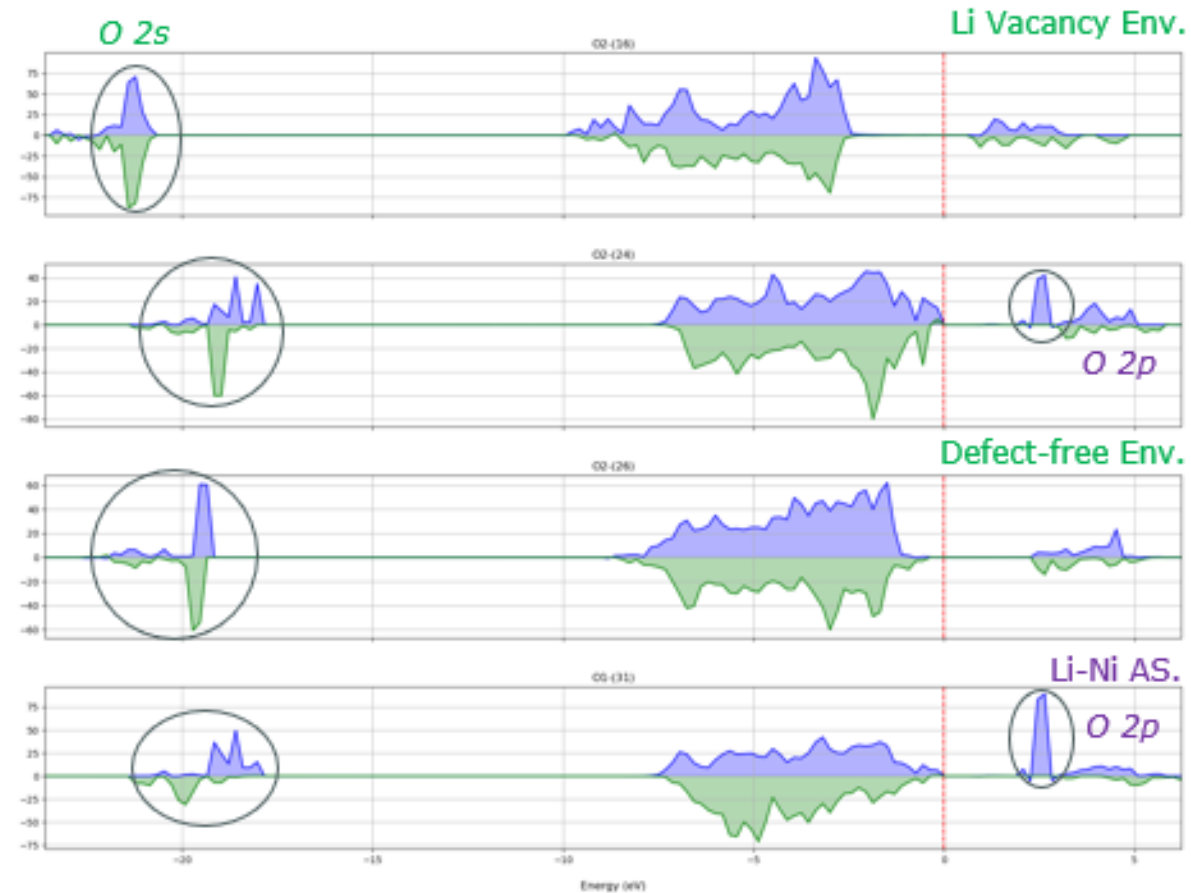


OXYGEN activation

Density of States analysis shows a **difference between O ions in defect-free vs anti-site environments.**

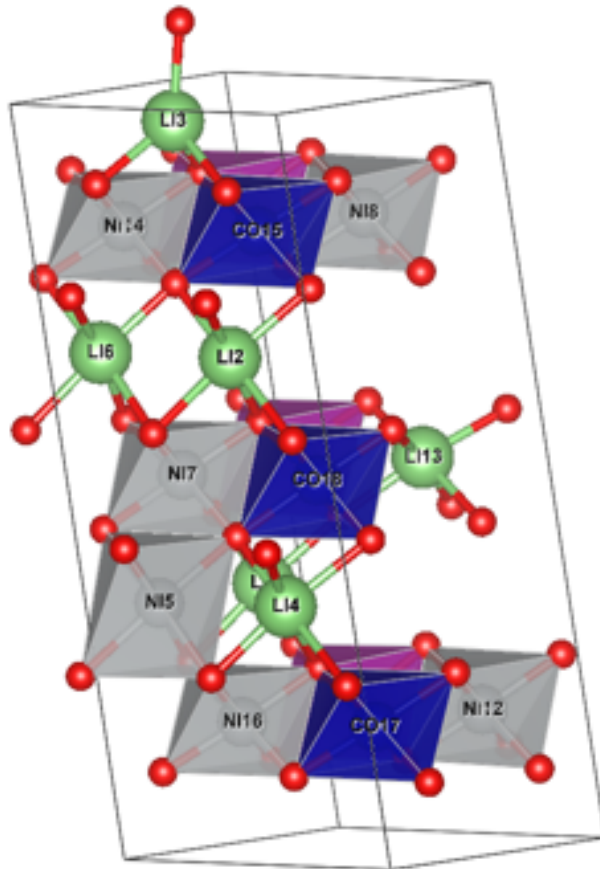


25% Lith.

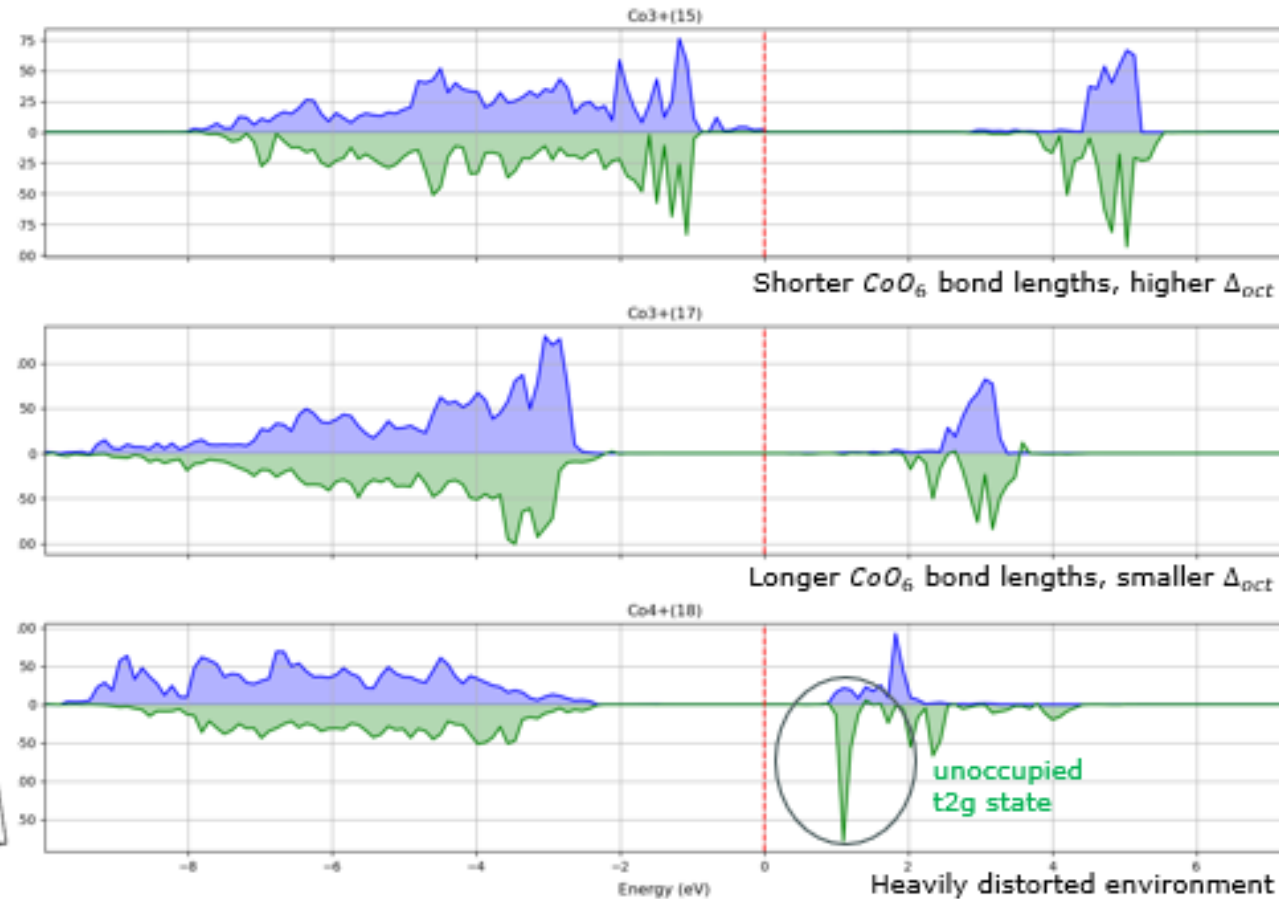


Co-protects oxygen activation

There is a threshold for Co activation also: at 50% lith. no O activation, but Cobalt goes to 4+ oxidation state (initially 3+).



50% Lith.



A Hybrid DFT-CTM Method for Theoretical Spectroscopy

1. DFT:

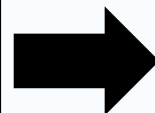
$$\hat{H}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

2. CTM:

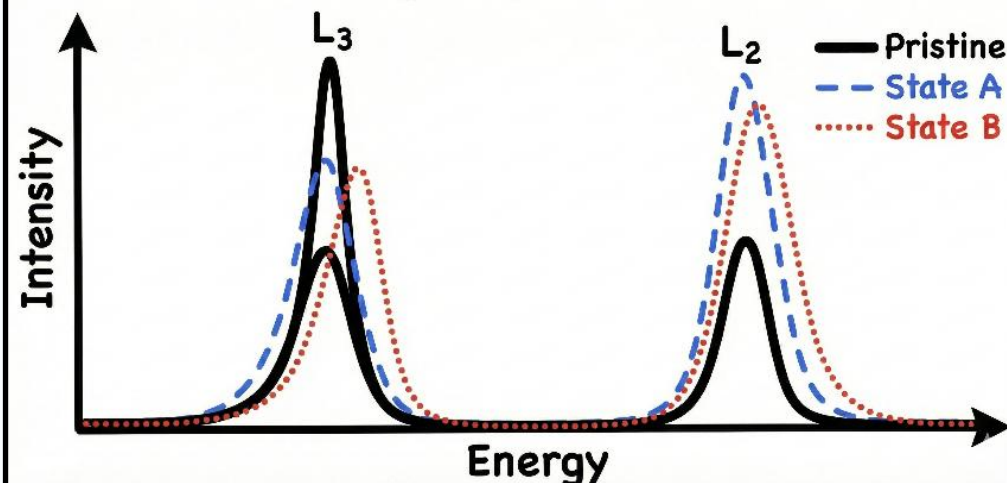
$$\hat{H}_{\text{CTM}} = \hat{H}_{\text{atom}} + \hat{H}_{\text{CF}} + V_{\text{mix}} \sum_{\mathbf{k}} (\hat{c}_{\text{d}}^{\dagger} \hat{c}_{\mathbf{k}} + \hat{c}_{\mathbf{k}}^{\dagger} \hat{c}_{\text{d}}) + \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}}$$

3. FGR:

$$\Gamma_{\text{fi}} = \frac{2\pi}{\hbar} |\langle f | \hat{H}' | i \rangle|^2 \delta(E_{\text{f}} - E_{\text{i}})$$

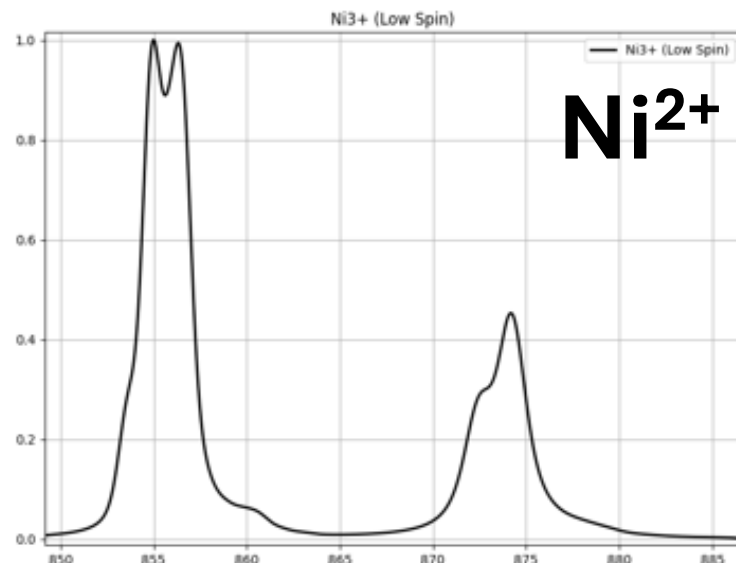


Nickel L-edge Spectra (NMC622)



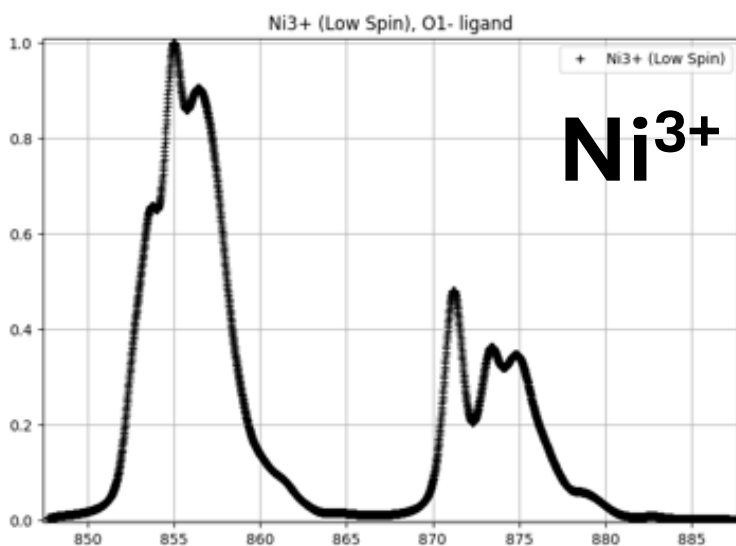
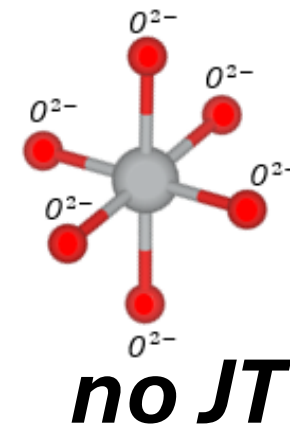
**Using electron density in 3D structure
from CRYSTAL-code to predict K- and L-edge spectra**

Ni - Theoretical L_{23} – edge transitions



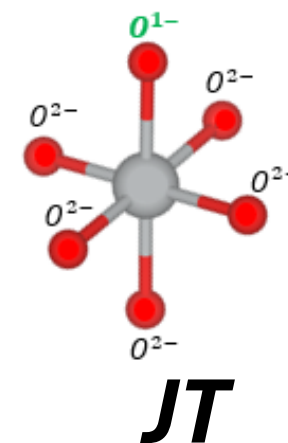
• Octahedral Symmetry O_h :

- $6 \times O^{2-}$ ligands
- Charge-transfer $\Delta_{CT} = 3.5$ eV
- $10Dq = 2$ eV
- Slater-Condon screening at 50%
- Hybridization:
 $V_{pds}: 1.8$ eV
 $V_{pdp}: 1.0$ eV



• Expectations: Broken O_h Symmetry:

- $5 \times O^{2-} + 1 \times O^{-}$
- Larger charge-transfer $\Delta_{CT} = 5$ eV
- Smaller $10Dq = 1.2$ eV
- Slater-Condon screening at 90%
- Less hybridization:
 $V_{pds}: 1.0$ eV
 $V_{pdp}: 0.8$ eV



**Difference
in L_3 -edge
spectra
between
 Ni^{2+} and JT-
distorted
 Ni^{3+}**

Theoretical L_{23} – edge transitions

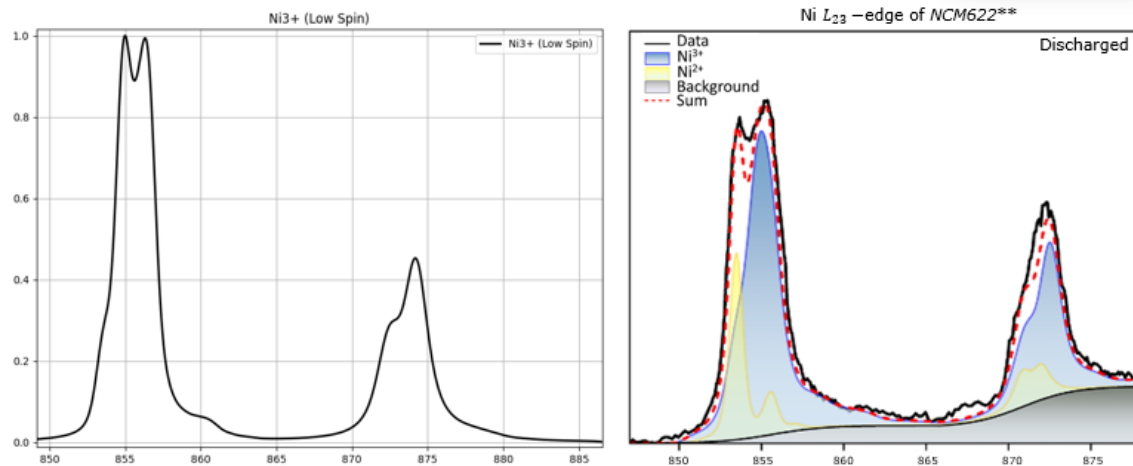
To write down the absorption spectrum use **Fermi's Golden Rule**:

$$W_{fi} \propto \sum_q |\langle \Phi_f | \mathbf{e}_q \cdot \mathbf{r} | \Phi_i \rangle|^2 \delta(\hbar\Omega - E_f + E_i).$$

Drives transition between initial state and final state

Ensures conservation of energy

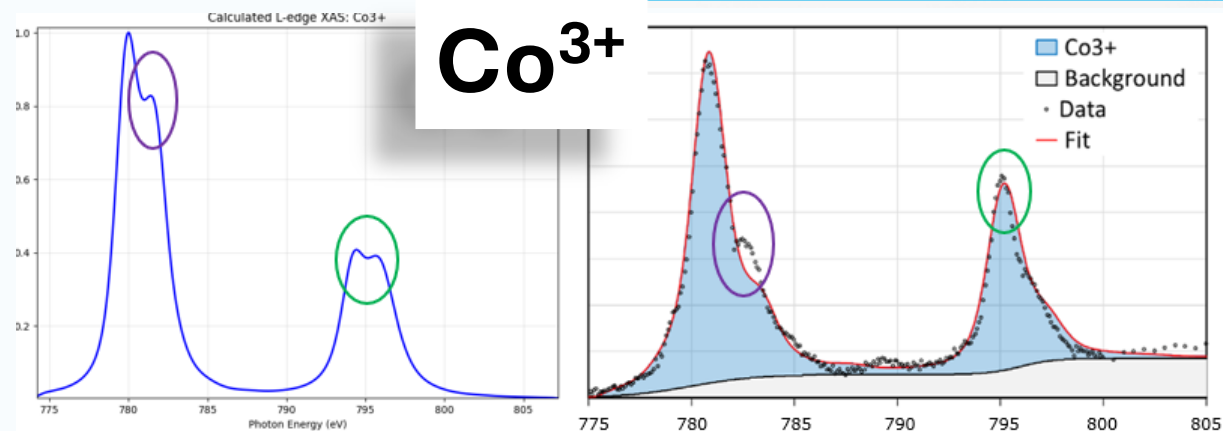
Ni²⁺



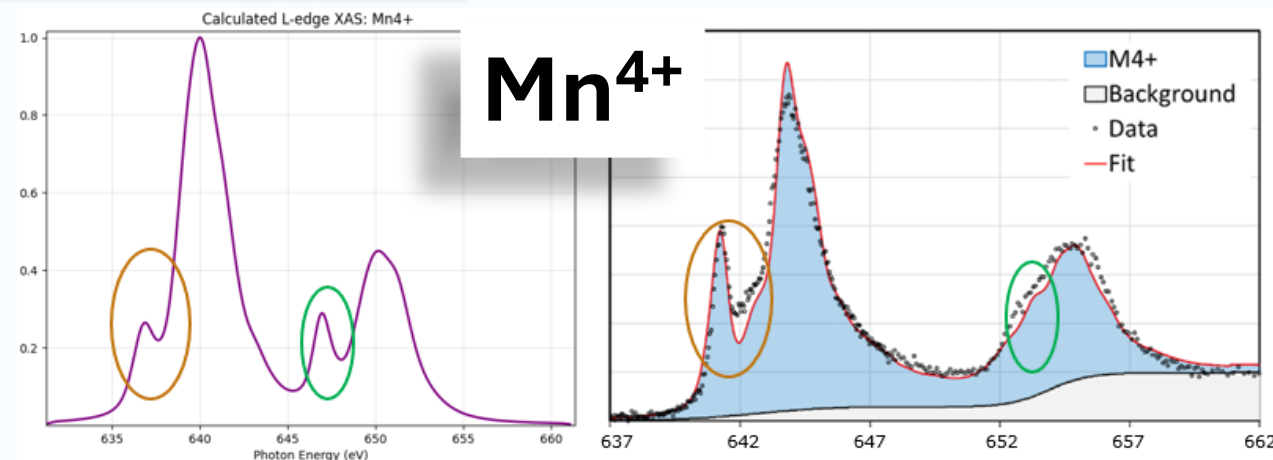
** Kleiner et. Al., A review and outlook on anionic and cationic redox in Ni-, Li- and Mn-rich layered oxides LiMeO2

- Ni L₃-edge agree with experiment
- **Co and Mn L-edge still need more work**

Co³⁺



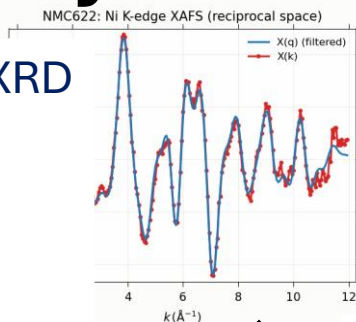
Mn⁴⁺



Importance of choosing the correct set of CTM parameters!

Case study: Creating Database - ML tools - AI

- Experimental XRD and XAS data
- Simulations of structural parameters

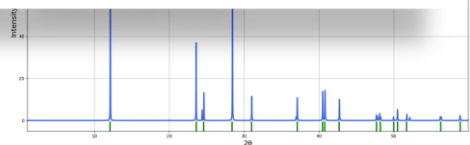


- Training Set

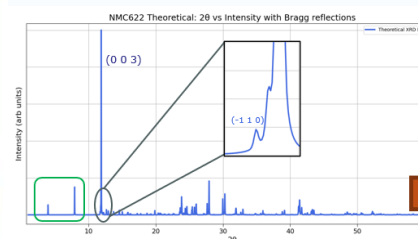
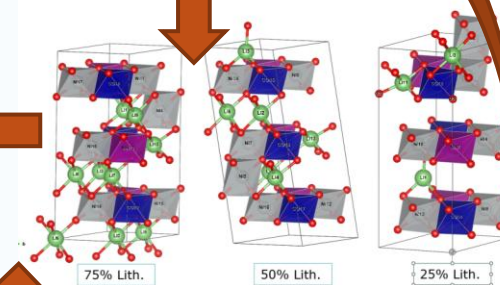
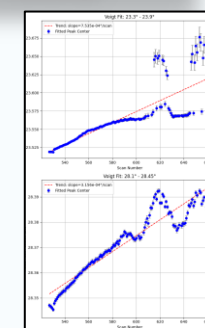
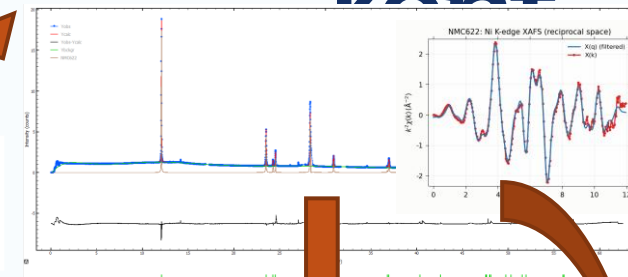
DATABASE

FAIR

- Experimental XRD data
- Simulations of XRD
- Validation

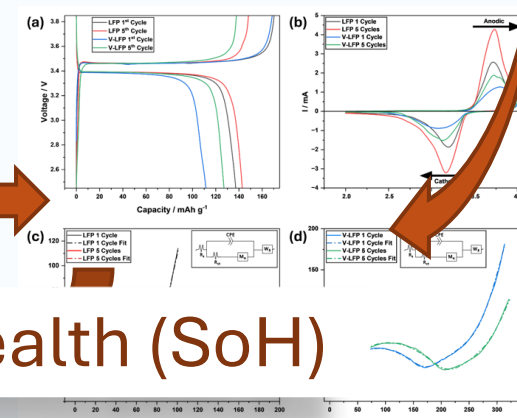


- Visualisation Tools
- Statistical Tools



- State-of-Health (SoH)

- Machine Learning (ML) tools
- Predictive tools – Artificial Intelligence (AI)



Example OpMetBat: Creating Database - ML tools - AI

Generate TM bond lengths
(random or by DFT)

Construct simulation data

```
{"Sim_ID": 1,  
  "Bond_Lengths": {  
    "TM": {  
      "13": [1.881, 1.886, ...]  
    }  
  }  
}
```

SQL
Database

Neural Network using Tensor Flow

$$\text{Loss} = -\frac{1}{N} \sum_{i=1}^N [y_i \log(\hat{y}_i) + (1 - y_i) \log(1 - \hat{y}_i)]$$

- y_i = actual label (0 or 1)
- $\hat{y}_i$ = predicted probability from your network
- N = number of training samples

SQL Database

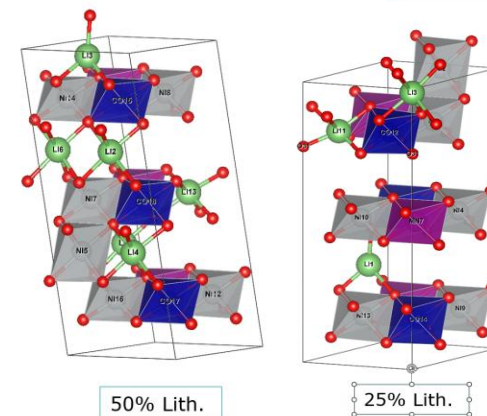
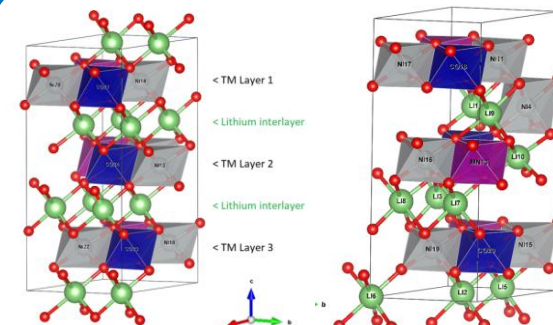
Train on simulation
data

Neural Network

JT classification

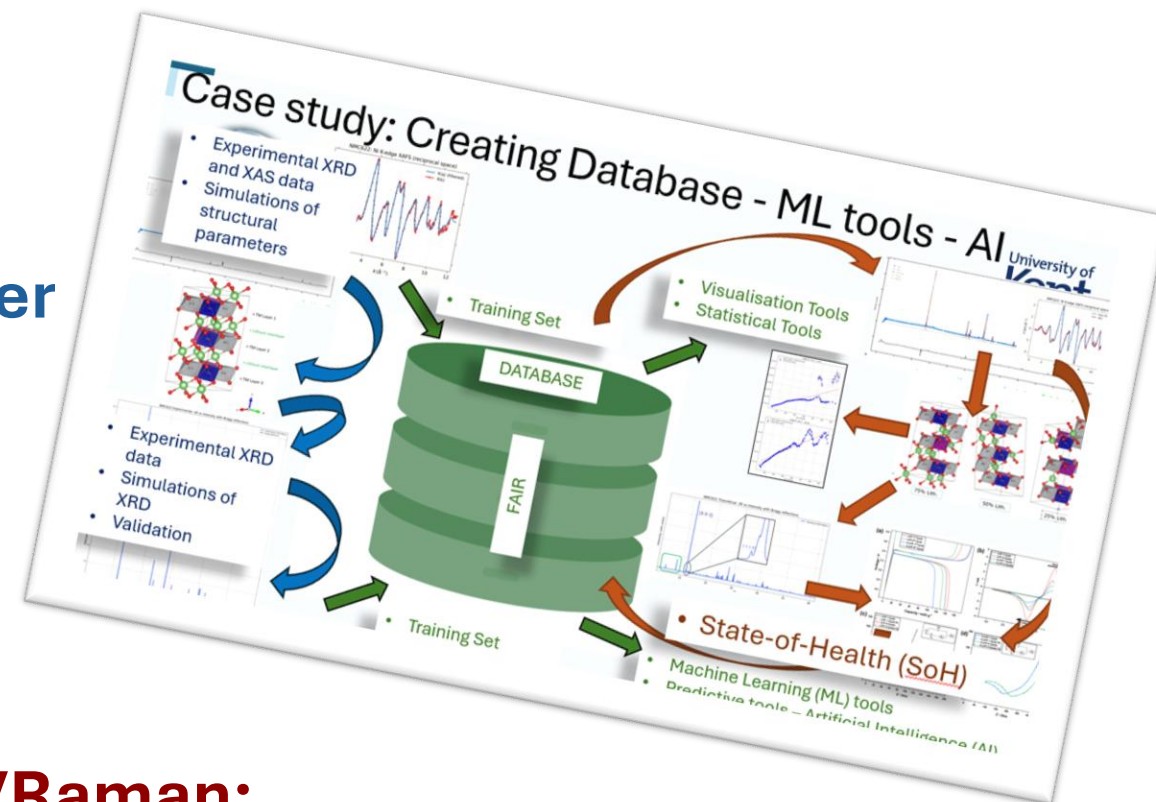
Fetch
bond lengths

```
1/1 0s 52ms/step  
TM_01: predicted Distorted (p=0.89) | actual: Distorted | bonds: [1.874, 1.879, 1.934, 1.935, 2.057, 2.065]  
TM_02: predicted Distorted (p=0.98) | actual: Distorted | bonds: [1.883, 1.89, 1.897, 1.902, 2.105, 2.109]  
TM_03: predicted Distorted (p=0.73) | actual: Distorted | bonds: [1.915, 1.919, 1.942, 1.948, 2.151, 2.159]  
TM_04: predicted Distorted (p=0.93) | actual: Distorted | bonds: [1.871, 1.872, 1.923, 1.933, 2.07, 2.07]  
TM_05: predicted -- (p=0.02) | actual: -- | bonds: [1.903, 1.906, 1.907, 1.913, 1.92, 1.921]  
TM_06: predicted Distorted (p=0.90) | actual: Distorted | bonds: [1.868, 1.876, 1.944, 1.947, 2.072, 2.074]  
TM_07: predicted Distorted (p=0.96) | actual: Distorted | bonds: [1.879, 1.884, 1.912, 1.915, 2.092, 2.093]  
TM_08: predicted -- (p=0.01) | actual: -- | bonds: [2.004, 2.01, 2.04, 2.043, 2.055, 2.056]  
TM_09: predicted -- (p=0.05) | actual: -- | bonds: [1.928, 1.928, 1.931, 1.931, 1.932, 1.938]  
TM_10: predicted Distorted (p=0.80) | actual: Distorted | bonds: [1.913, 1.918, 1.935, 1.937, 2.154, 2.169]  
TM_11: predicted -- (p=0.07) | actual: -- | bonds: [1.931, 1.932, 1.933, 1.938, 1.938, 1.942]  
TM_12: predicted -- (p=0.05) | actual: -- | bonds: [1.917, 1.925, 1.926, 1.928, 1.94, 1.943]
```



Take away message

- $\text{Ni}^{2+}/\text{Mn}^{4+}$ disproportions if in same layer
- Polarons forms as metastable states, leading to battery degradation
- **Oxygen shows redox activity in presence of Ni anti-sites**
- **Co protects oxygen activity**
- **Hybrid XRD/XAS; XAS/SAXS; XAS/XRD/Raman; XAS/XRD/EIS**
- **Collect standardised data in database**
- **ML tools applied to structural (experiment/theory) and electrochemical battery properties**





Stand for ambition.
kent.ac.uk

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Dr Marcus Bertuzzo

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Sally Pang

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Prof Erik M. Kelder (TUD)

Prof Jawwad Darr (UCL)

Prof Markys Cain (Electrosoci LTD)

MEE Group

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Award

Alistore-ERI

OpMetBat/HyMetBat The EU
Partnership on Metrology

Summary and Aims of WP4

The aim of this work package is to develop computational tools to support the experimental metrology that is to be developed in WP1, WP2 and WP3.

Develop modelling and computational tools - large datasets - enabled by hybrid metrology.



Task 4.1

Theoretical calculations to aid in the interpretation of experimental data generated in WPs 1-3

Task 4.2

Establishment of a database and associated tools to handle the accompanied large datasets

Task 4.3

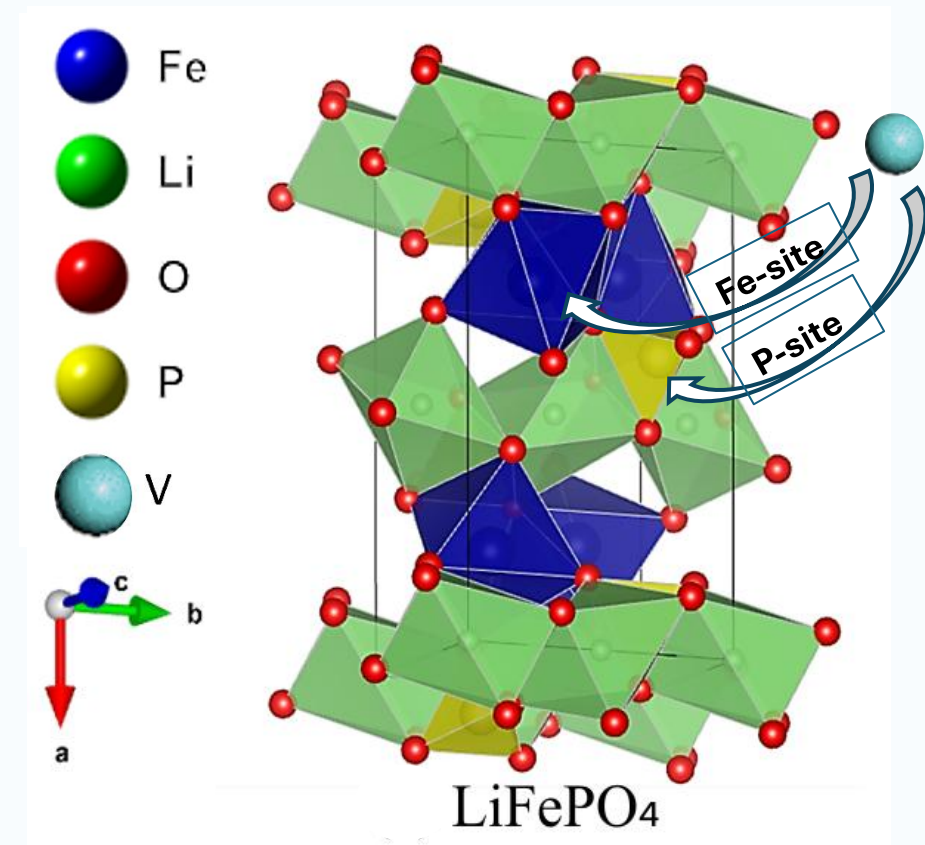
Application of ML approaches to enable automation of hybrid operando data handling.
Specifically targeting experimental outputs of WP3.

Why dope LFP?

- Doping can occur at Li, Fe, or P sites
- Improves electronic and ionic conductivity
- Creates defects in the unit cell
 - Facilitates Li-ion diffusion
 - Improves internal conductivity
- **Better rate performance, capacity retention, & cycling capability and stability**

Aims of the Study

- Use XAS K-edge data to follow electronic structure during battery cycling.
- Follow changes in the local structure for doped-LFP
- **Establish whether the PO_4^{3-} polyanion is electrochemically active**
- **Does the PO_4^{3-} polyanion contribute to extra capacity (induction effect)**



Materials

- Anode – Conversion/Displacement reaction



- Cathode

- Polyanionic compounds



- Layered Oxides



- Solid Oxide Fuel Cells (SOFCs)

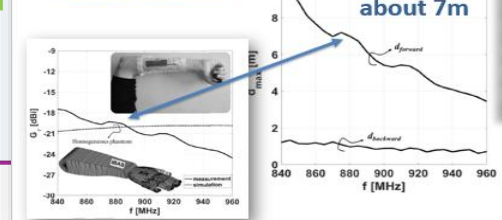


2D printed Flexible (Organic) Batteries

IEEE Antenna Transaction
Caccarami et al, 2018



Read Range

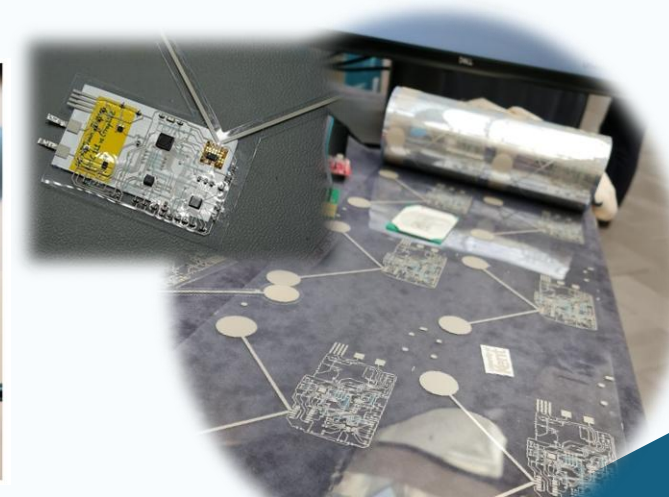
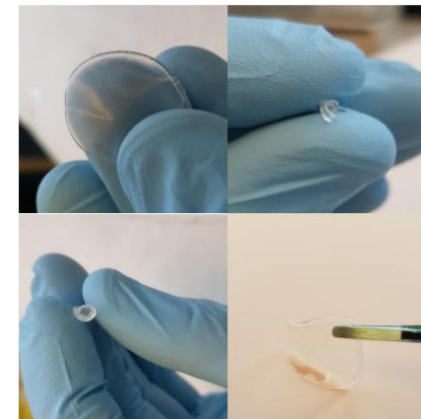


- 2D printed
- Materials cost reduction
- Manufacturing process
- Light weight
- Integrated flexible antenna/battery (transmitting/receiving signals)
- Integration with sensors
- Sustainable/biocompatible materials (Economic circle)

University of
Kent

AIMs

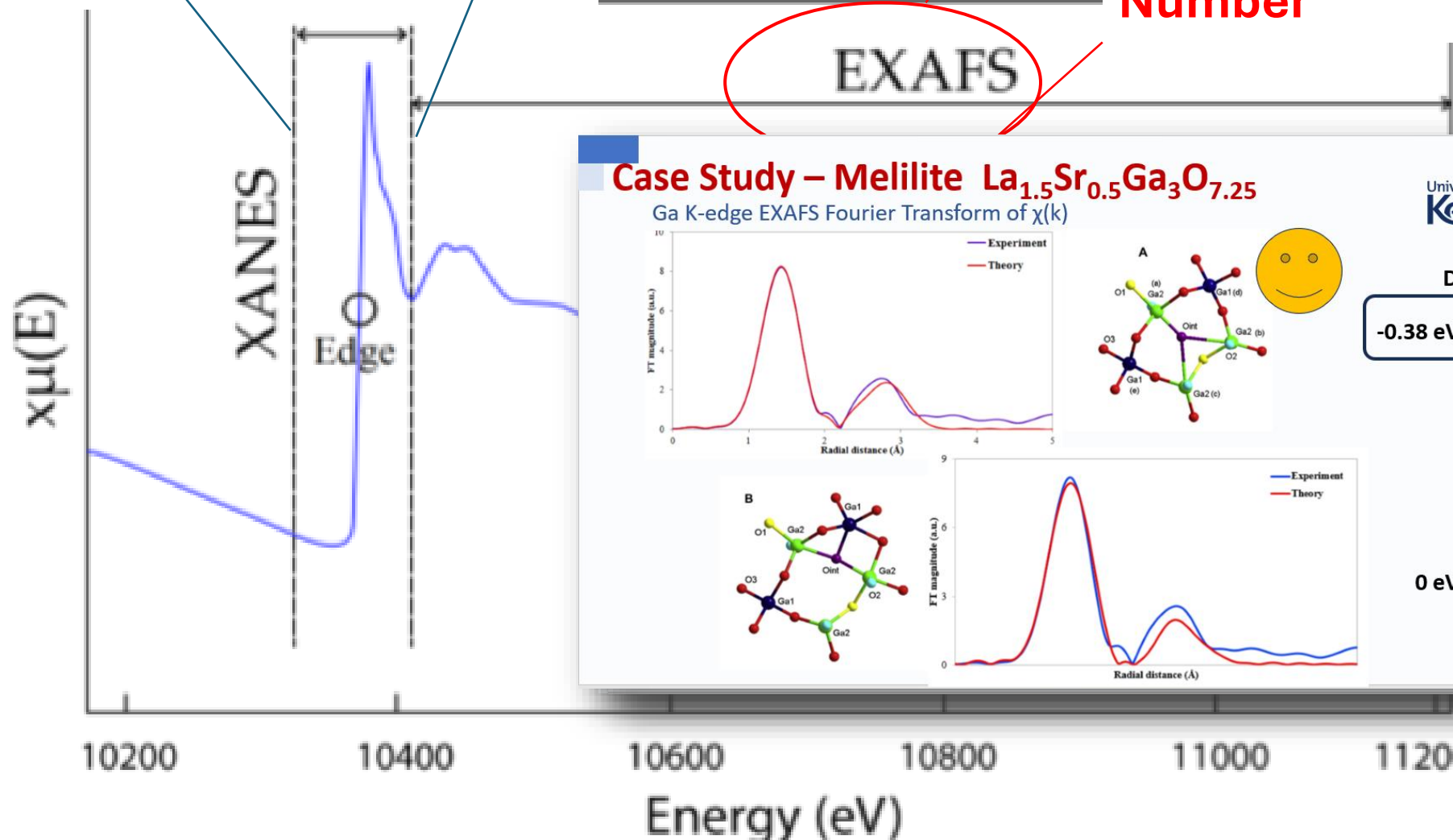
- Low cost
- Environmentally friendly
- Non-toxic
- Biodegradable
- Reduce energy consumption



XAS Spectrum

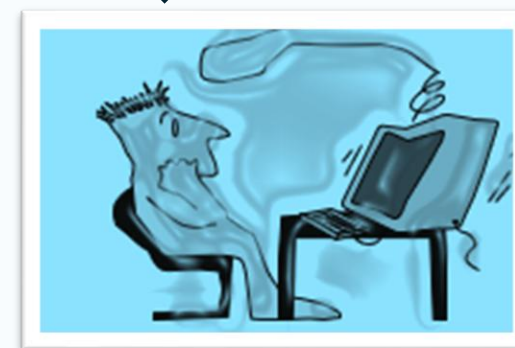
XANES Region:
Oxidation State
Coordination Number

EXAFS Region:
Bond distances
Neighbours
Coordination
Number



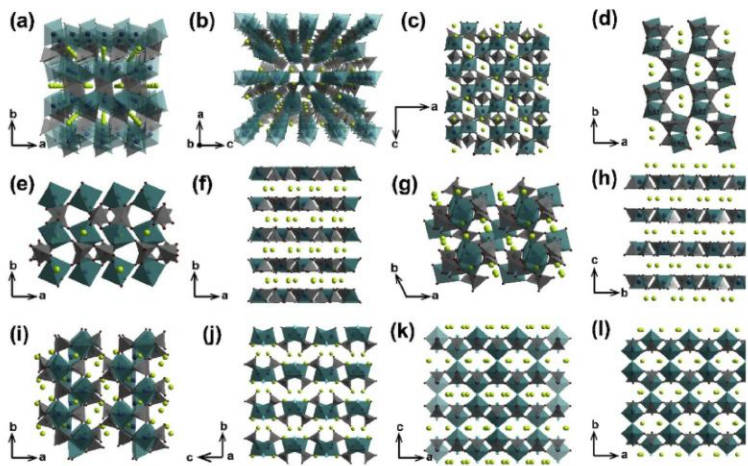
Layout

- Decoupling Polyanion Redox from Electrolyte Contributions in LiFePO_4 : Insights from Fe, Ho, V and **P K-Edge XANES**
- Oxygen redox in $\text{Li}_2\text{FeSiO}_4$: Insights from X-ray Raman Spectroscopy (XRS)
- How manage Oxygen redox in LiNiMnCoO_2 (NMC): Insights from DFT simulations



Why Polyanions?

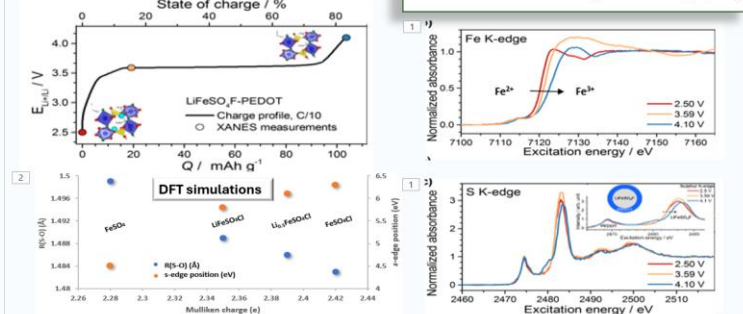
L.N. Zhao et al. / Materials Today Nano 10 (2020) 100072



LiFeSO₄F

LiFeSO₄F - PEDOT (XAS)

- S K-edge in the SO₄²⁻ anion is sensitive to changes in electron distribution
- Electron distribution changes with battery cycling

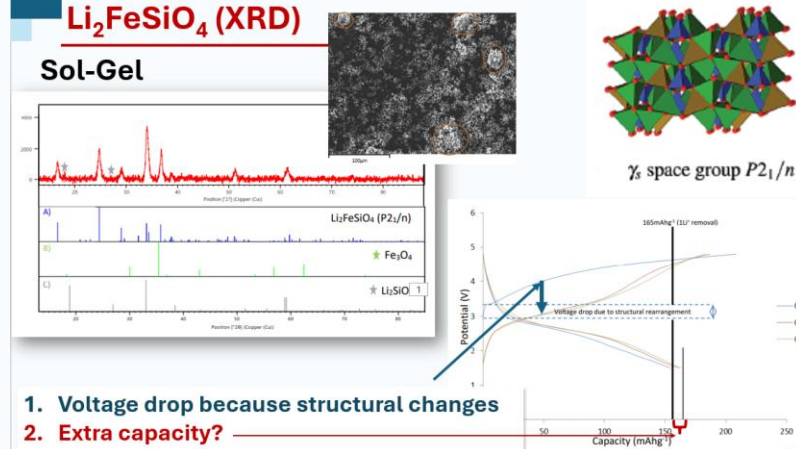


A. Blidberg et al., J. Power Sources, 418, 84 (2019).

Li₂FeSiO₄

Li₂FeSiO₄ (XRD)

Sol-Gel

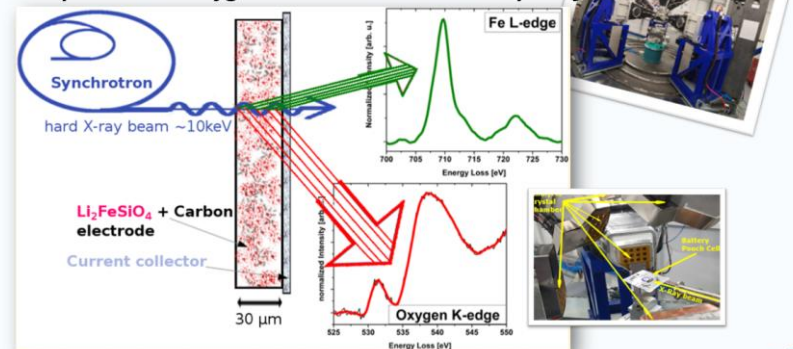


1. Voltage drop because structural changes
2. Extra capacity?

Li₂FeSiO₄ (XRS) – Oxygen edge

Question 3:

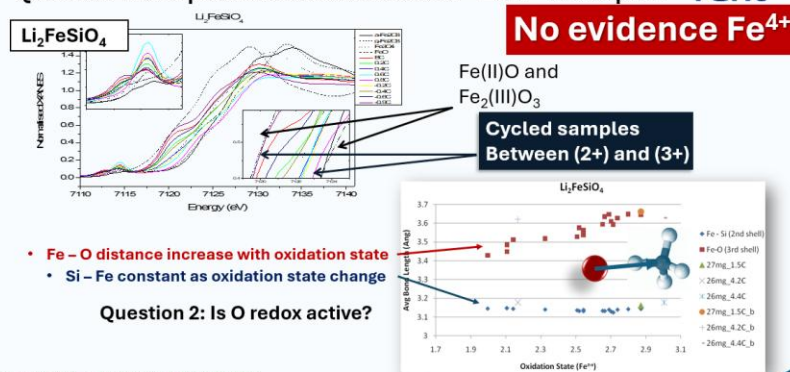
Is it possible to oxygen contributes to extra capacity?



Li₂FeSiO₄ (In operando XAS)

Question 1: Is it possible to access the Fe³⁺ ⇌ Fe⁴⁺ redox pair?

No evidence Fe⁴⁺



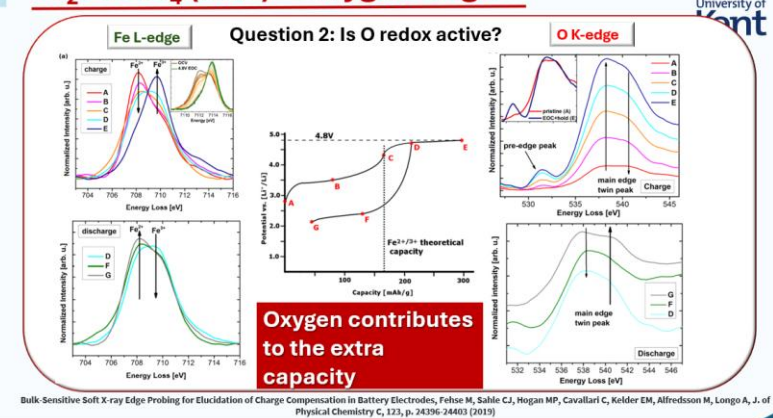
- Fe – O distance increase with oxidation state
- Si – Fe constant as oxidation state change

Question 2: Is O redox active?

Brownrigg et al., J. Mat. Chem. A, 3, 7314-7322 (2015)

Li₂FeSiO₄ (XRS) – Oxygen edge

Question 2: Is O redox active?

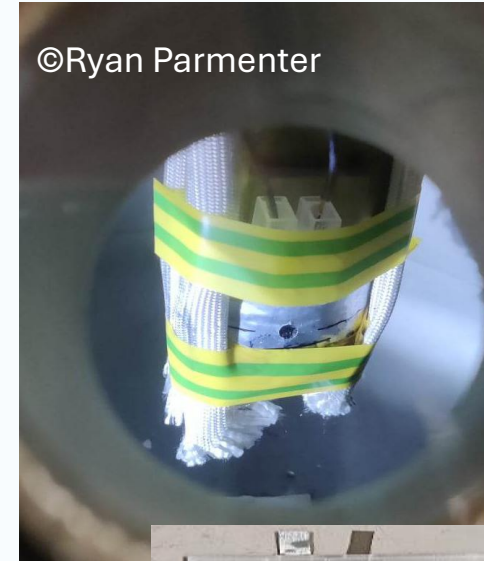
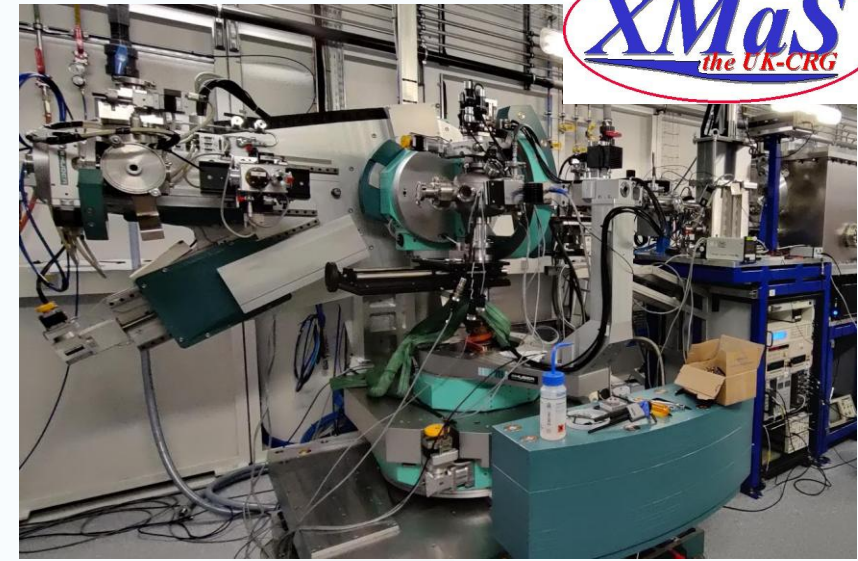


Oxygen contributes to the extra capacity

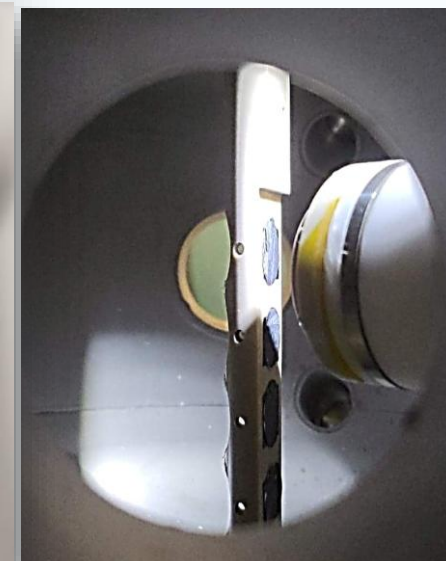
Bulk-Sensitive Soft X-ray Edge Probing for Elucidation of Charge Compensation in Battery Electrodes, Fehse M, Sable CJ, Hogan MP, Cavallari C, Kelder EM, Alfreidsson M, Longo A, J. of Physical Chemistry C, 123, p. 24396-24403 (2019)

(Soft) X-Ray (XAS) Measurements

- Data collected @ BM28 (XMas, ESRF) and B18 (DLS) **P, Mn, V, & Fe K-edges**, and **Ho L_{III}-edge**
- **Ex-situ samples:** Chamber sealed under vacuum throughout experiment
- Fluorescence mode
- Data analysed using Athena, Larch
- **Operando cell:** in He-environment

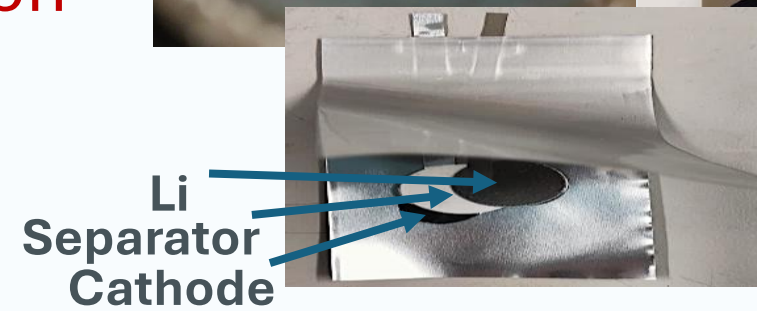


©Ryan Parmenter

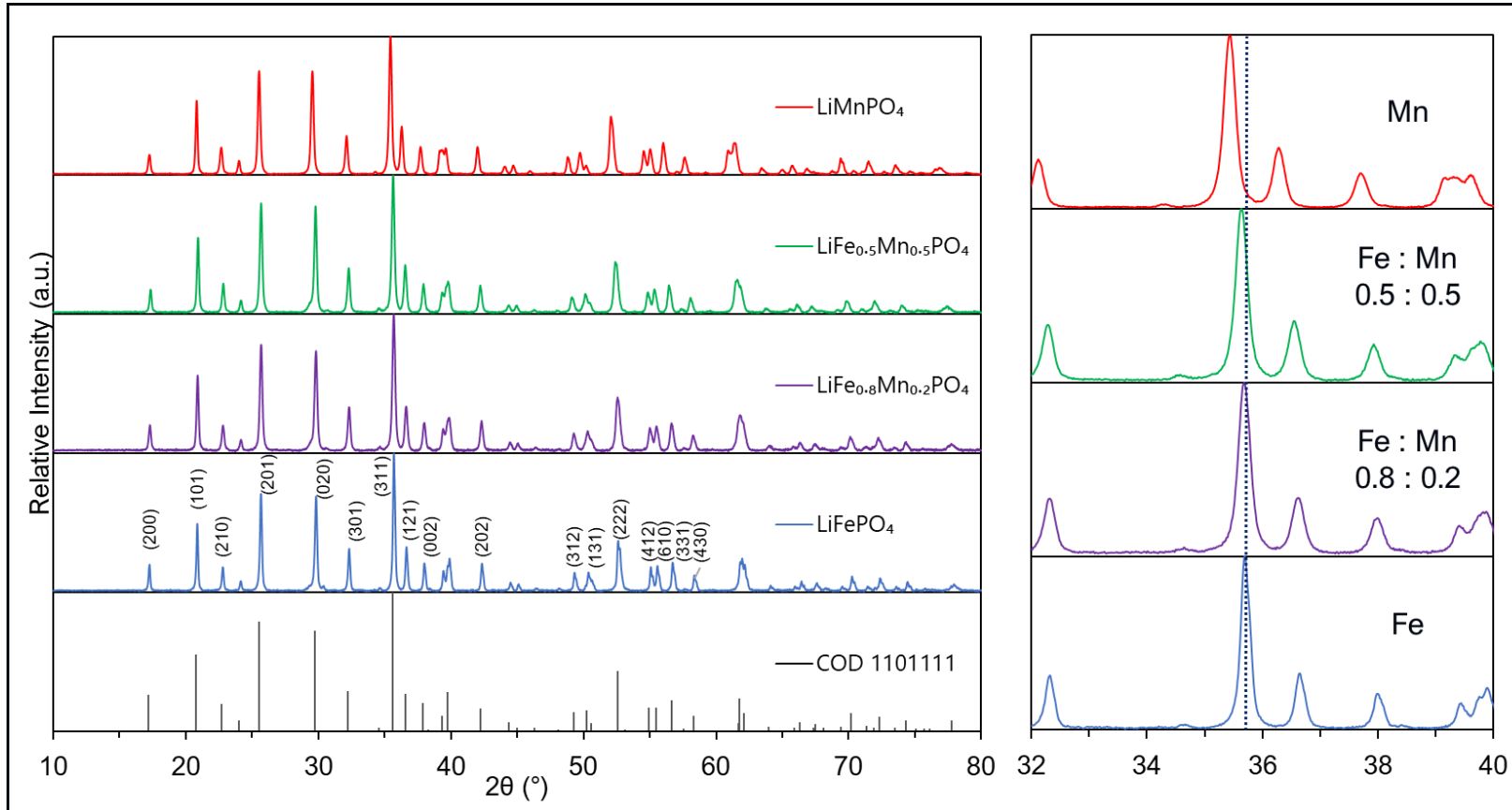


Battery Assembly

- Electrode slurries of LFP (active material): (PVDF) Binder: Carbon black made up – 90:5:5 ratio
- **Pouch cells**
- Conducting mylar window



Material Characterisation $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$

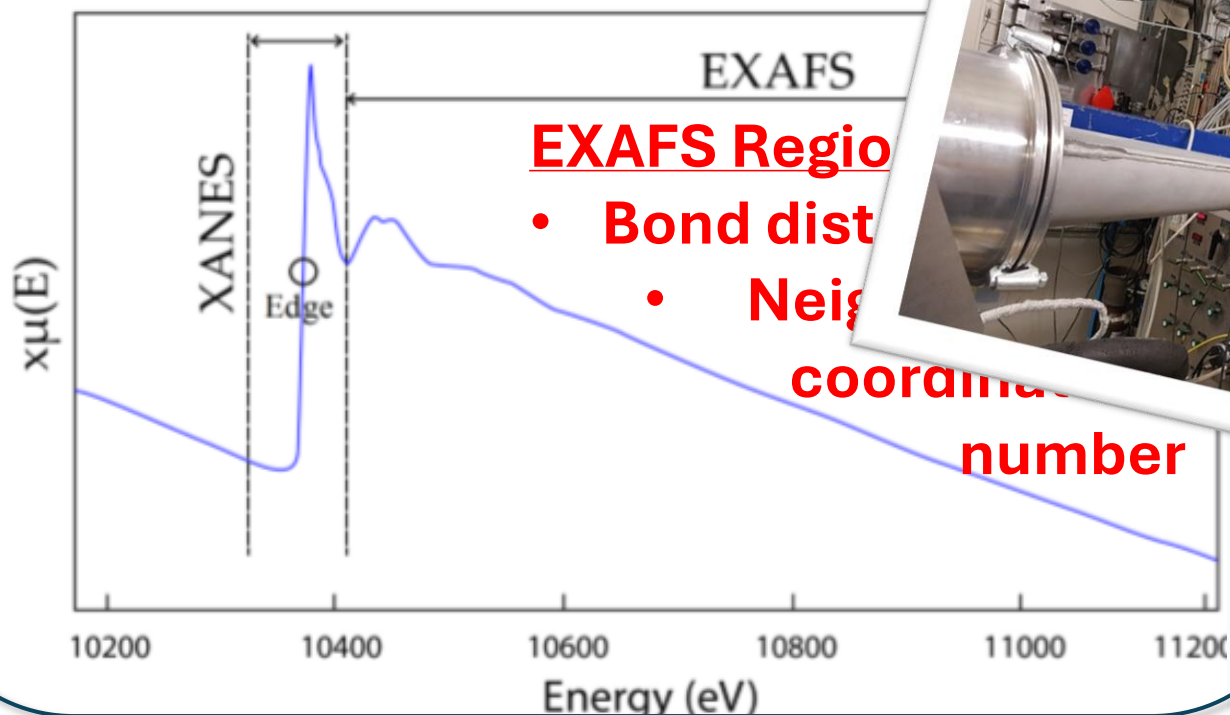


Sample	a (Å)	b (Å)	c (Å)	Vol. (Å ³)	R _{wp}	R _p
LiFePO ₄	10.326	6.004	4.693	290.9	3.72	2.42
LiFe _{0.8} Mn _{0.2} PO ₄	10.353	6.023	4.705	293.4	3.42	2.20
LiFe _{0.5} Mn _{0.5} PO ₄	10.397	6.052	4.727	297.5	4.65	2.90
LiMnPO ₄	10.452	6.103	4.749	302.9	8.57	5.57

Tools

simultaneously

XANES Region:
Oxidation State
Coordination Number



SAXS:
Particle distribution



Atomistic Simulations

CRYSTAL [2]
Gaussian type Basis Functions
Hybrid functionals

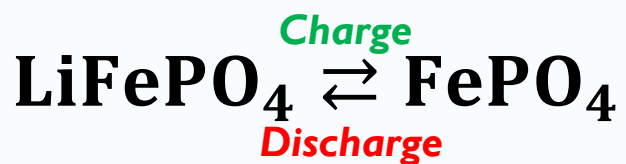
GULP [3]
Inter-atomic potentials
Shell models
Molecular dynamics

Other techniques:
electrochemistry; XRD; XES; XRS etc

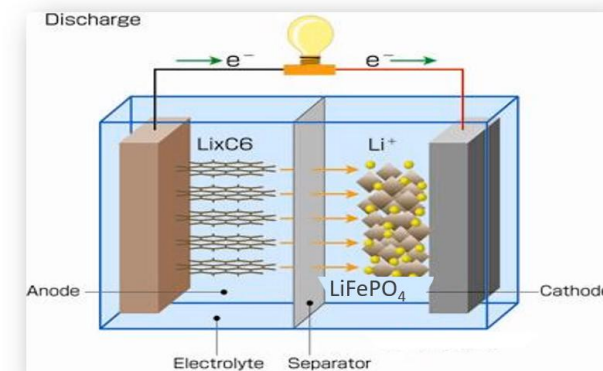
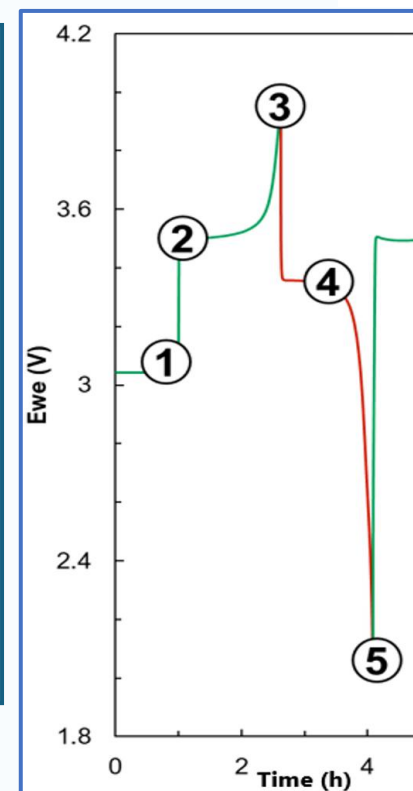
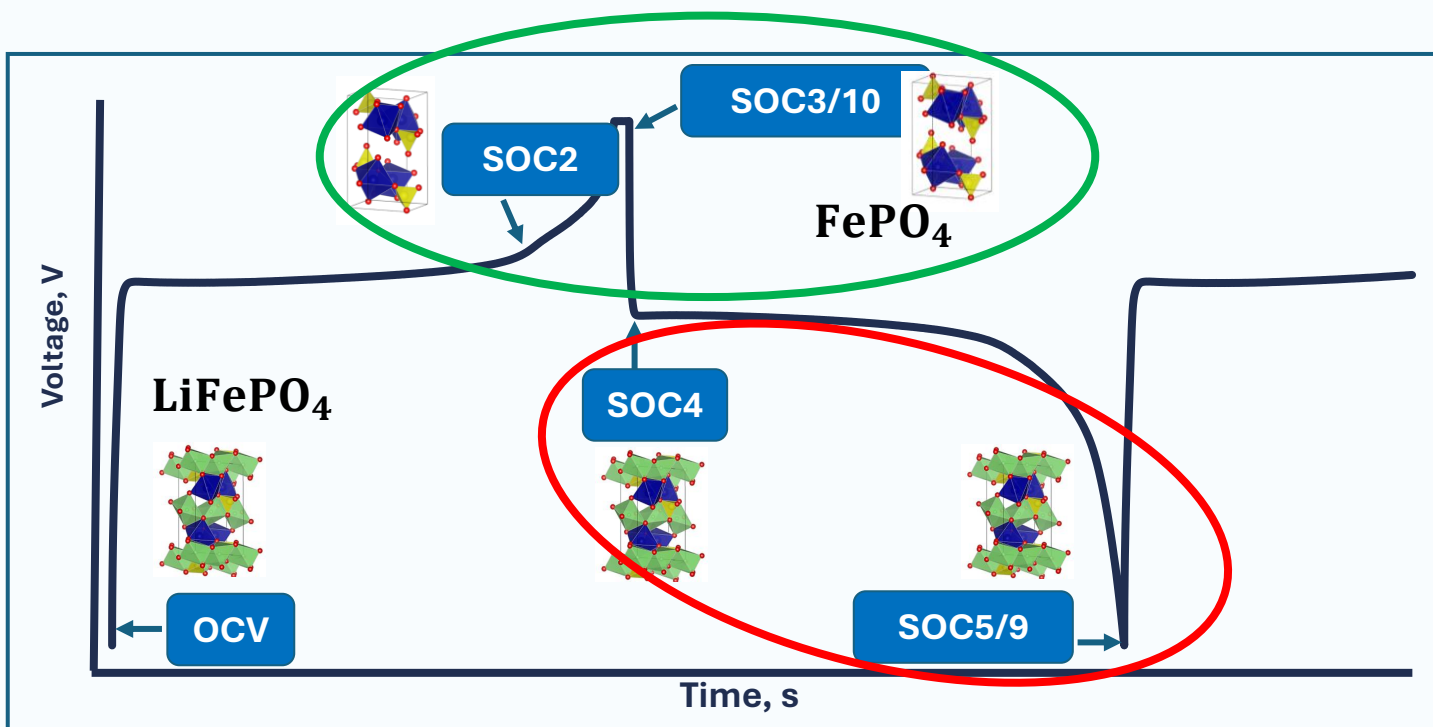
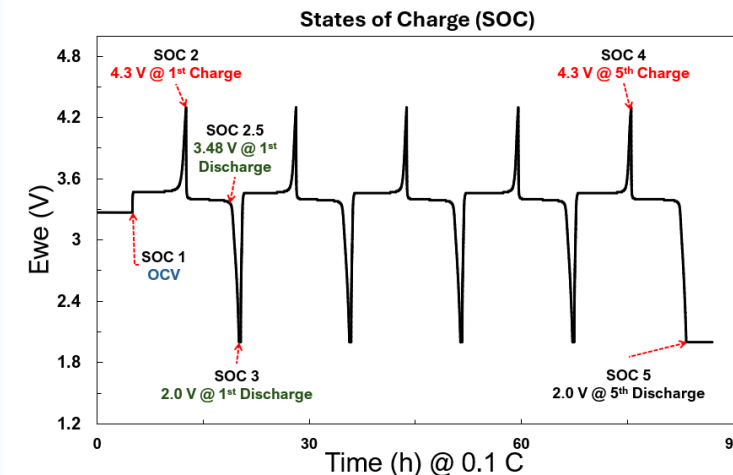


[1] *Quantum espresso*: P. Giannozzi et al., J.Phys.:Condens.Matter **21**, 035502 (2009); P. Giannozzi et al., J.Phys.:Condens.Matter **29**, 465901 (2017)
[2] *CRYSTAL 17 User's Manual*, V.R. Saunders, R. Dovesi, C. Roetti, M. Causà, N.M. Harrison, R. Orlando and C.M. Zicovich-Wilson, et al., University of Turin, Turin (1999)
[3] *GULP*: J.D. Gale, JCS Faraday Trans., **93**, 629 (1997)

Battery Cycling/States of Charge (SOC)



- Galvanostatic Cycling: between 2-4.3 V
- C-rate: 0.1C



- Upon charging, LFP is delithiated
- Upon discharging, LFP is lithiated

- Batteries cycled up to 5.5 times

Battery Cycling V-LFP

Galvanostatic curves

- Capacity is lower in V-LFP than LFP
- Capacity increases as batteries are cycled

CV- Curves

- V-LFP double peak: surface and bulk sites
- V-LFP distorted structure

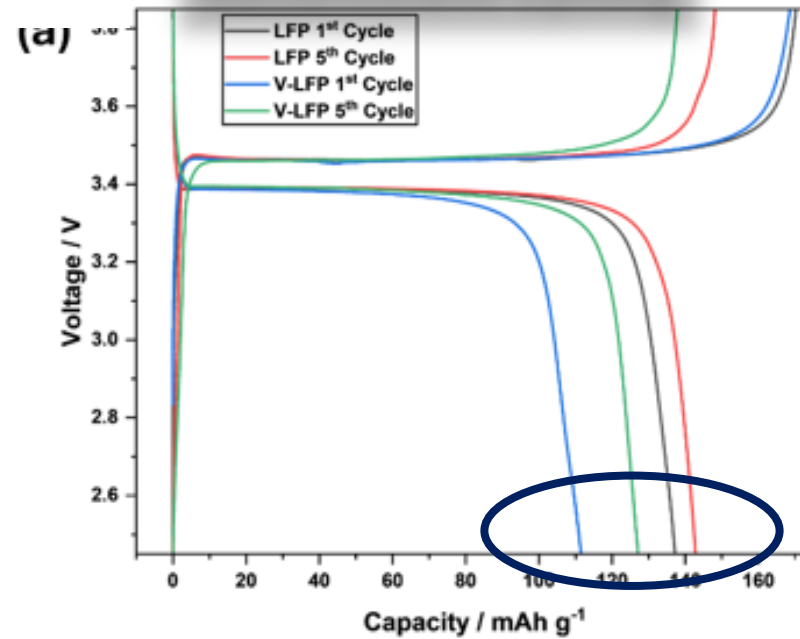
EIS – LFP

- Second semi-circle due to CEI formation

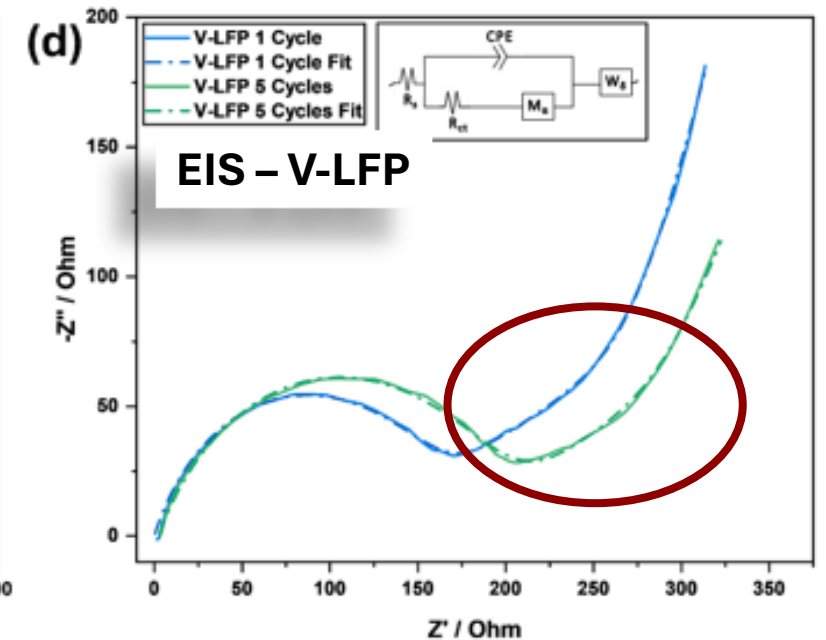
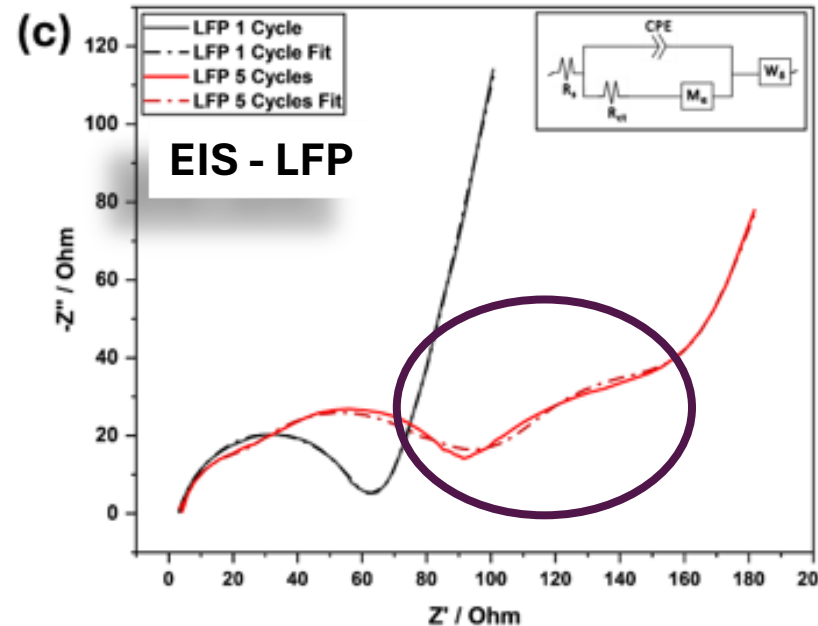
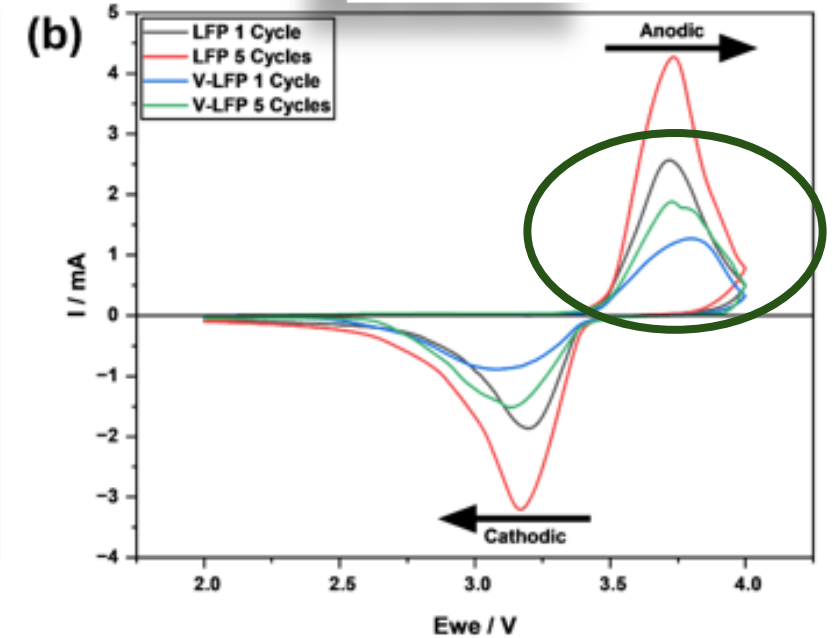
EIS – V-LFP

- Semi-circle in 1st cycle due to CEI or space charging

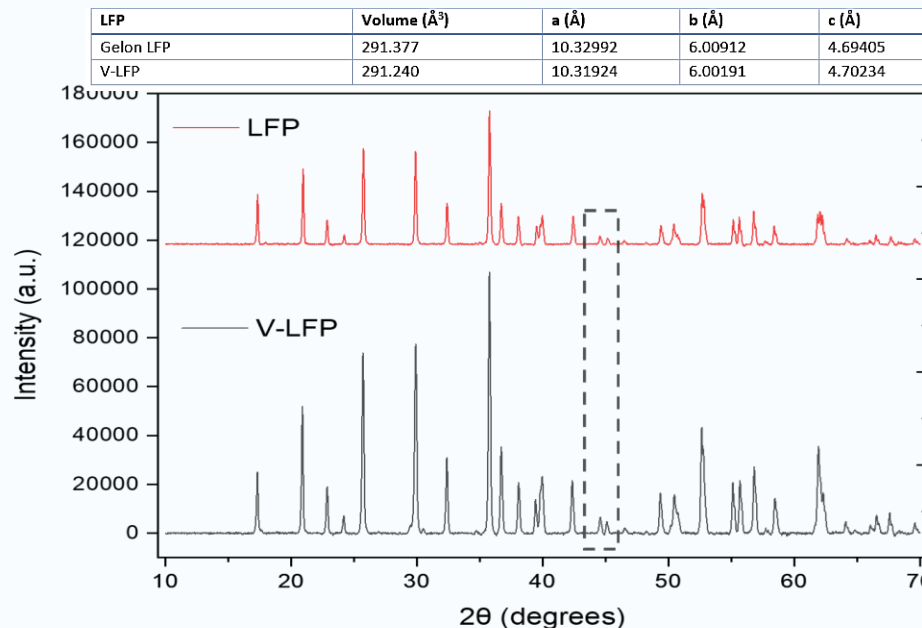
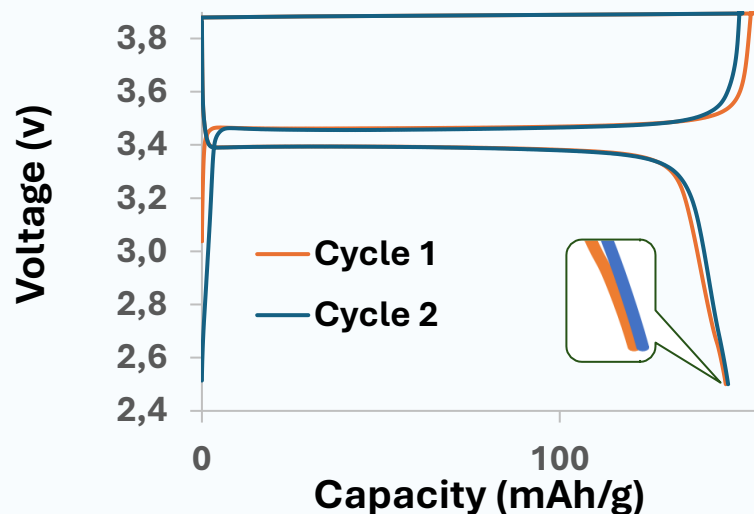
Galvanostatic Cycling



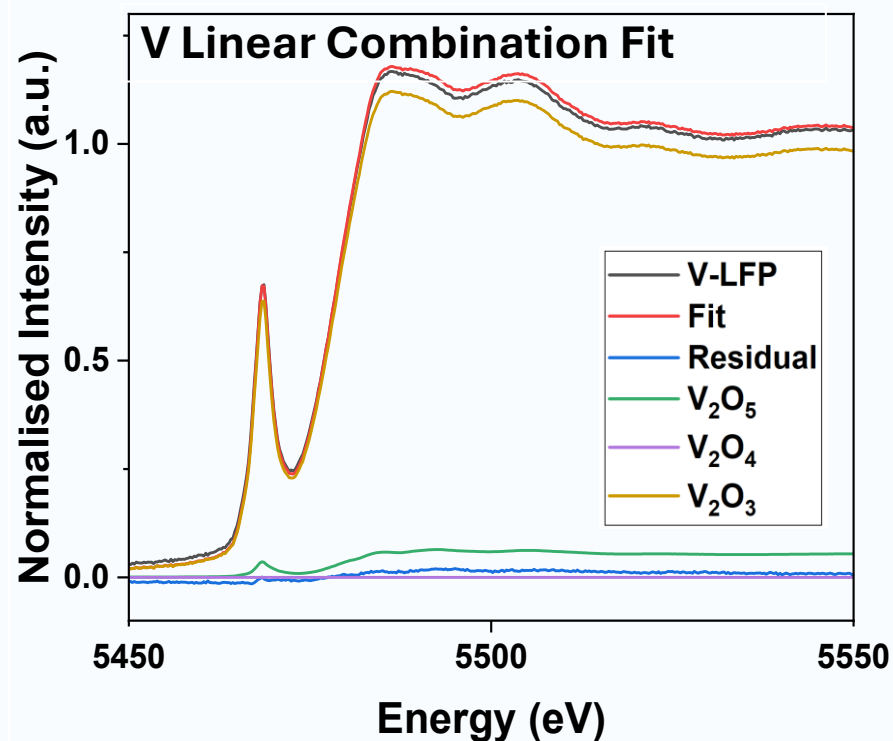
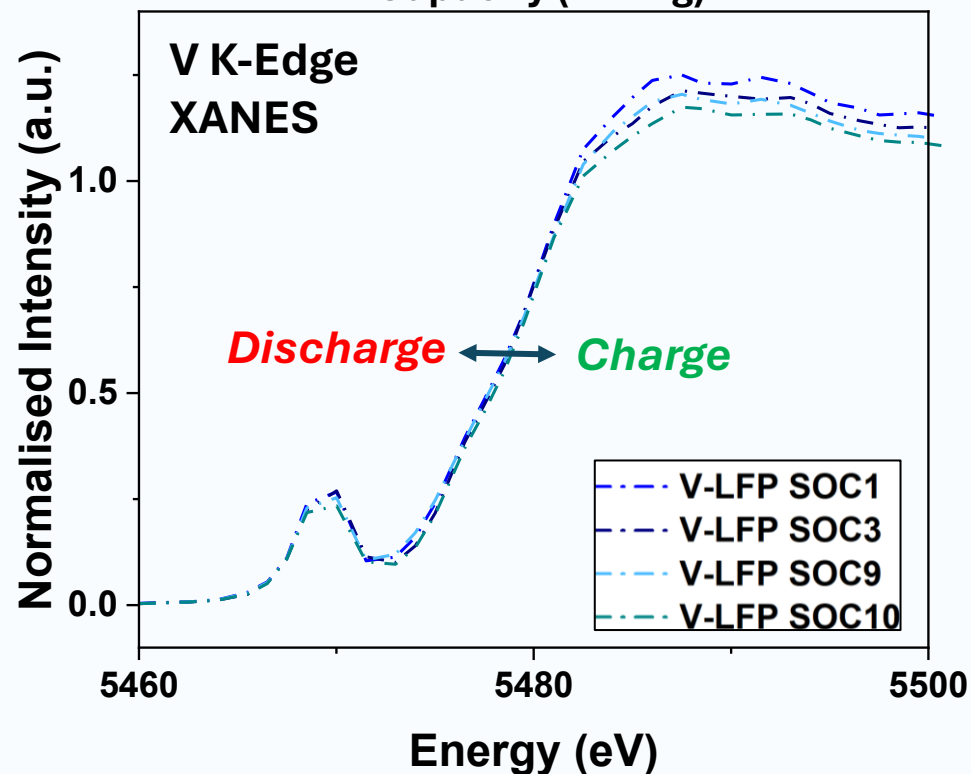
CV-curves



V K-edge in V-LFP



- V(III) is occupying an Fe-site



- V is redox inactive during battery cycling
- Linear combination fittings indicate that V is in the (III) oxidation state

Bond Distances from Radial Distribution Function V-LFP

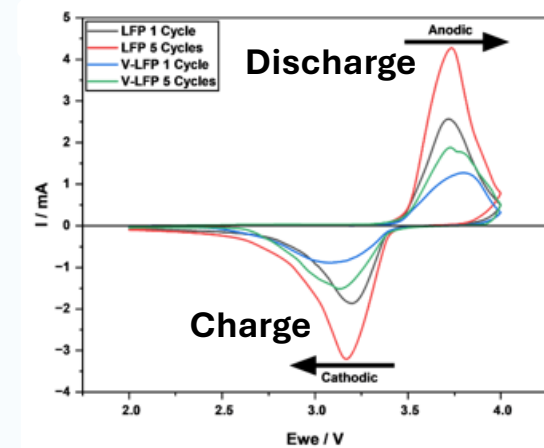
State of Charge (SOC)	Fe Oxidation State	LFP	V-LFP	
		R(Fe–O), Å	R(Fe–O), Å	R(V–O), Å
OCV	Fe ²⁺	2.16 ± 0.05	2.14 ± 0.05	2.08 ± 0.03
SOC3(DC)	Fe ³⁺	1.99 ± 0.04	1.99 ± 0.04	2.05 ± 0.03
SOC9(C)	Fe ²⁺	2.15 ± 0.04	2.10 ± 0.03	2.08 ± 0.03
SOC10(DC)	Fe ³⁺	1.99 ± 0.04	2.00 ± 0.02	2.06 ± 0.02

- Bond distance decreases with Fe oxidation from Fe(II) to Fe(III)
- R(Fe–O) similar in both doped & undoped LFP
- R(Fe–O) shorter in V-LFP after cycling
- R(V–O) changes very slightly – confirming redox inactivity

Diffusion Coefficients V-LFP

Randles–Ševčík equation

$$i_p = \pm (2.69 \times 10^5) n^{3/2} AC \sqrt{D_{app} v}$$



Diffusion Coefficients	LFP (1 cycle)	LFP (5 cycle)	V-LFP (1 cycle)	V-LFP (5 cycle)
Anodic D_{app} (cm ² /s)	2.79×10^{-10}	7.61×10^{-10}	0.69×10^{-10}	1.38×10^{-10}
Cathodic D_{app} (cm ² /s)	1.50×10^{-10}	4.45×10^{-10}	0.34×10^{-10}	0.89×10^{-10}



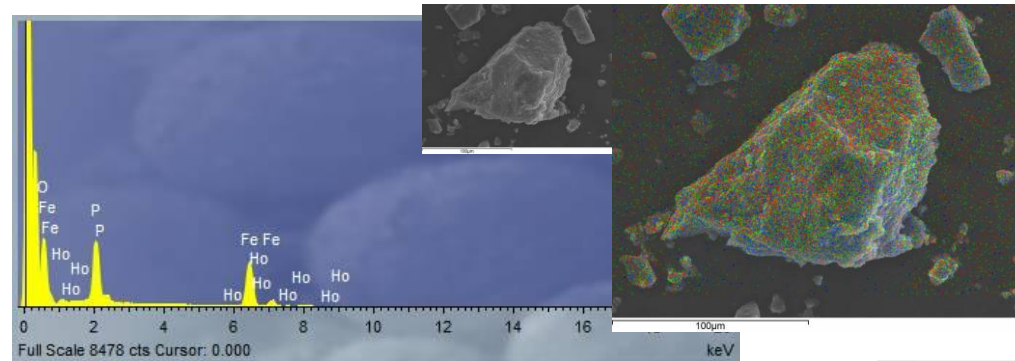
- Diffusion lower in V-LFP than LFP



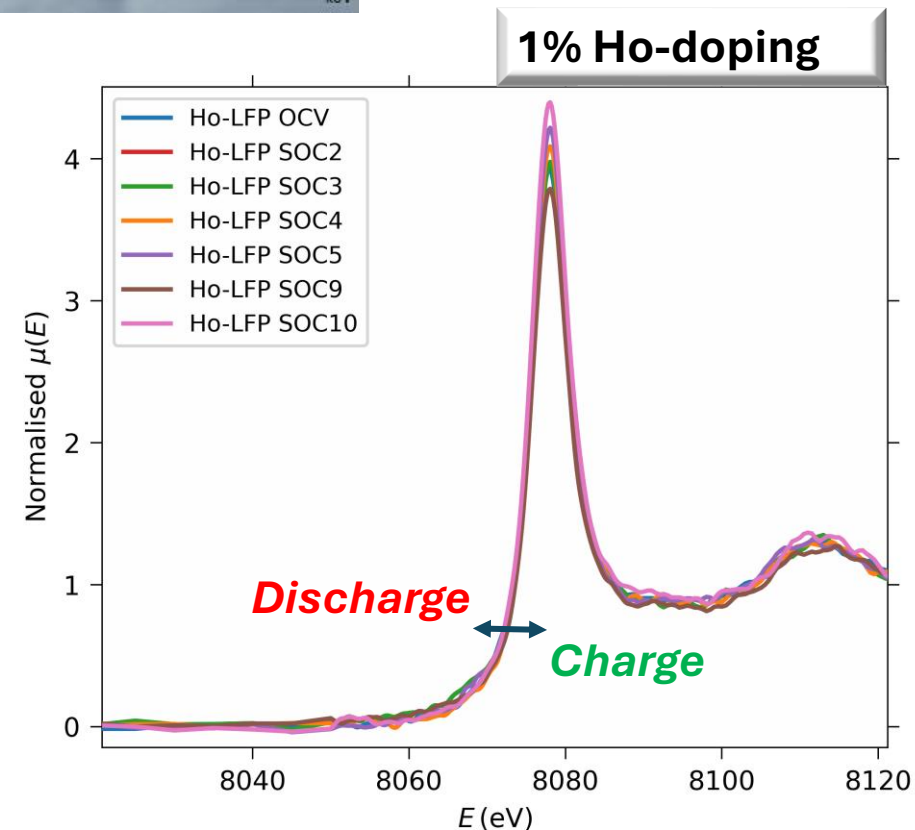
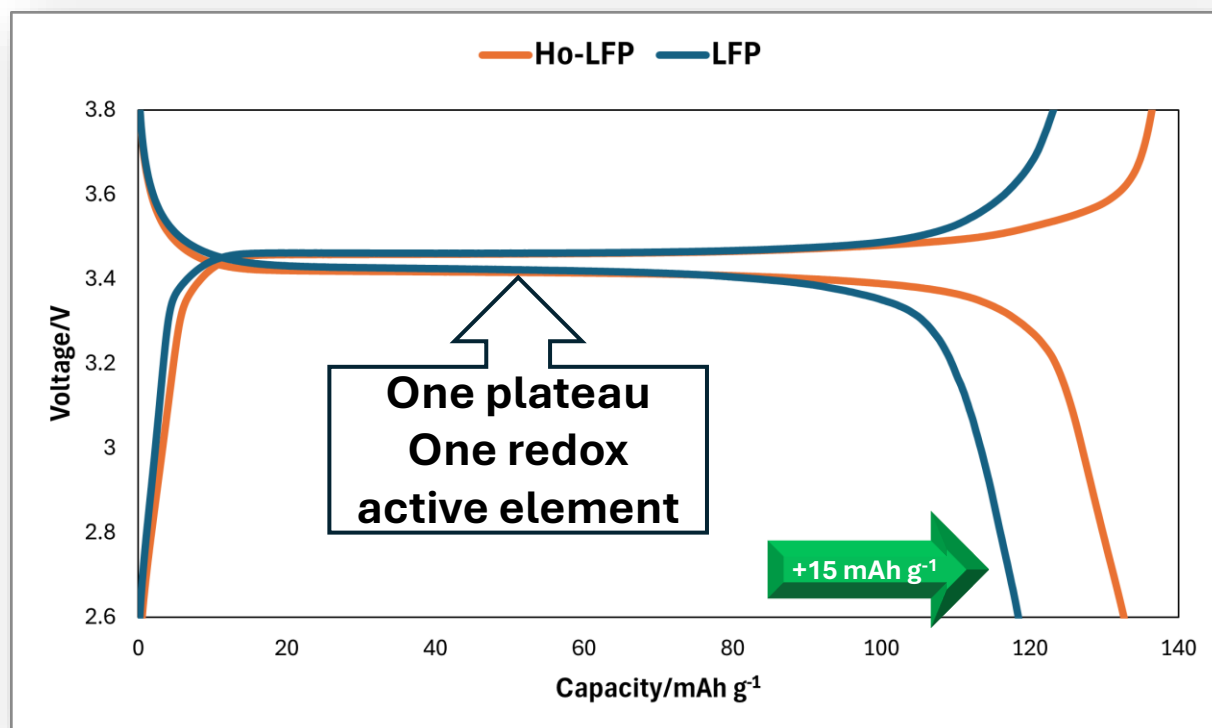
- Diffusion faster for Discharge in both materials
- Diffusion rate increases by cycling in both materials

Ho L_{III}-Edge XANES

- EDX analysis indicated that Ho was present in the LFP sample



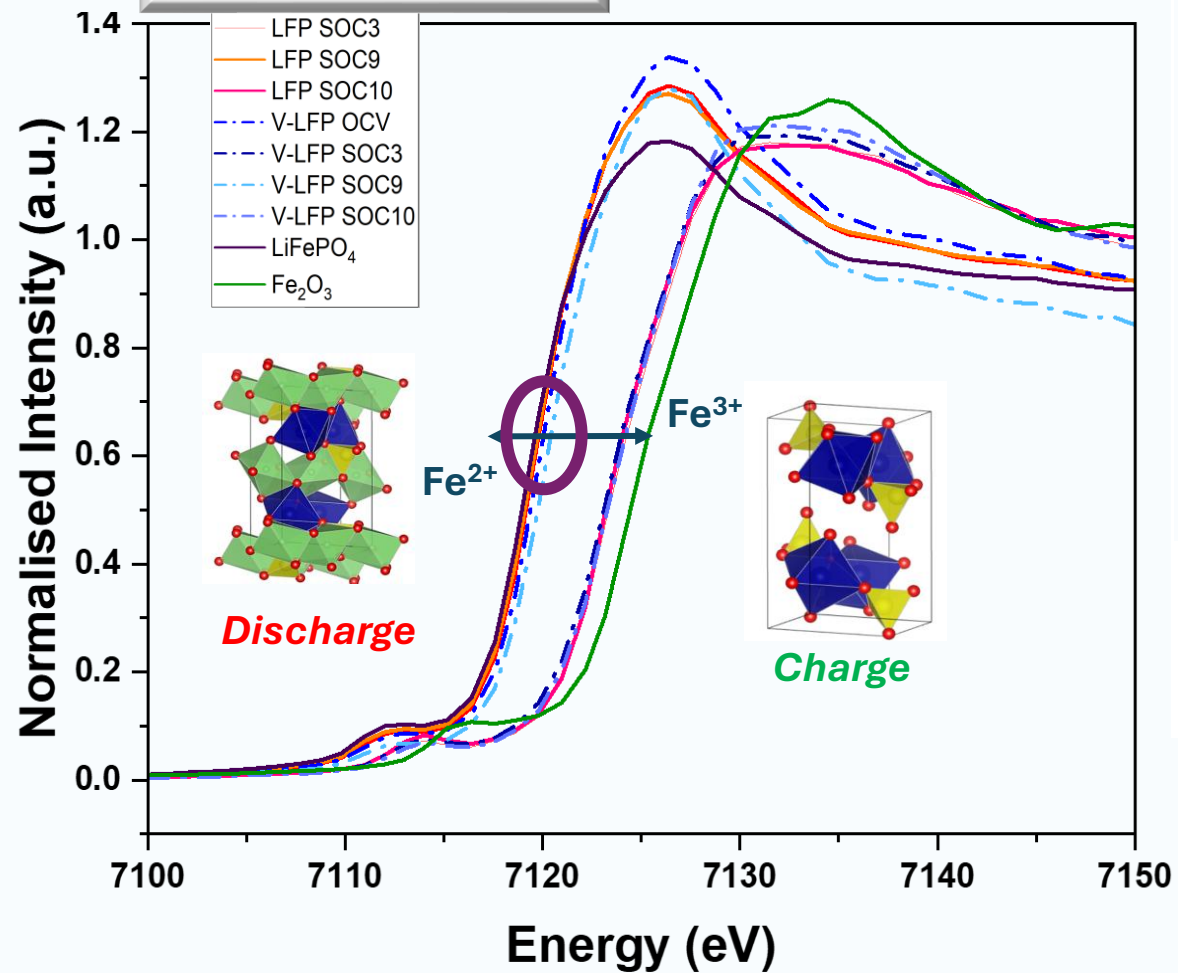
Synthesised Ln-doped LFP	Volume (Å ³)	a (Å)	b (Å)	c (Å)
Undoped LFP	290.435	10.31462	5.99651	4.69567
1% Ho	290.686	10.31458	6.00224	4.69526



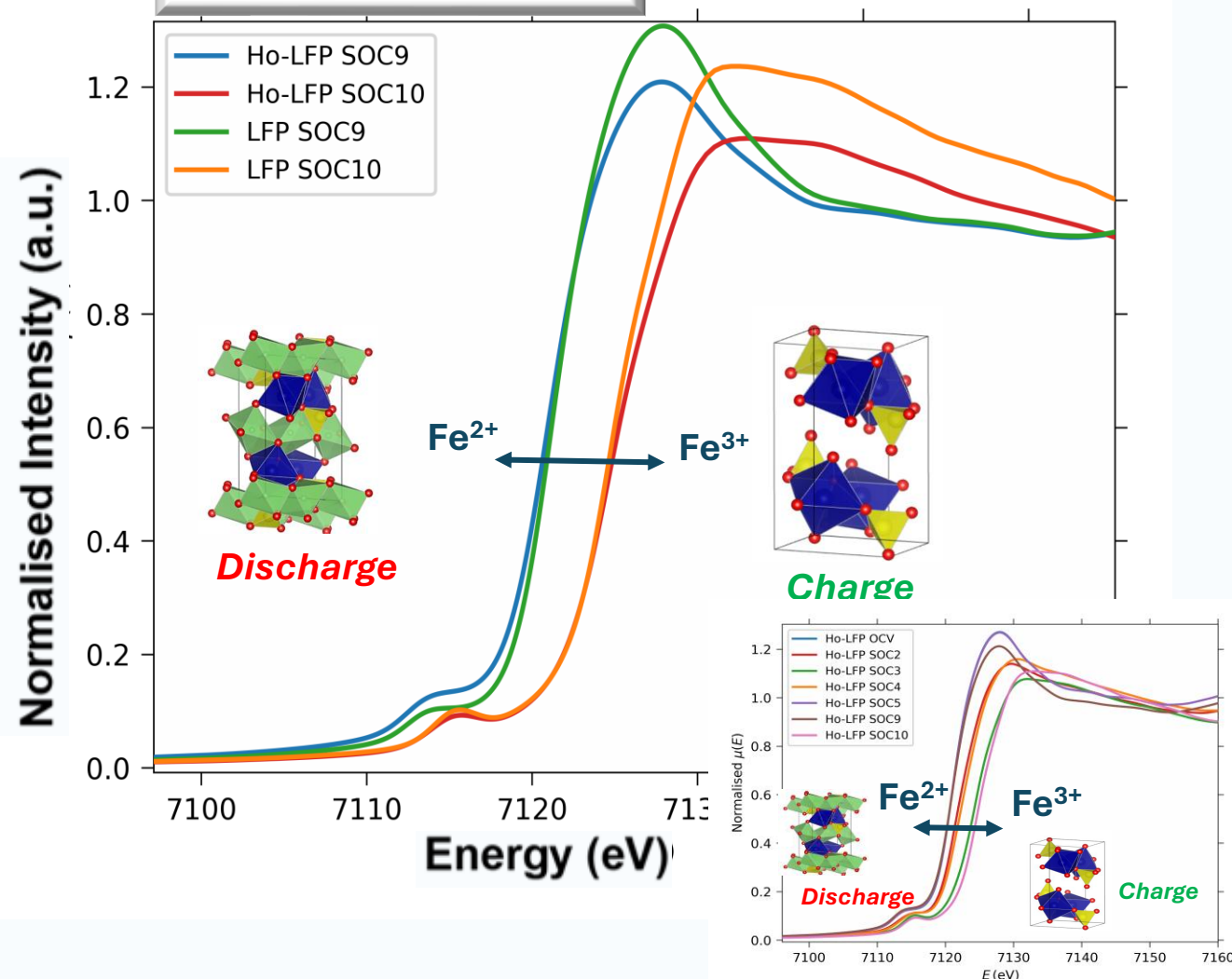
- No shift in the edge
- Ho is not redox active

Fe K-Edge XANES

V-doped LFP

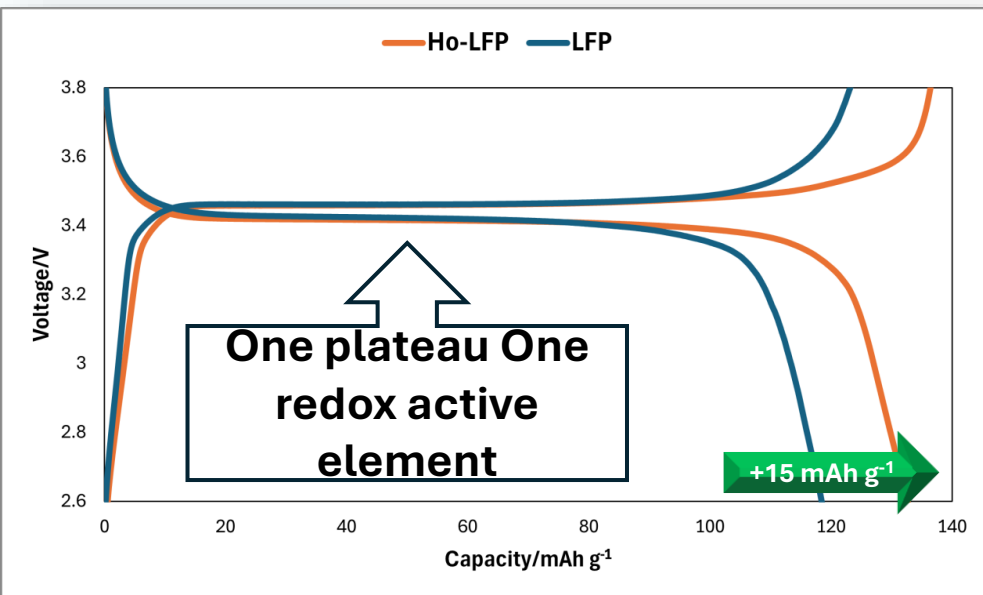
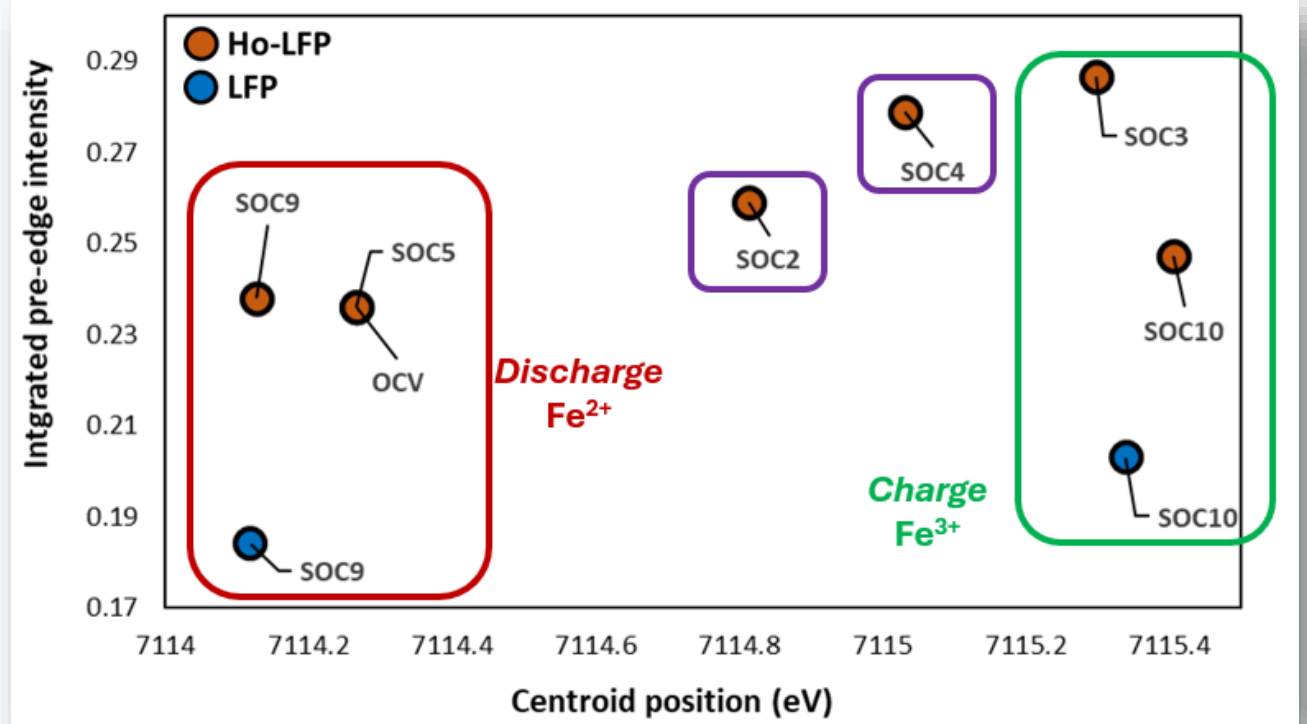
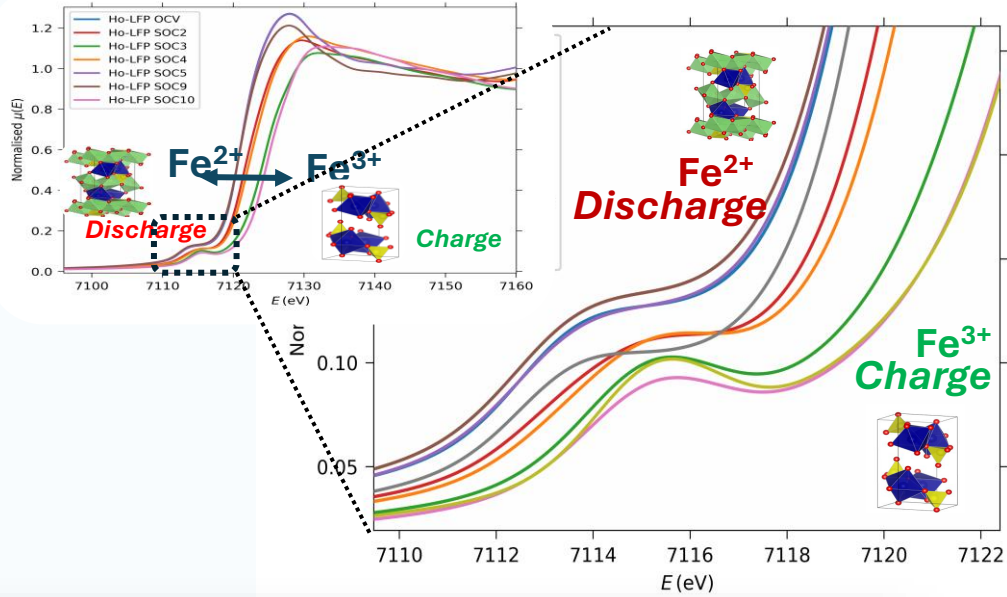


Ho-doped LFP



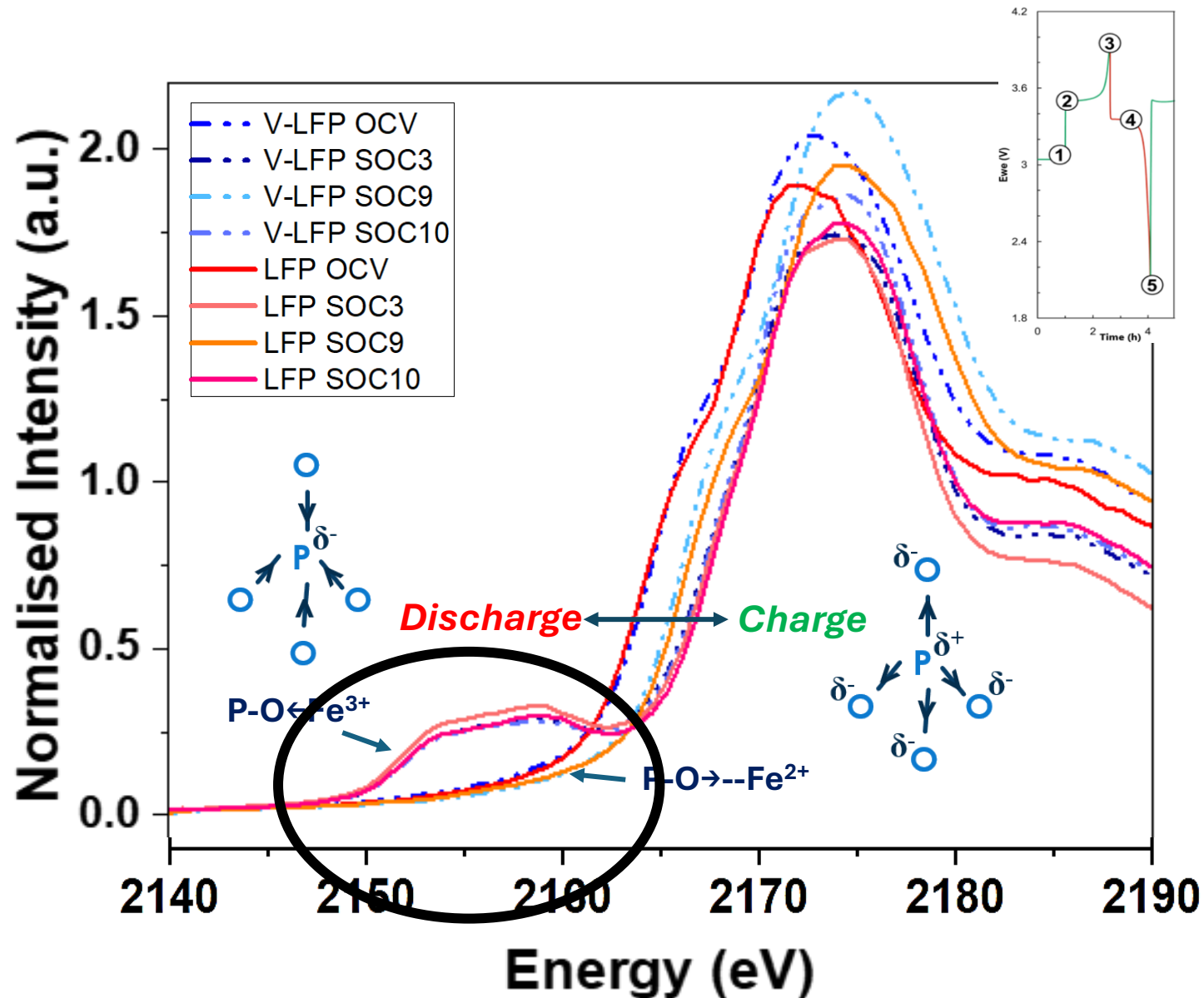
- No clear change in the K-edge position between LFP and the doped materials

Fe K-edge and correlation XANES



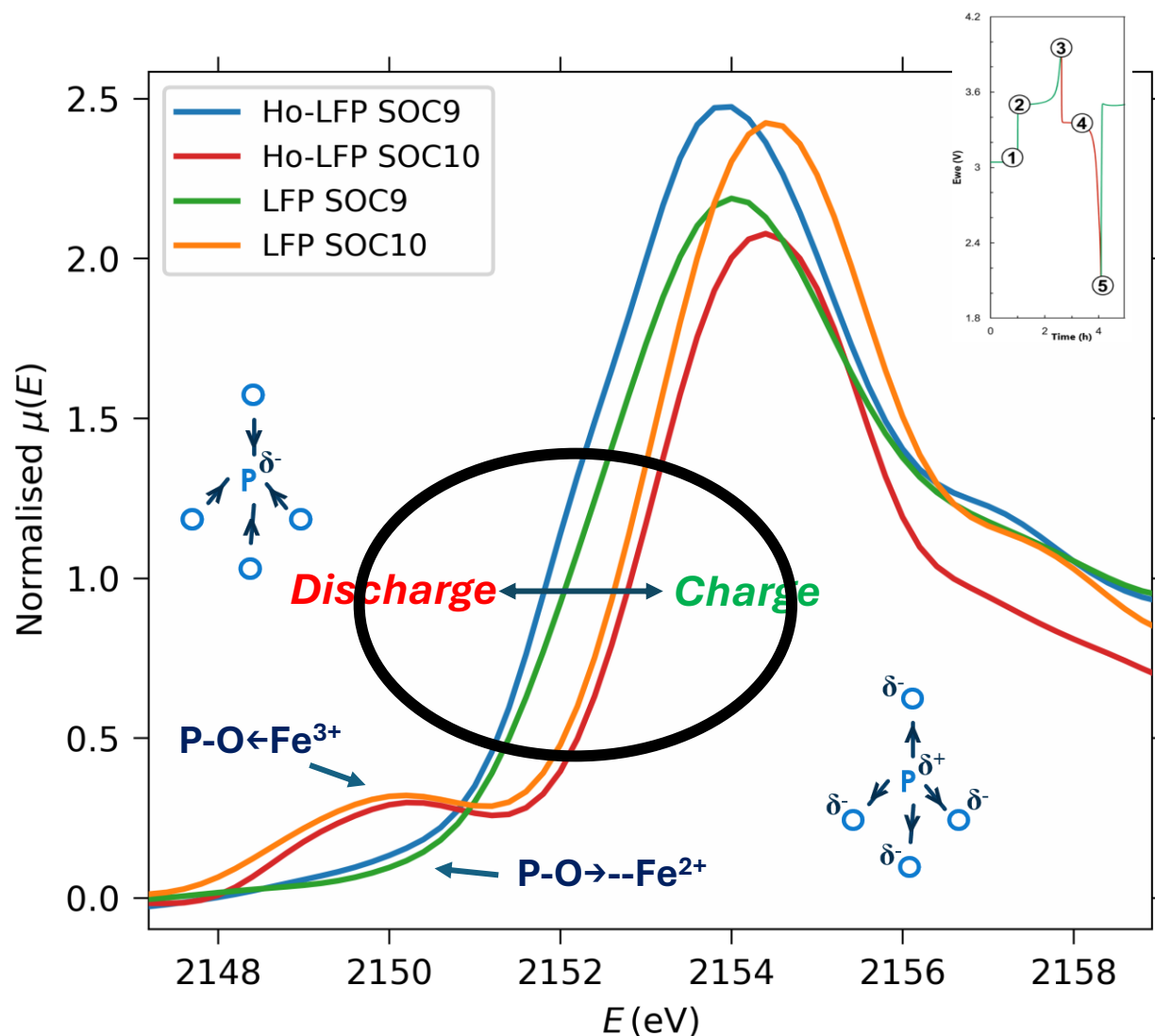
- Pre-edge intensities are higher in Ho-LFP than LFP
- Indicating higher disorder in Ho-LFP than LFP
- Increased Li-ion diffusion

P K-Edge XANES; V-LFP

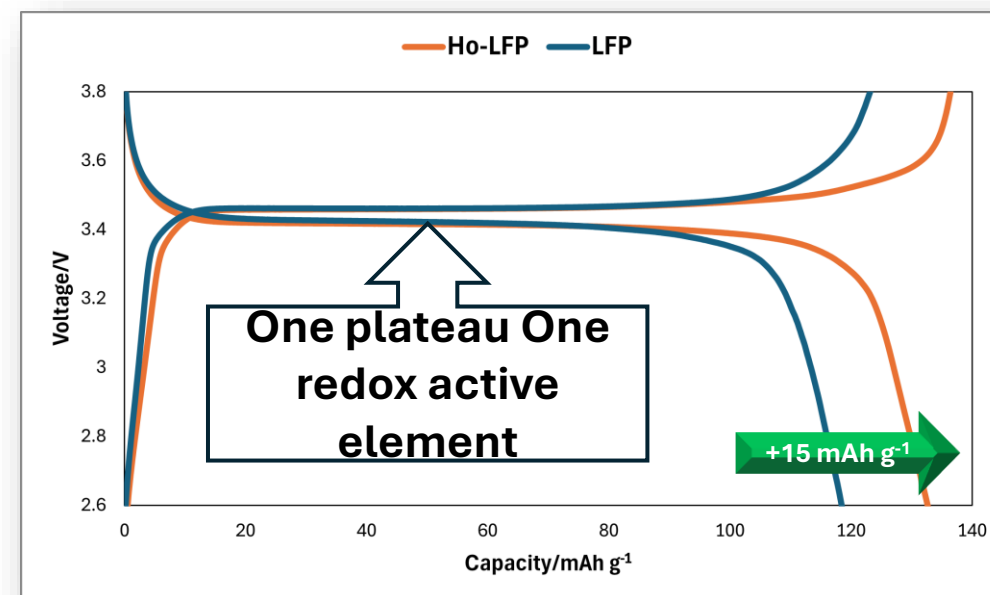


- K-edge energy values are upshifted during delithiation
- **Change in pre-edge feature due to electron redistribution**
- **Caused by hybridization between P (*p-orbitals*) and Fe (*d-orbitals*) (DFT-calculations)**
- No discernable change between LFP & V-LFP

P K-Edge XANES; Ho-LFP



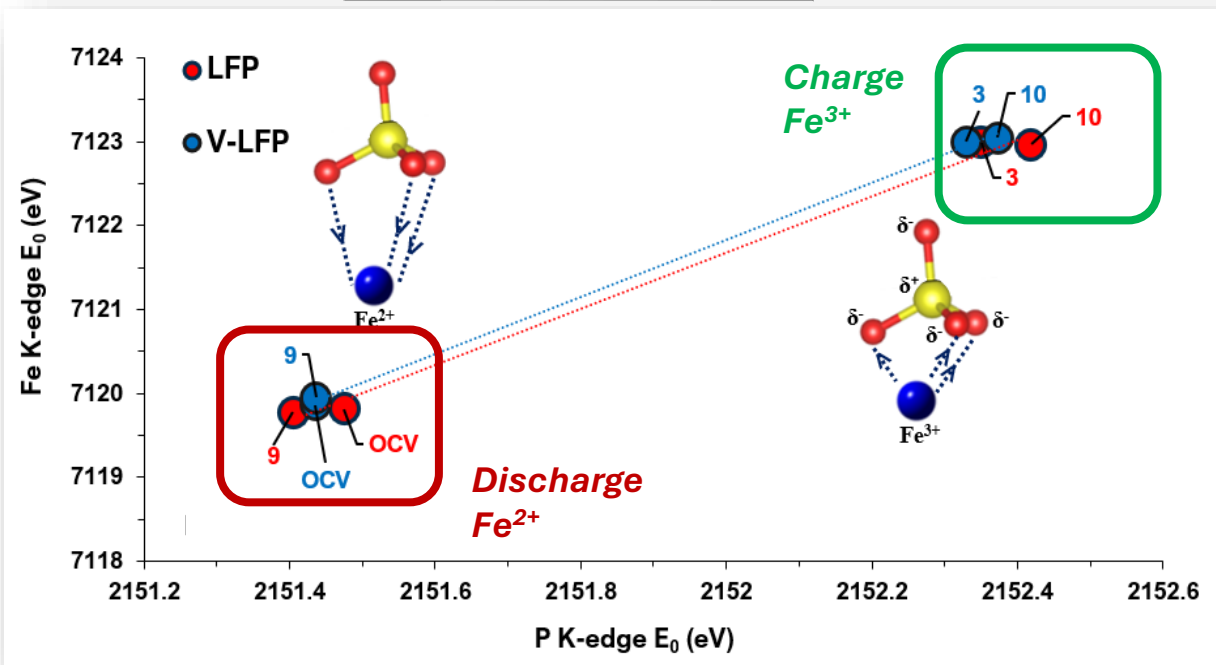
- K-edge energy values are upshifted during delithiation
- Change in pre-edge feature due to electron redistribution
- **Ho-LFP K-edge down(II)/up(III)-shifted compared to LFP**
- **Higher polarization (induction effect) in PO_4^{3-} anion in Ho-LFP than LFP**



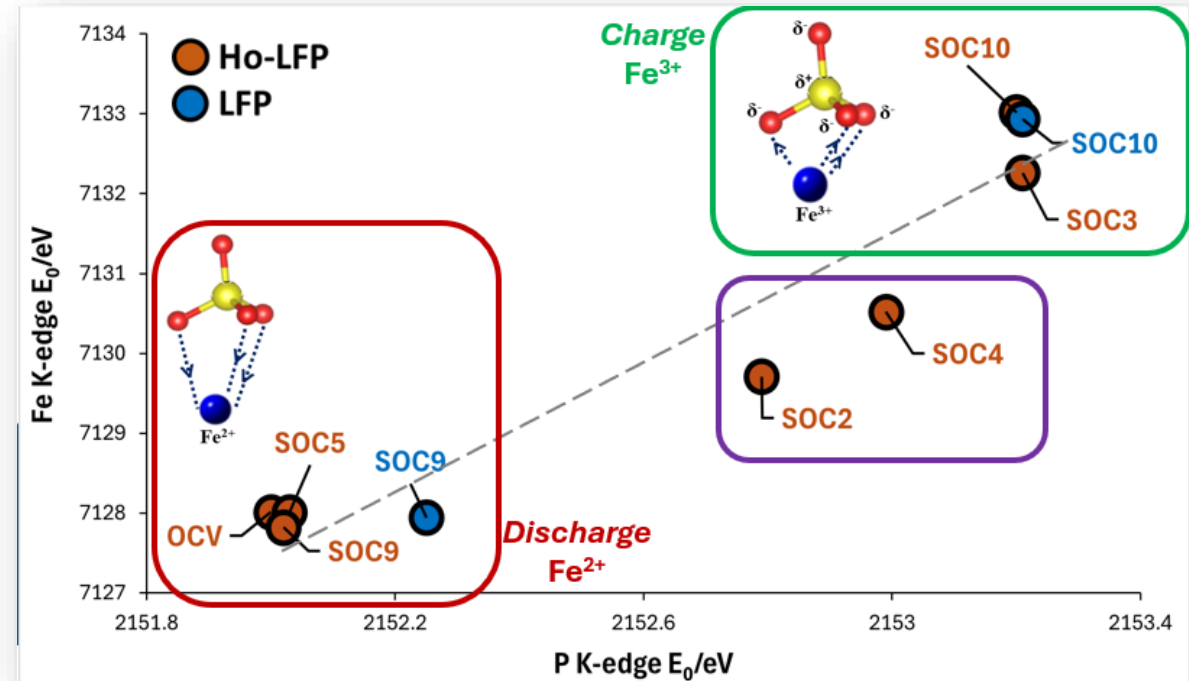
Conclusions V- and Ho-LFP

Fe and P K-edge correlation

V-doped LFP



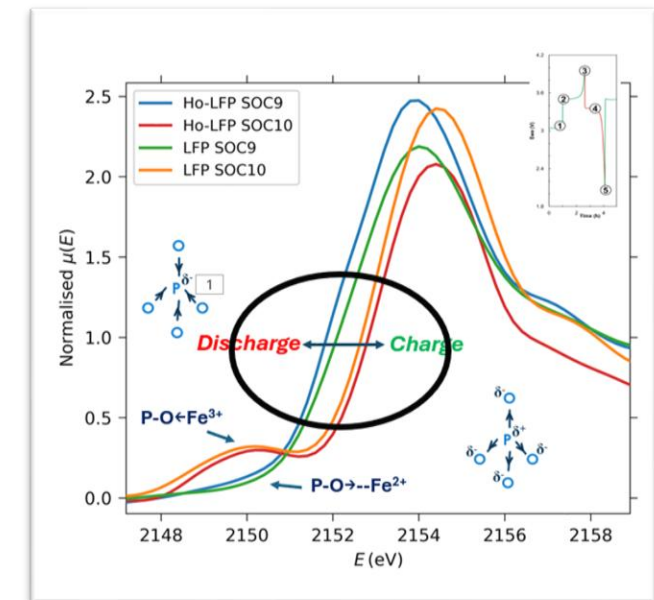
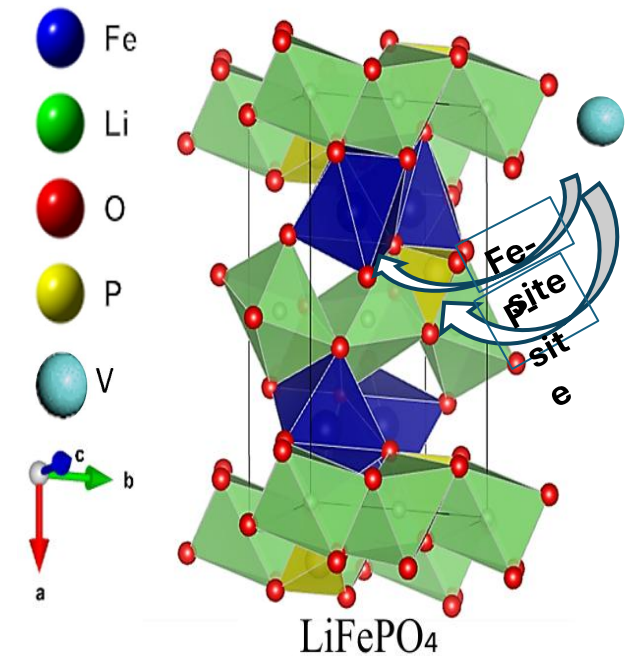
Ho-doped LFP



- P K-edge Linear Correlation with the Fe K-edge
- PO_4^{3-} is active in the material enhancing inductive effect
- Higher capacity due to inductive effect

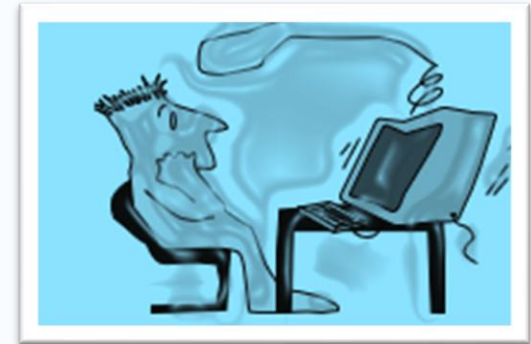
Take away message

- **V and Ho are redox inactive** and does not contribute to the induction effect during battery cycling
- **V-LFP** introduce an up-shift in the K-edge position resulting in shorter **Fe-O bond distance** – **improved Li-ion diffusion**
- **Ho-LFP** shows **higher disorder** in the local structure than LFP
- Lattice defects due to presence of V and Ho may improve rate capability as b-axis shorter
- **P is active in the redox mechanism** during battery cycling
- P K-edge in **Ho-LFP** is upshifted compared to LFP indicating **higher polarisation** (induction effect) - **higher specific capacities**.



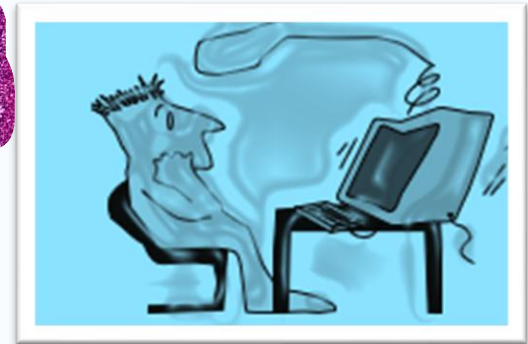
Layout

- Decoupling Polyanion Redox from Electrolyte Contributions in LiFePO_4 : Insights from Fe, Ho, V and **P K-Edge XANES**
- Oxygen redox in $\text{Li}_2\text{FeSiO}_4$: Insights from X-ray Raman Spectroscopy (XRS)
- How manage Oxygen redox in LiNiMnCoO_2 (NMC): Insights from DFT simulations

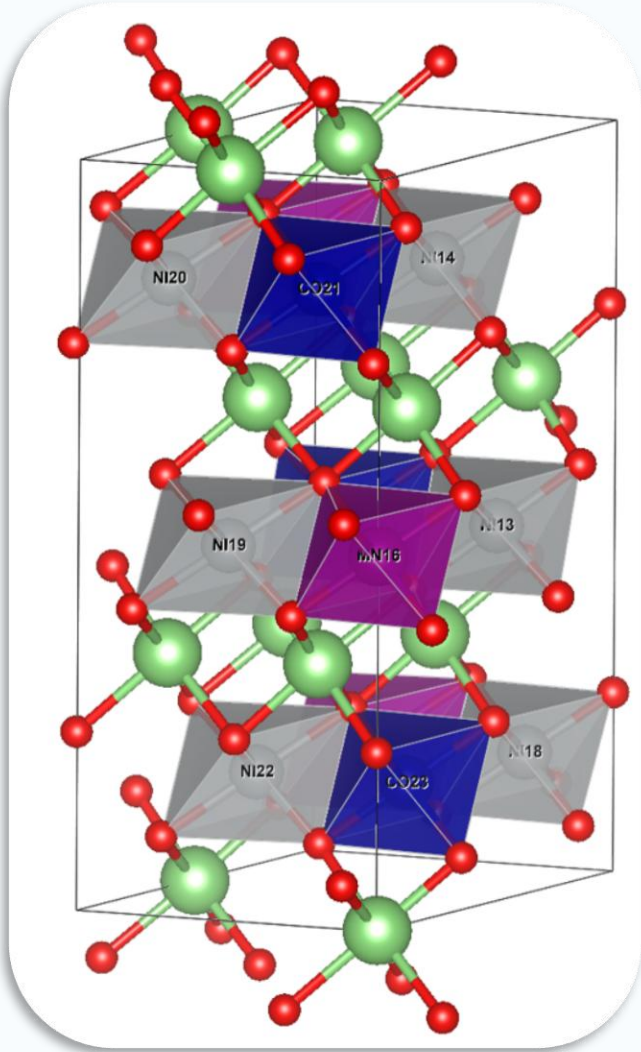


Layout

- Decoupling Polyanion Redox from Electrolyte Contributions in LiFePO_4 : Insights from Fe, Ho, V and **P K-Edge XANES**
- Oxygen redox in $\text{Li}_2\text{FeSiO}_4$: Insights from X-ray Raman Spectroscopy (XRS)
- How manage Oxygen redox in LiNiMnCoO_2 (NMC): Insights from DFT simulations



Aims of study



Our aims are:

- Understand the activation of oxygen for different stoichiometries of NMC and
- Understand its effects on electrochemical performance



HyXeBat
Metrology Project



Gen-AI
Ontologies

Summary and Aims of WP4

The aim of this work package is to develop computational tools to support the experimental metrology that is to be developed in WP1, WP2 and WP3.

Develop modelling and computational tools - large datasets - enabled by hybrid metrology.



Task 4.1

Theoretical calculations to aid in the interpretation of experimental data generated in WPs 1-3

Task 4.2

Establishment of a database and associated tools to handle the accompanied large datasets

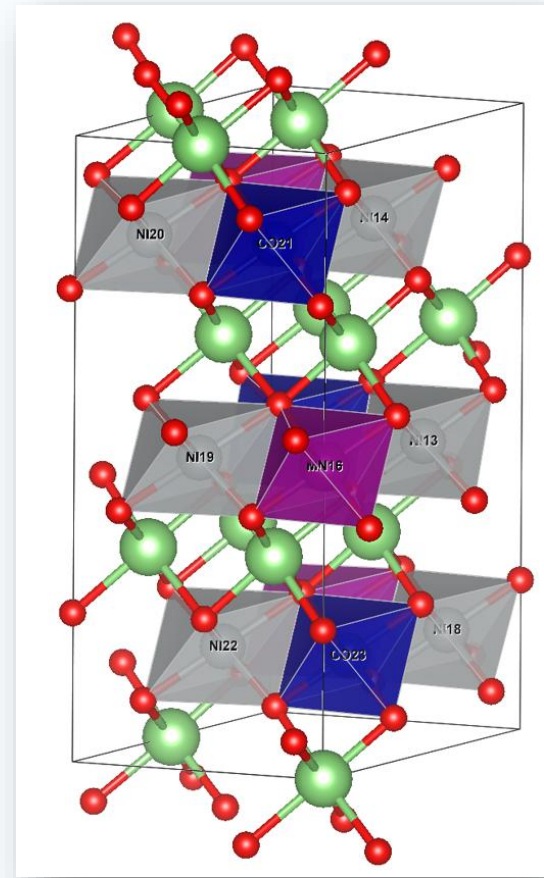
Task 4.3

Application of ML approaches to enable automation of hybrid operando data handling.
Specifically targeting experimental outputs of WP3.

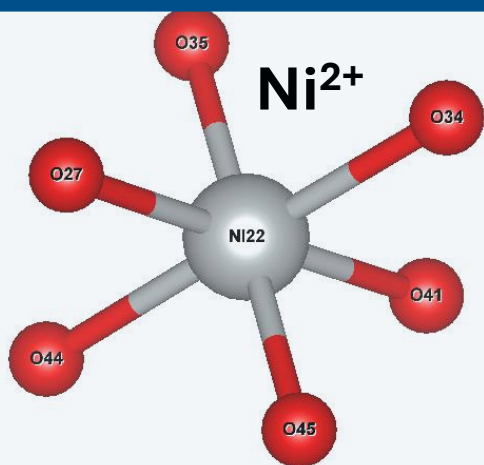
Computational Setup

Computational Set-up

- *CRYSTAL2023¹ – All electron Gaussian basis set*
- **PBE0** – hybrid functional
- 2x2x1 cell contains 12 transition metal (TM) sites.
- We thus refer to it as the *12-formula unit cell*.
 - **NMC633**: Ni-poor NMC phase compare NMC622
 - **NMC1011**: Ni-rich NMC phases compare NMC811



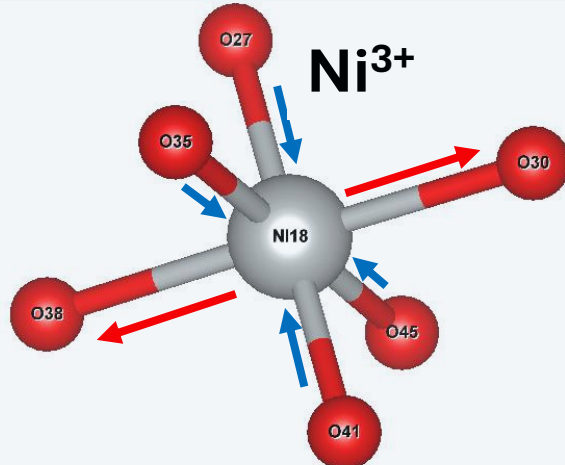
Jahn-Teller Distortion – Validation of method



Ni²⁺ Bond lengths (Å)

Ni-O	2.014
Ni-O	2.018
Ni-O	2.025
Ni-O	2.032
Ni-O	2.051
Ni-O	2.059

**6 x
Similar
Ni-O**



Ni³⁺ Bond lengths (Å)

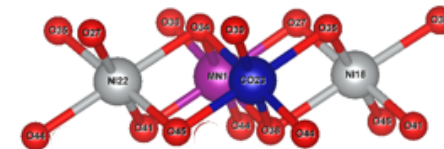
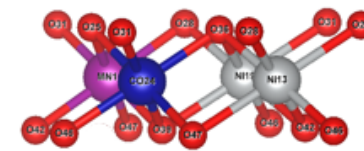
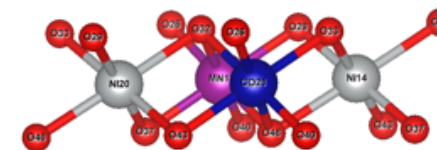
Ni-O	1.879
Ni-O	1.881
Ni-O	1.907
Ni-O	1.914
Ni-O	2.097
Ni-O	2.103

**4 x & 2 x
Similar
Ni-O**

- Local distortion and spin state of the TM ions are **strongly correlated**. Even if composition is the same, **different layers have different local structures**.

- 1st and 3rd layer:
 - **Ni²⁺** **HS**, JT inactive
 - **Ni³⁺** **LS**, **JT active**
 - **Co³⁺** **LS**, JT inactive
 - **Mn⁴⁺** **HS**, JT inactive

- 2nd layer:
 - **Ni²⁺** **HS**, JT inactive
 - **Ni³⁺** **LS**, **JT active**
 - **Co³⁺** **LS**, JT inactive
 - **Mn⁴⁺** **HS**, JT inactive



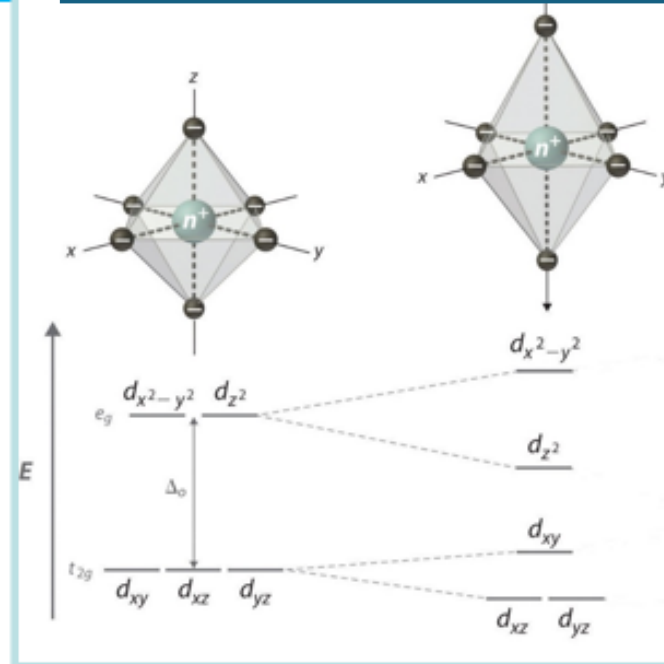
PBE0 using the CRYSTAL23 code correctly identify local geometries

Polarons

NMC633: Observed Metastable State

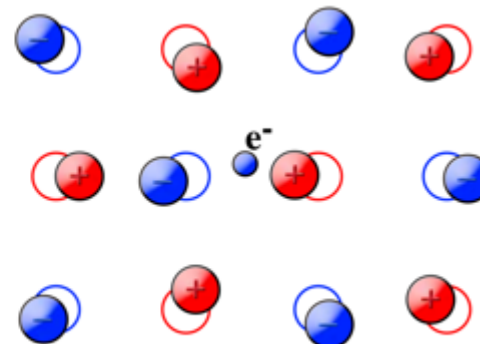
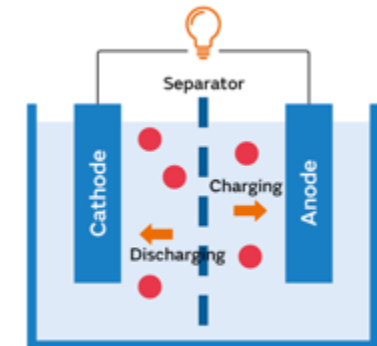
- **Intermediate state** (IS) observed for Co^{3+} (d^6) in NMC633, when Co is located in a distorted environment.
- The structure is **metastable** relative to the low spin (LS) solution, but a local minimum in the energy surface could be formed as transient species during cycling.
- **Importance of polaron-induced distortions.**
- $\Delta E_{LS-IS} \sim 0.5 \text{ eV}$ per Cobalt ion.
 - **Oxidation and electronic state of the TMs adapt to the local environment.**
 - Local distortions induced by **polarons** can force ions to adopt a different spin-configuration, even if other configurations are energetically more favorable.

$$\Delta E_{LS-IS} \sim 0.56 \text{ eV per Cobalt ion.}$$



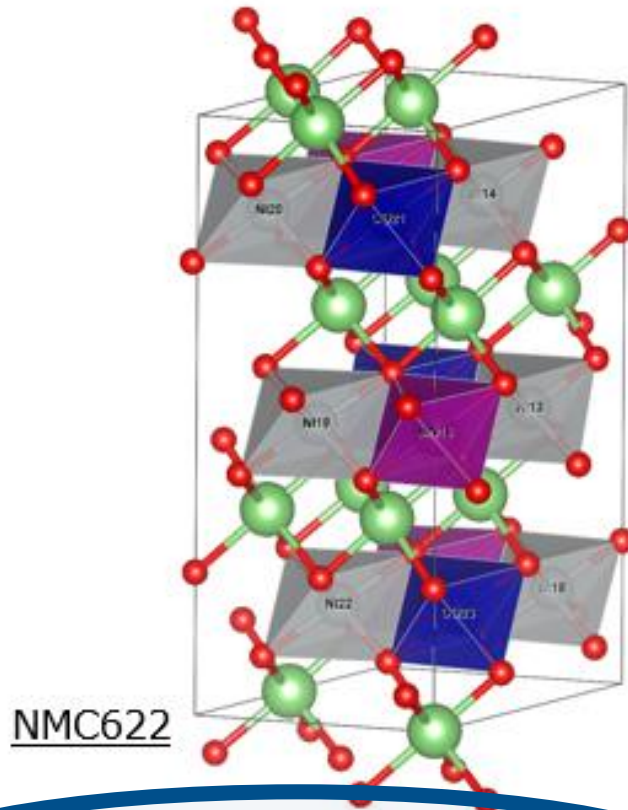
Why is this important?

- e^- are added and removed from the d -orbitals upon battery cycling. If the local environment permits, some e^- may be pulled from and added to TM sites where the JT distortion is not the most stable.
- **Could be important in the degradation of a battery.**



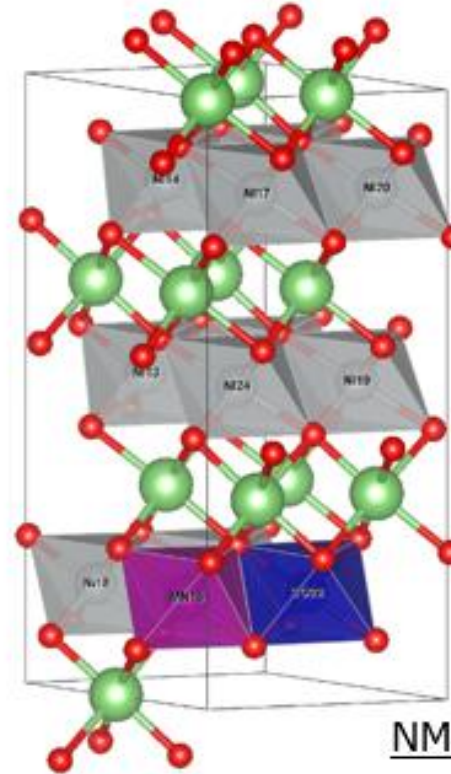
Ion distribution

Our focus is on **Nickel-poor** and **-rich** $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC) cathodes.



NMC622

- Ni/Mn disproportionation is present in each TM layer.
- Each layer occupied evenly by 1Ni^{2+} , 1Ni^{3+} , 1Mn^{4+} and 1Co^{3+} .



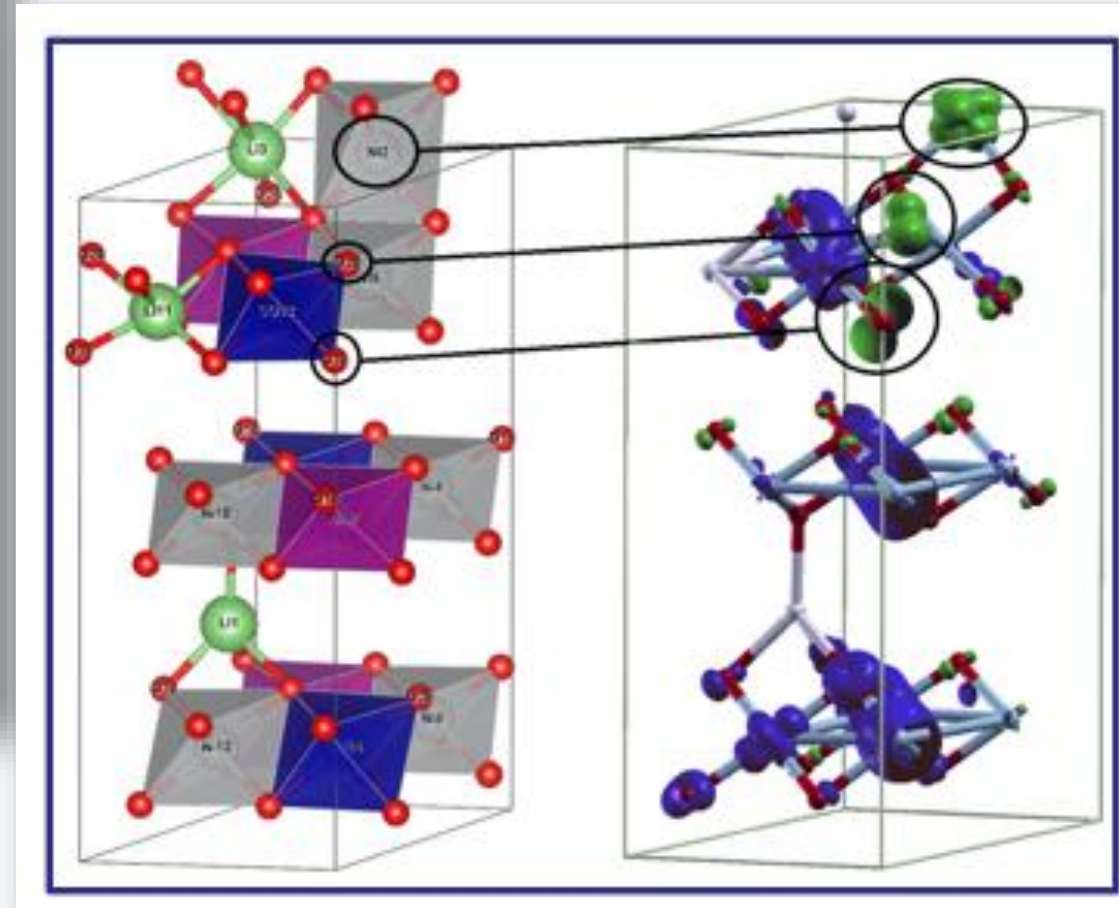
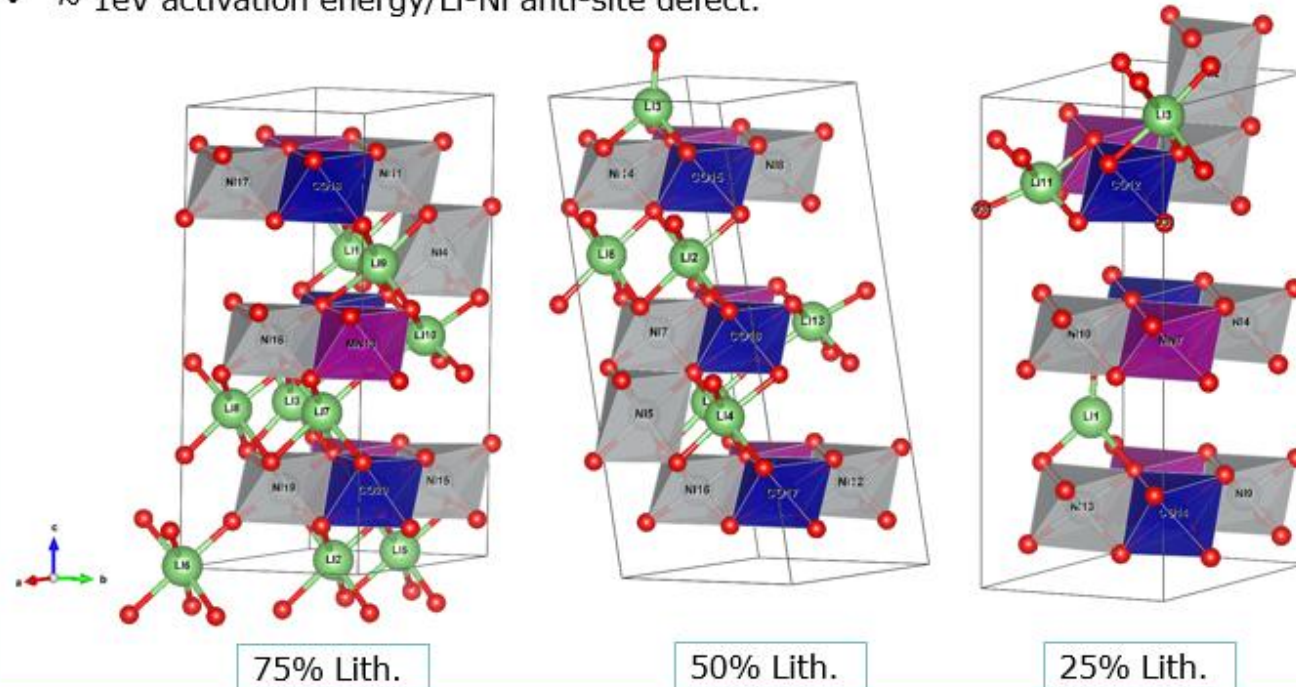
NMC811

- Configuration with Mn and Co in same layer is more favorable.
- A 12-formula unit cell is used in both cases.

De-lithiation – OXYGEN redox

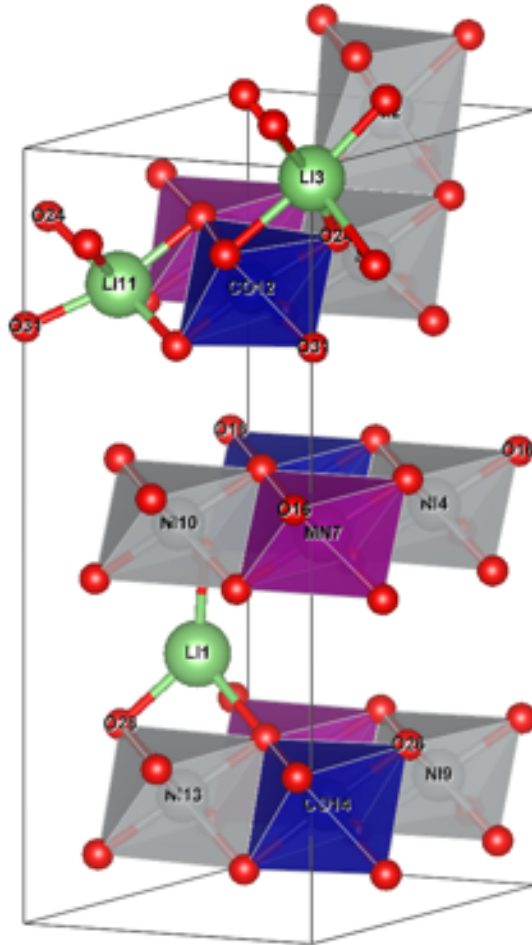
Local threshold for O activation: at 75% and 50% lithiation no O activation.
Once the cell reaches 25% lith. Oxygen will participate in a redox reaction.

- ~ 1eV activation energy/Li-Ni anti-site defect.

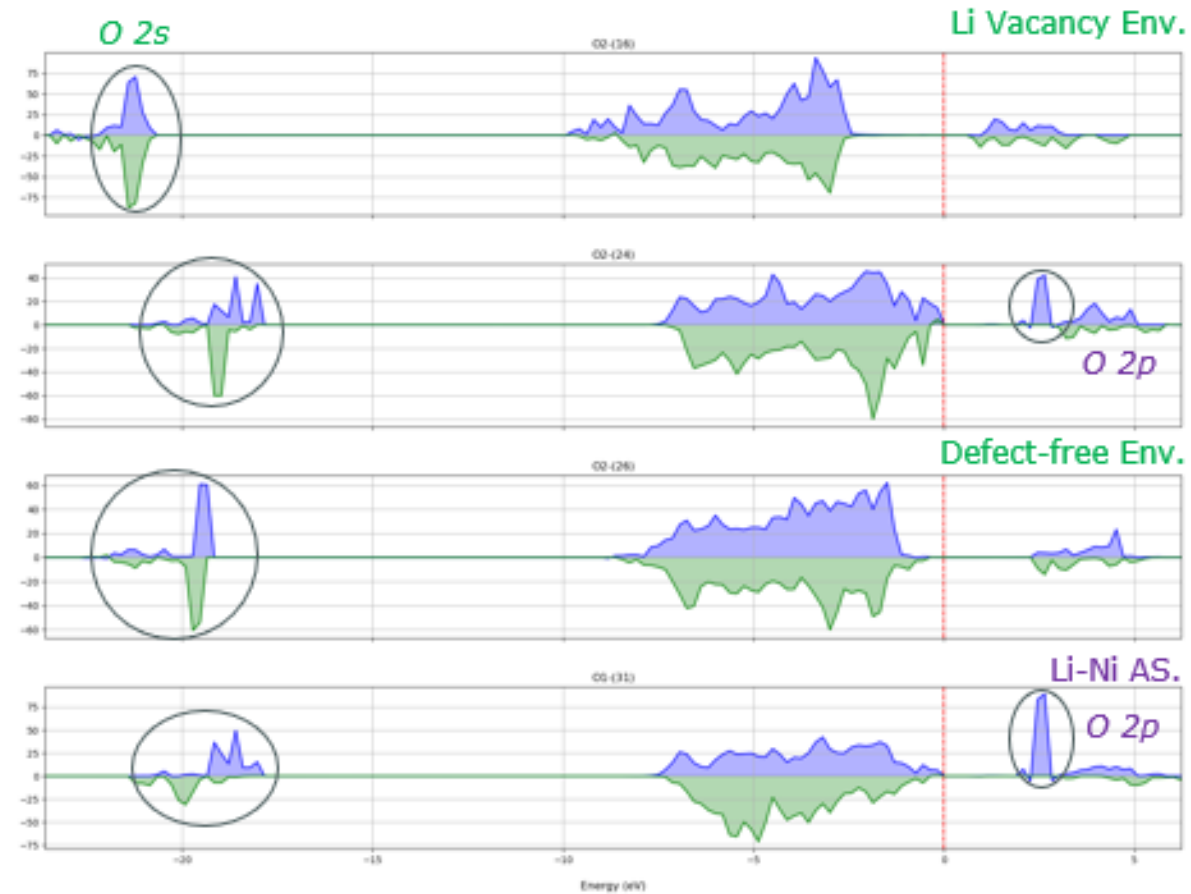


OXYGEN activation

Density of States analysis shows a **difference between O ions in defect-free vs anti-site environments.**

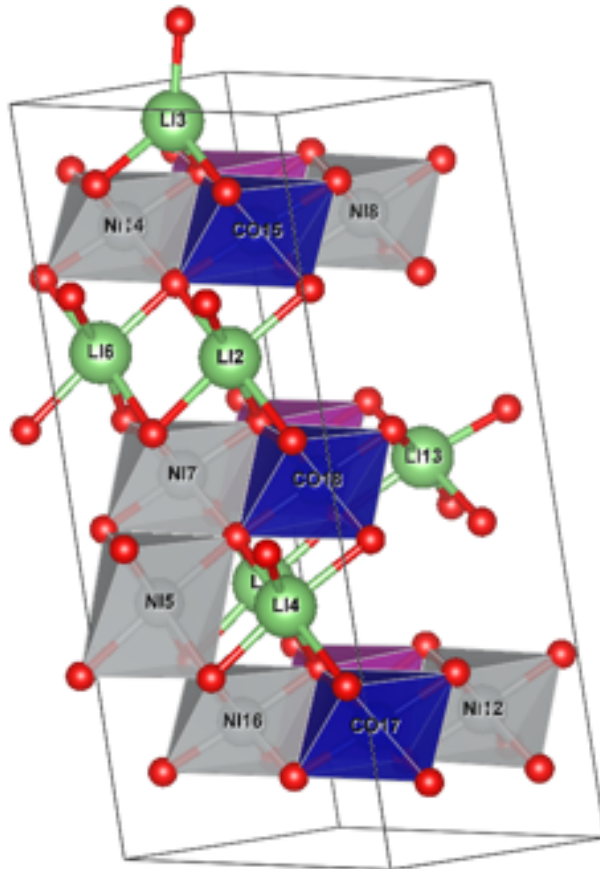


25% Lith.

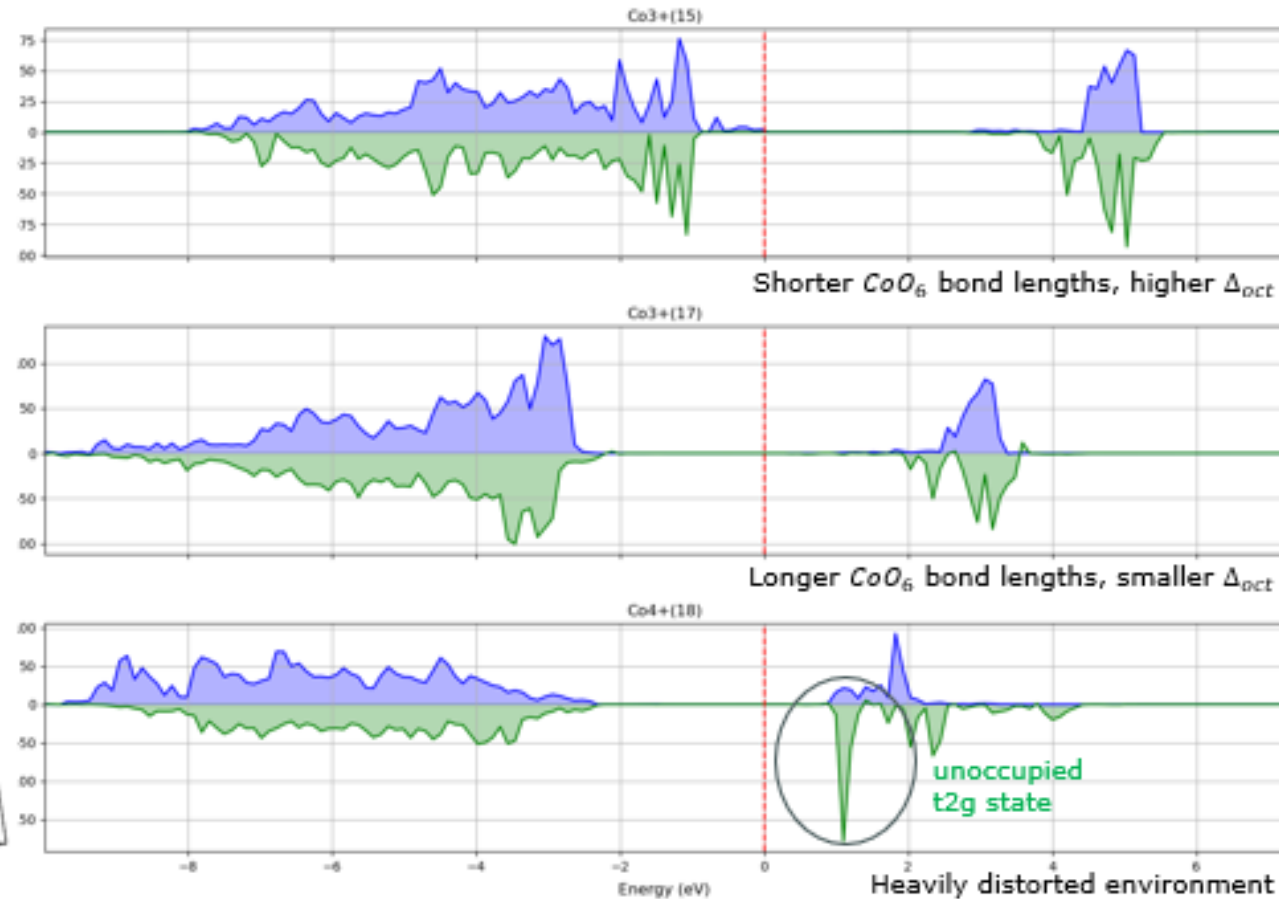


Co-protects oxygen activation

There is a threshold for Co activation also: at 50% lith. no O activation, but Cobalt goes to 4+ oxidation state (initially 3+).



50% Lith.



A Hybrid DFT-CTM Method for Theoretical Spectroscopy

1. DFT:

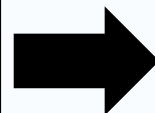
$$\hat{H}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

2. CTM:

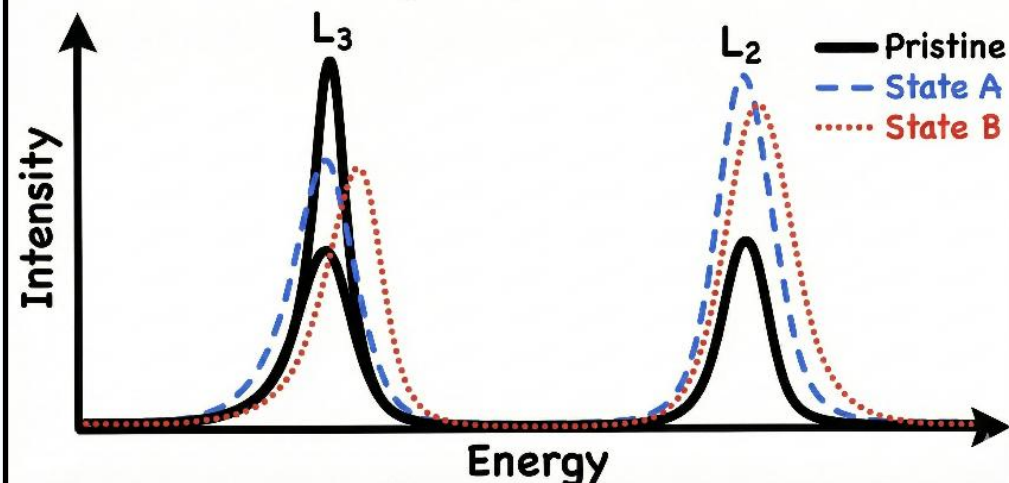
$$\hat{H}_{\text{CTM}} = \hat{H}_{\text{atom}} + \hat{H}_{\text{CF}} + V_{\text{mix}} \sum_{\mathbf{k}} (\hat{c}_{\text{d}}^{\dagger} \hat{c}_{\mathbf{k}} + \hat{c}_{\mathbf{k}}^{\dagger} \hat{c}_{\text{d}}) + \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}}$$

3. FGR:

$$\Gamma_{\text{fi}} = \frac{2\pi}{\hbar} |\langle f | \hat{H}' | i \rangle|^2 \delta(E_f - E_i)$$

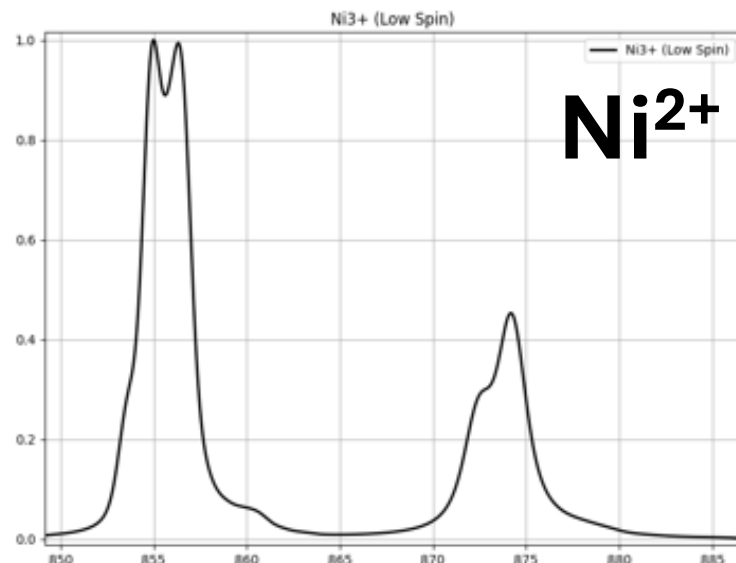


Nickel L-edge Spectra (NMC622)



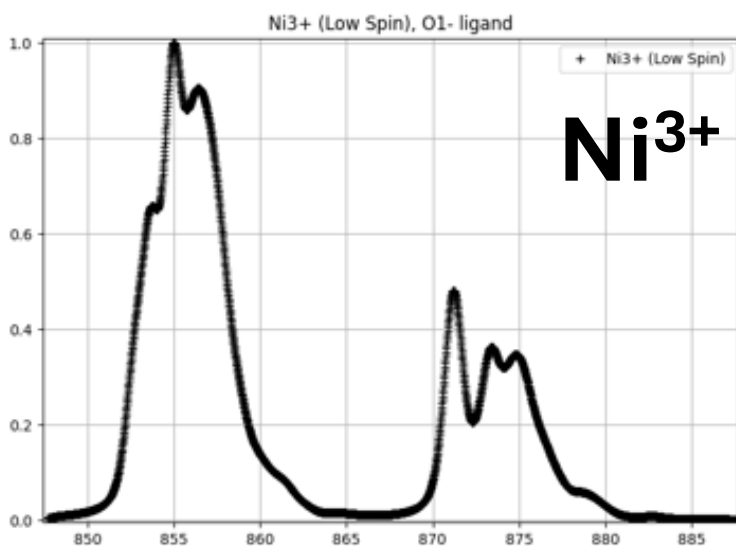
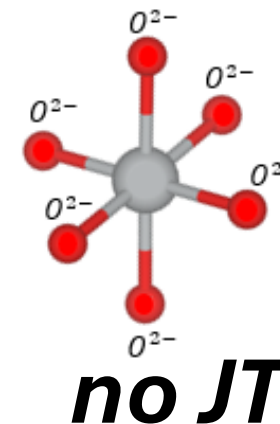
**Using electron density in 3D structure
from CRYSTAL-code to predict K- and L-edge spectra**

Ni - Theoretical L_{23} – edge transitions



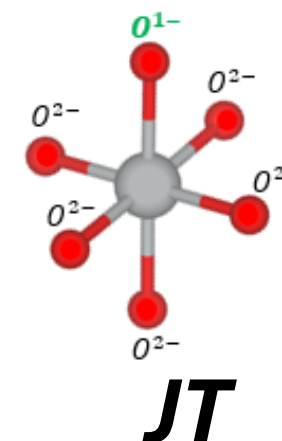
• Octahedral Symmetry O_h :

- $6 \times O^{2-}$ ligands
- Charge-transfer $\Delta_{CT} = 3.5$ eV
- $10Dq = 2$ eV
- Slater-Condon screening at 50%
- Hybridization:
 $V_{pds}: 1.8$ eV
 $V_{pdp}: 1.0$ eV



• Expectations: Broken O_h Symmetry:

- $5 \times O^{2-} + 1 \times O^{-}$
- Larger charge-transfer $\Delta_{CT} = 5$ eV
- Smaller $10Dq = 1.2$ eV
- Slater-Condon screening at 90%
- Less hybridization:
 $V_{pds}: 1.0$ eV
 $V_{pdp}: 0.8$ eV



**Difference
in L_3 -edge
spectra
between
 Ni^{2+} and JT-
distorted
 Ni^{3+}**

Theoretical L_{23} – edge transitions

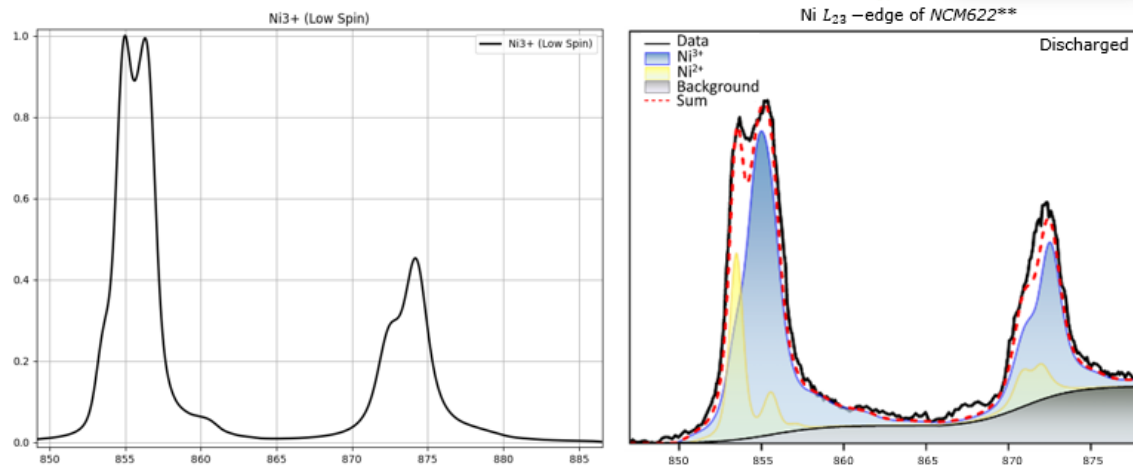
To write down the absorption spectrum use **Fermi's Golden Rule**:

$$W_{fi} \propto \sum_q |\langle \Phi_f | \mathbf{e}_q \cdot \mathbf{r} | \Phi_i \rangle|^2 \delta(\hbar\Omega - E_f + E_i).$$

Drives transition between initial state and final state

Ensures conservation of energy

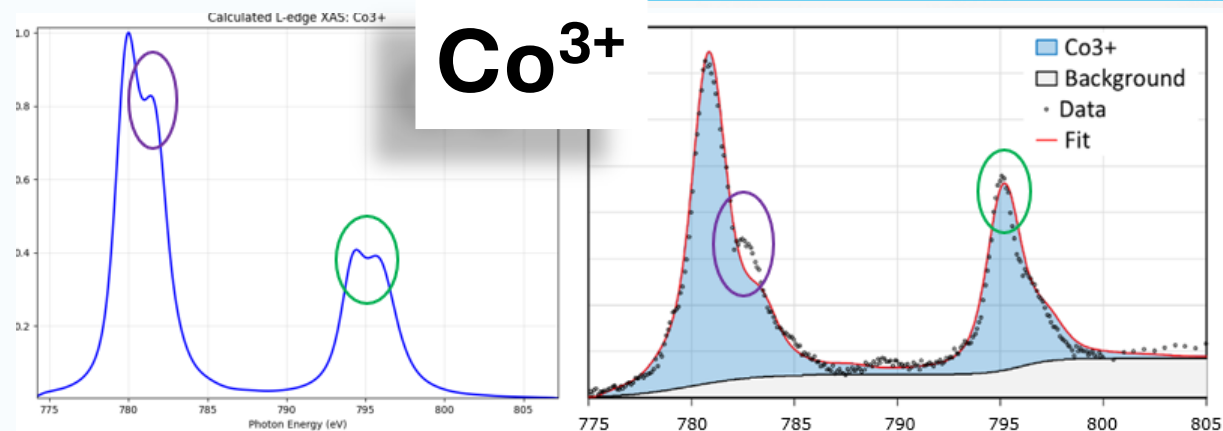
Ni²⁺



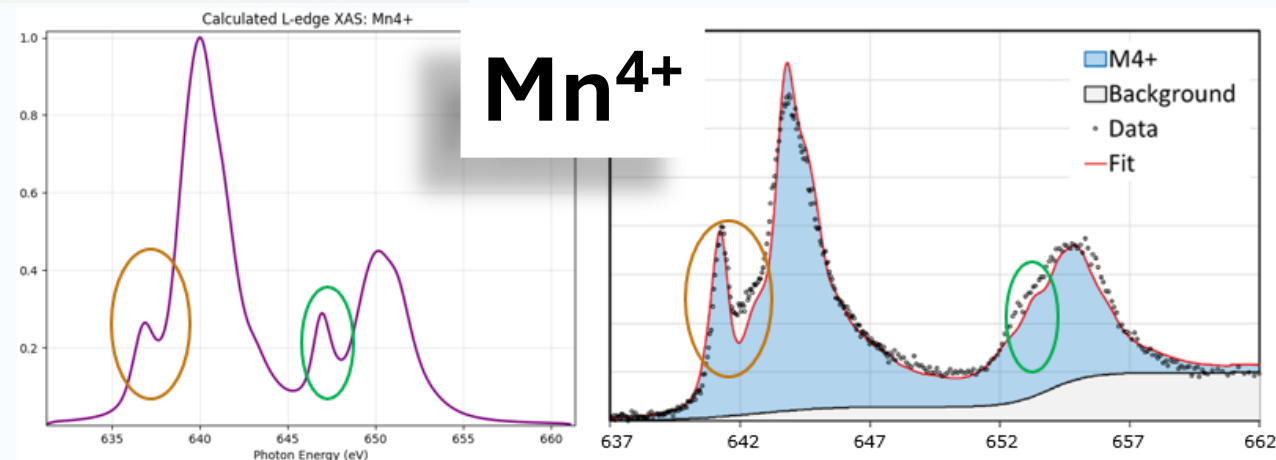
** Kleiner et. Al., A review and outlook on anionic and cationic redox in Ni-, Li- and Mn-rich layered oxides LiMeO2

- Ni L₃-edge agree with experiment
- **Co and Mn L-edge still need more work**

Co³⁺



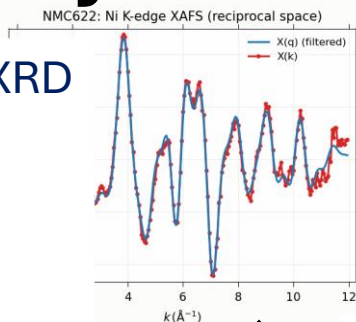
Mn⁴⁺



Importance of choosing the correct set of CTM parameters!

Case study: Creating Database - ML tools - AI

- Experimental XRD and XAS data
- Simulations of structural parameters

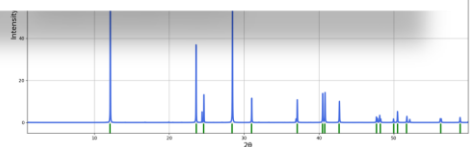


- Training Set

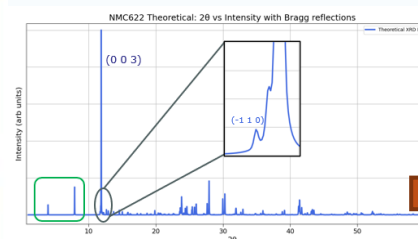
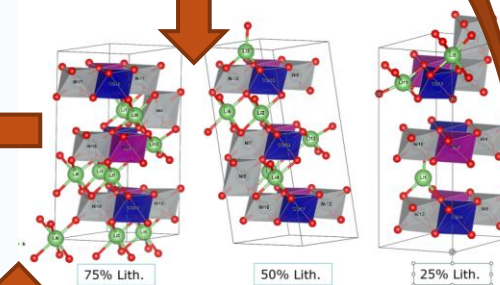
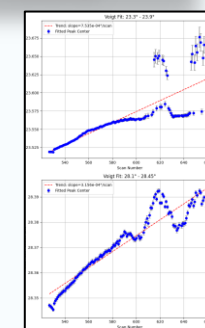
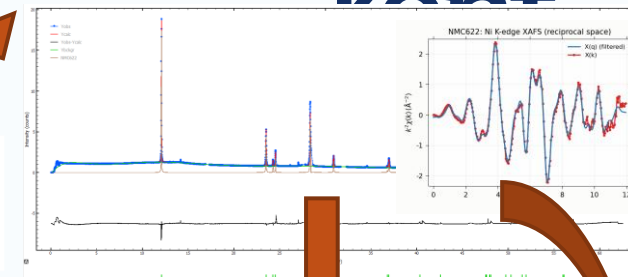
DATABASE

FAIR

- Experimental XRD data
- Simulations of XRD
- Validation

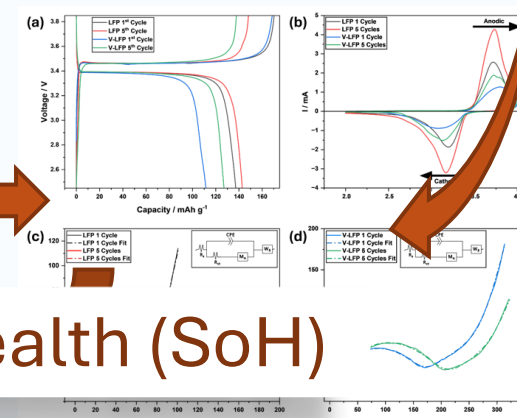


- Visualisation Tools
- Statistical Tools



- State-of-Health (SoH)

- Machine Learning (ML) tools
- Predictive tools – Artificial Intelligence (AI)



Example OpMetBat: Creating Database - ML tools - AI

Generate TM bond lengths
(random or by DFT)

Construct simulation data

```
{"Sim_ID": 1,  
  "Bond_Lengths": {  
    "TM": {  
      "13": [1.881, 1.886, ...]  
    }  
  }  
}
```

SQL
Database

Neural Network using Tensor Flow

$$\text{Loss} = -\frac{1}{N} \sum_{i=1}^N [y_i \log(\hat{y}_i) + (1 - y_i) \log(1 - \hat{y}_i)]$$

- y_i = actual label (0 or 1)
- $\hat{y}_i$ = predicted probability from your network
- N = number of training samples

SQL Database

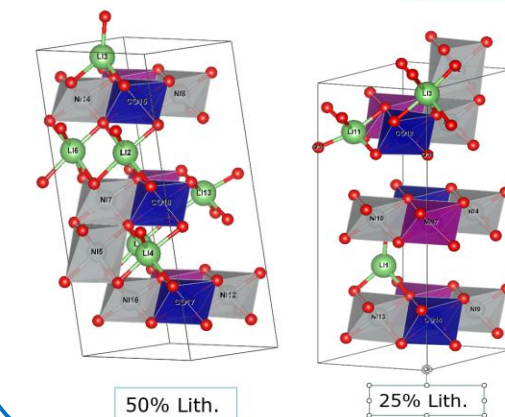
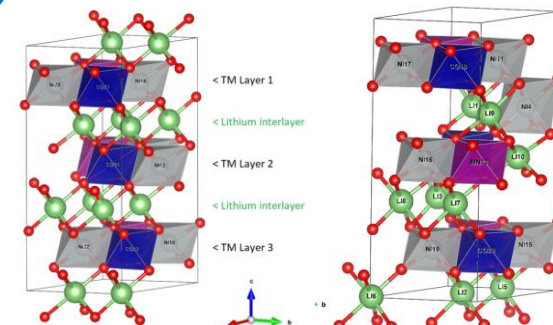
Train on simulation
data

Neural Network

JT classification

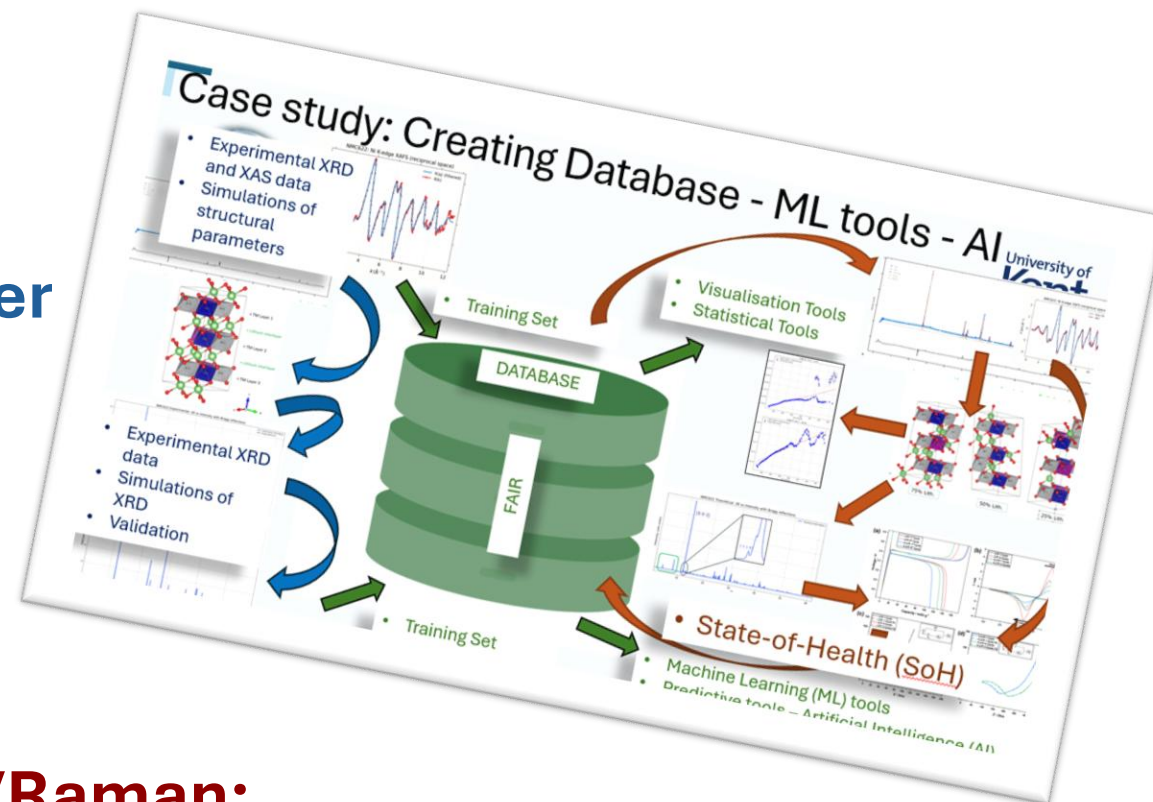
Fetch
bond lengths

```
1/1 0s 52ms/step  
TM_01: predicted Distorted (p=0.89) | actual: Distorted | bonds: [1.874, 1.879, 1.934, 1.935, 2.057, 2.065]  
TM_02: predicted Distorted (p=0.98) | actual: Distorted | bonds: [1.883, 1.89, 1.897, 1.902, 2.105, 2.109]  
TM_03: predicted Distorted (p=0.73) | actual: Distorted | bonds: [1.915, 1.919, 1.942, 1.948, 2.151, 2.159]  
TM_04: predicted Distorted (p=0.93) | actual: Distorted | bonds: [1.871, 1.872, 1.923, 1.933, 2.07, 2.07]  
TM_05: predicted -- (p=0.02) | actual: -- | bonds: [1.903, 1.906, 1.907, 1.913, 1.92, 1.921]  
TM_06: predicted Distorted (p=0.90) | actual: Distorted | bonds: [1.868, 1.876, 1.944, 1.947, 2.072, 2.074]  
TM_07: predicted Distorted (p=0.96) | actual: Distorted | bonds: [1.879, 1.884, 1.912, 1.915, 2.092, 2.093]  
TM_08: predicted -- (p=0.01) | actual: -- | bonds: [2.004, 2.01, 2.04, 2.043, 2.055, 2.056]  
TM_09: predicted -- (p=0.05) | actual: -- | bonds: [1.928, 1.928, 1.931, 1.931, 1.932, 1.938]  
TM_10: predicted Distorted (p=0.80) | actual: Distorted | bonds: [1.913, 1.918, 1.935, 1.937, 2.154, 2.169]  
TM_11: predicted -- (p=0.07) | actual: -- | bonds: [1.931, 1.932, 1.933, 1.938, 1.938, 1.942]  
TM_12: predicted -- (p=0.05) | actual: -- | bonds: [1.917, 1.925, 1.926, 1.928, 1.94, 1.943]
```



Take away message

- $\text{Ni}^{2+}/\text{Mn}^{4+}$ disproportions if in same layer
- Polarons forms as metastable states, leading to battery degradation
- **Oxygen shows redox activity in presence of Ni anti-sites**
- **Co protects oxygen activity**
- **Hybrid XRD/XAS; XAS/SAXS; XAS/XRD/Raman; XAS/XRD/EIS**
- **Collect standardised data in database**
- **ML tools applied to structural (experiment/theory) and electrochemical battery properties**





Stand for ambition.
kent.ac.uk

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Prof Erik M. Kelder (TUD)

Prof Jawwad Darr (UCL)

MEE Group

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BM28, ESRF, France

B18, DLS, UK

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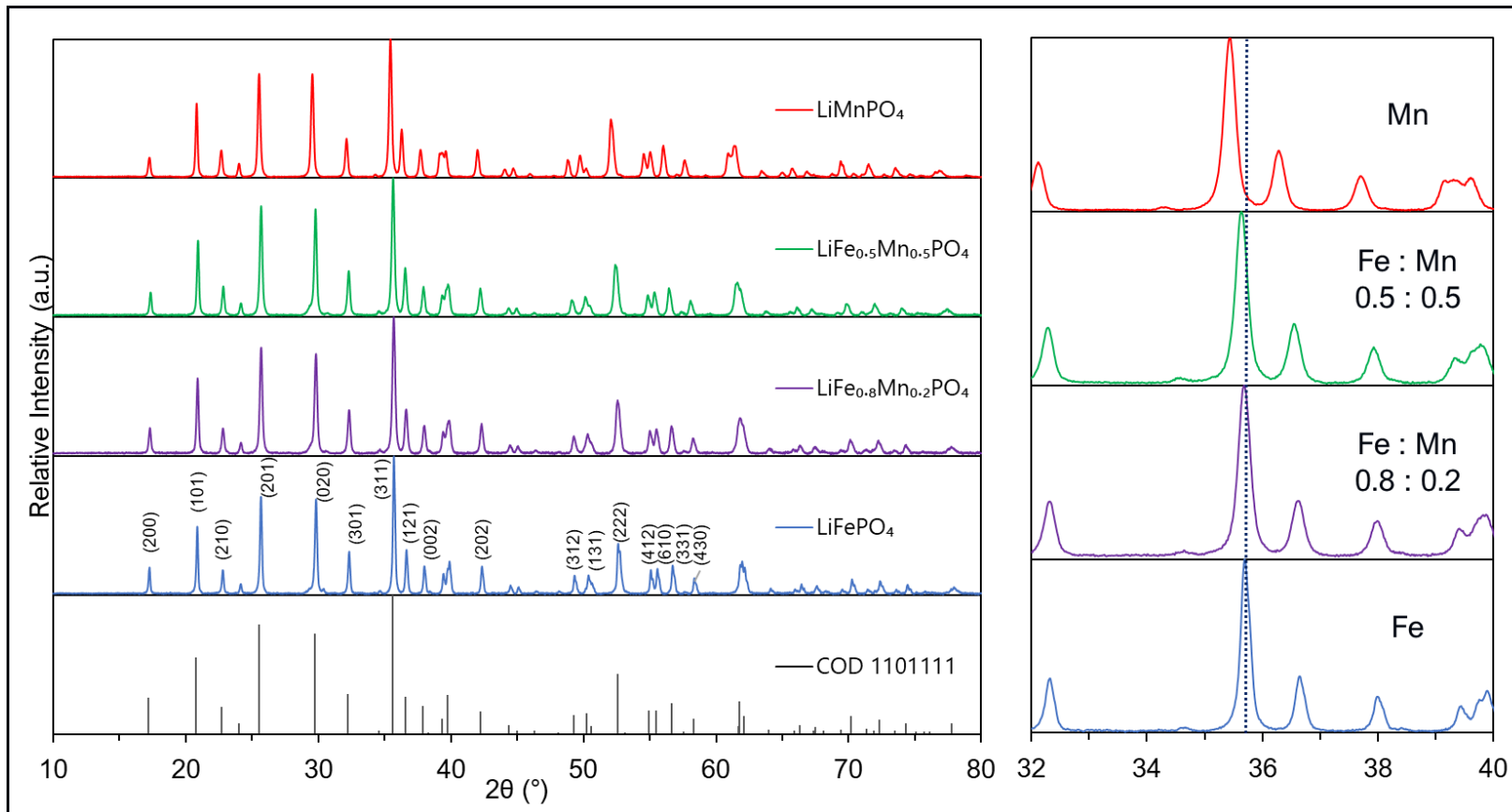
EPSRC for DTA PhD
Studentship

DSTL and EPSRC for CASE
Award

Alistore-ERI

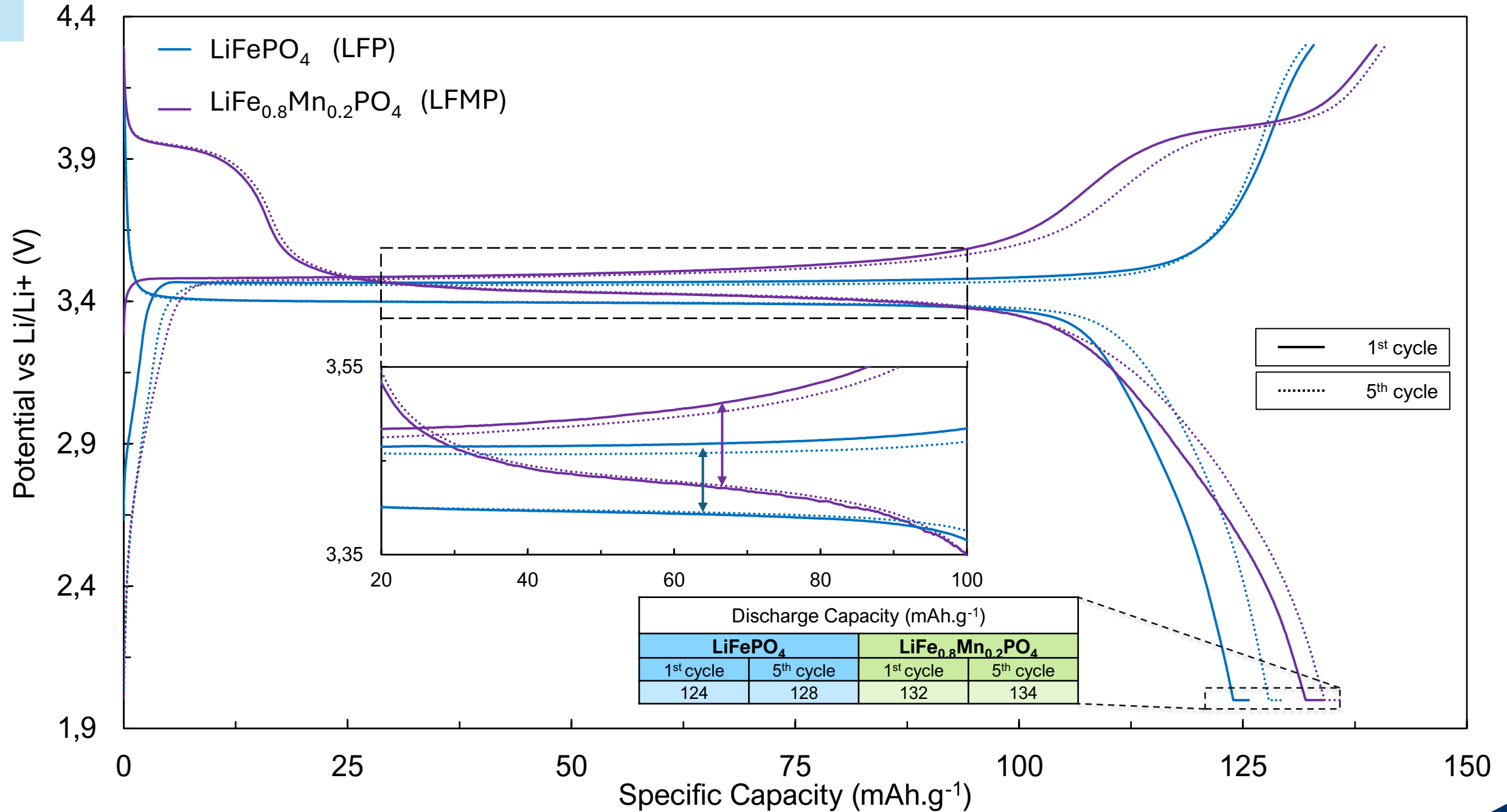
OpMetBat/HyMetBat The EU
Partnership on Metrology

Material Characterisation $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$

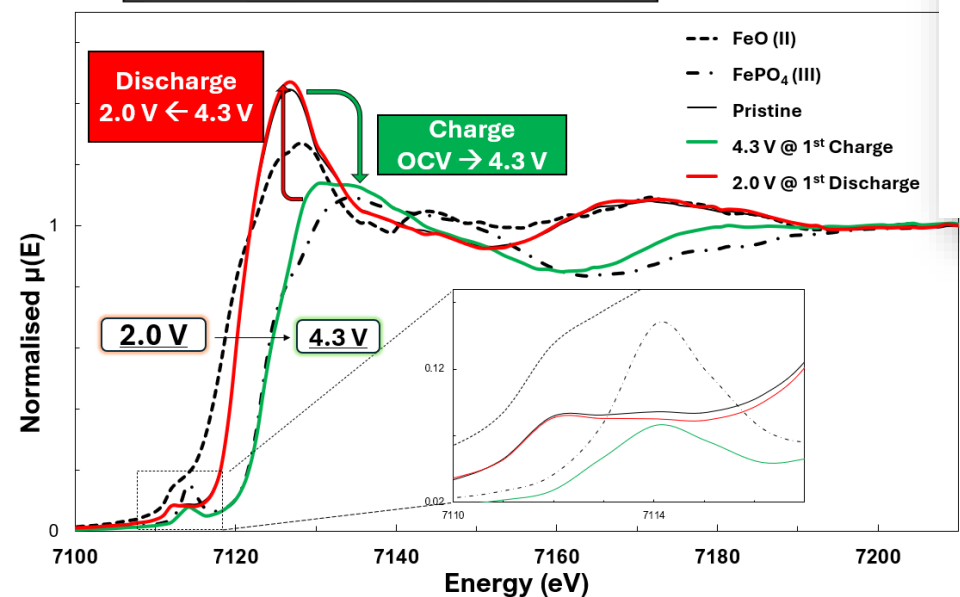


Sample	a (Å)	b (Å)	c (Å)	Vol. (Å ³)	R _{wp}	R _p
LiFePO ₄	10.326	6.004	4.693	290.9	3.72	2.42
LiFe _{0.8} Mn _{0.2} PO ₄	10.353	6.023	4.705	293.4	3.42	2.20
LiFe _{0.5} Mn _{0.5} PO ₄	10.397	6.052	4.727	297.5	4.65	2.90
LiMnPO ₄	10.452	6.103	4.749	302.9	8.57	5.57

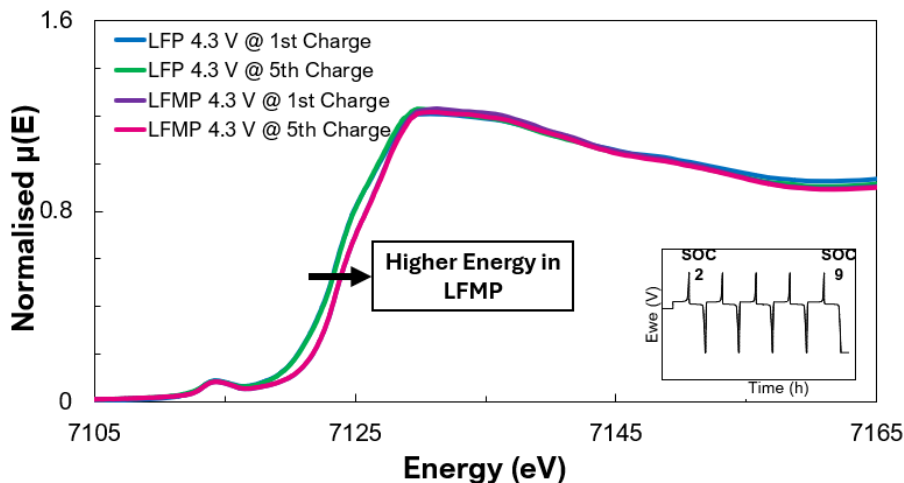
$\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ Theoretical Capacity = 170 mAh.g^{-1} ($x = 0-1$)



Fe K-Edge XANES

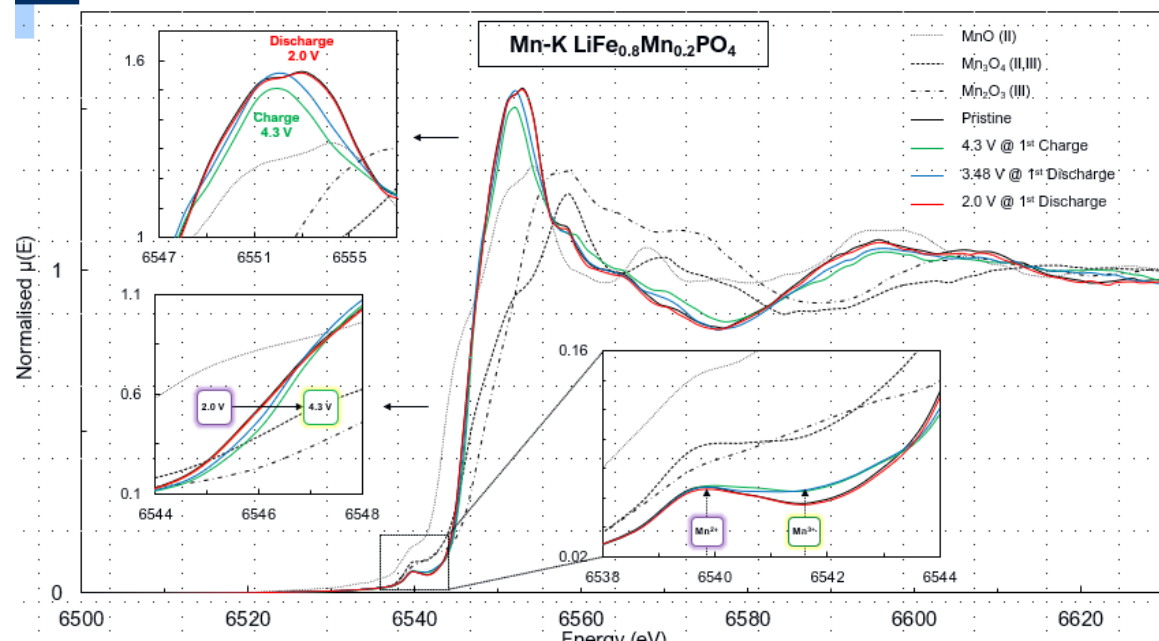


- No change in K-edge position
- Observable changes in pre-edge features

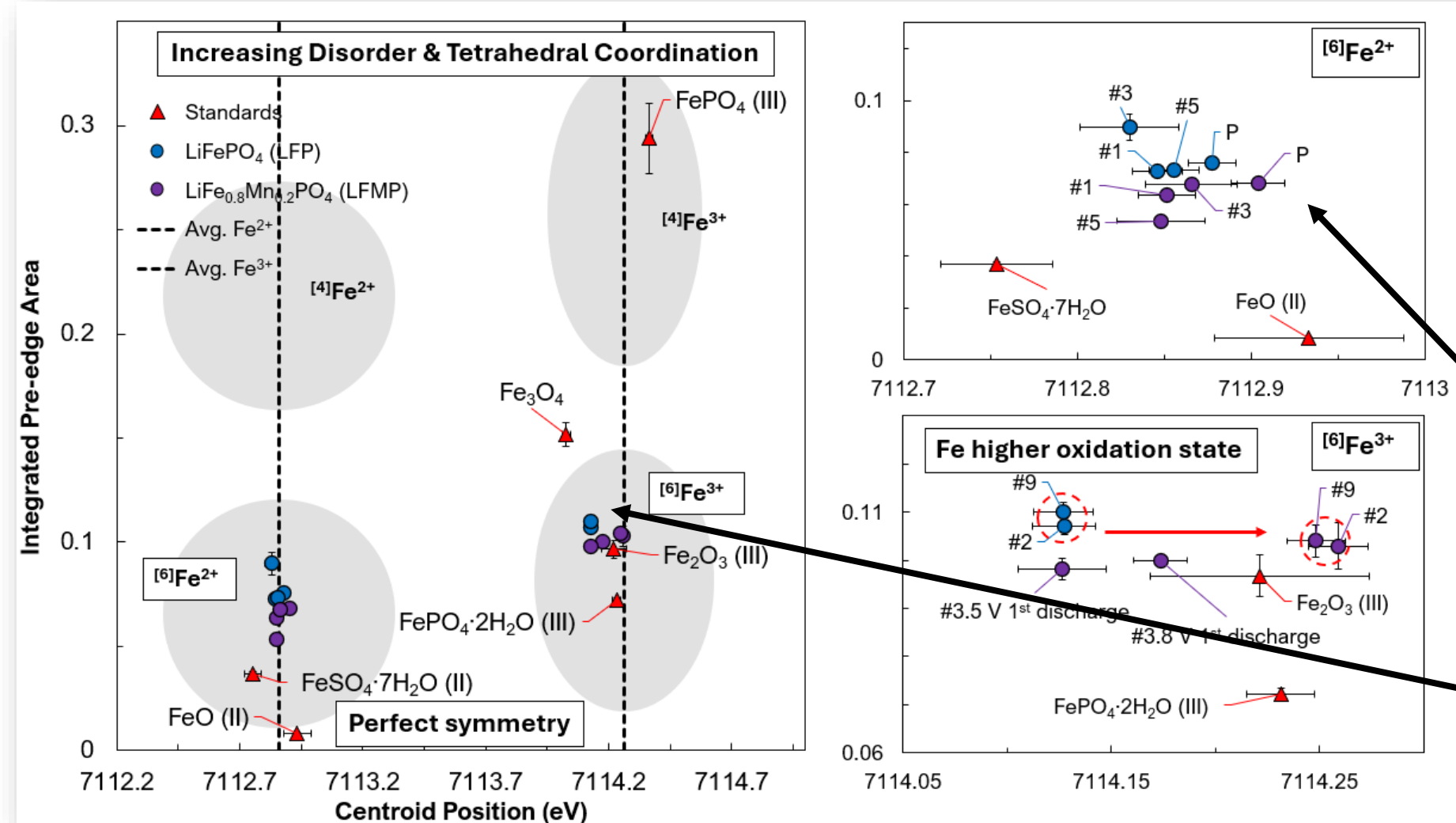


- Larger upshift in LFMP than in LFP
- Increased capacity during battery cycling?

Mn K-Edge XANES



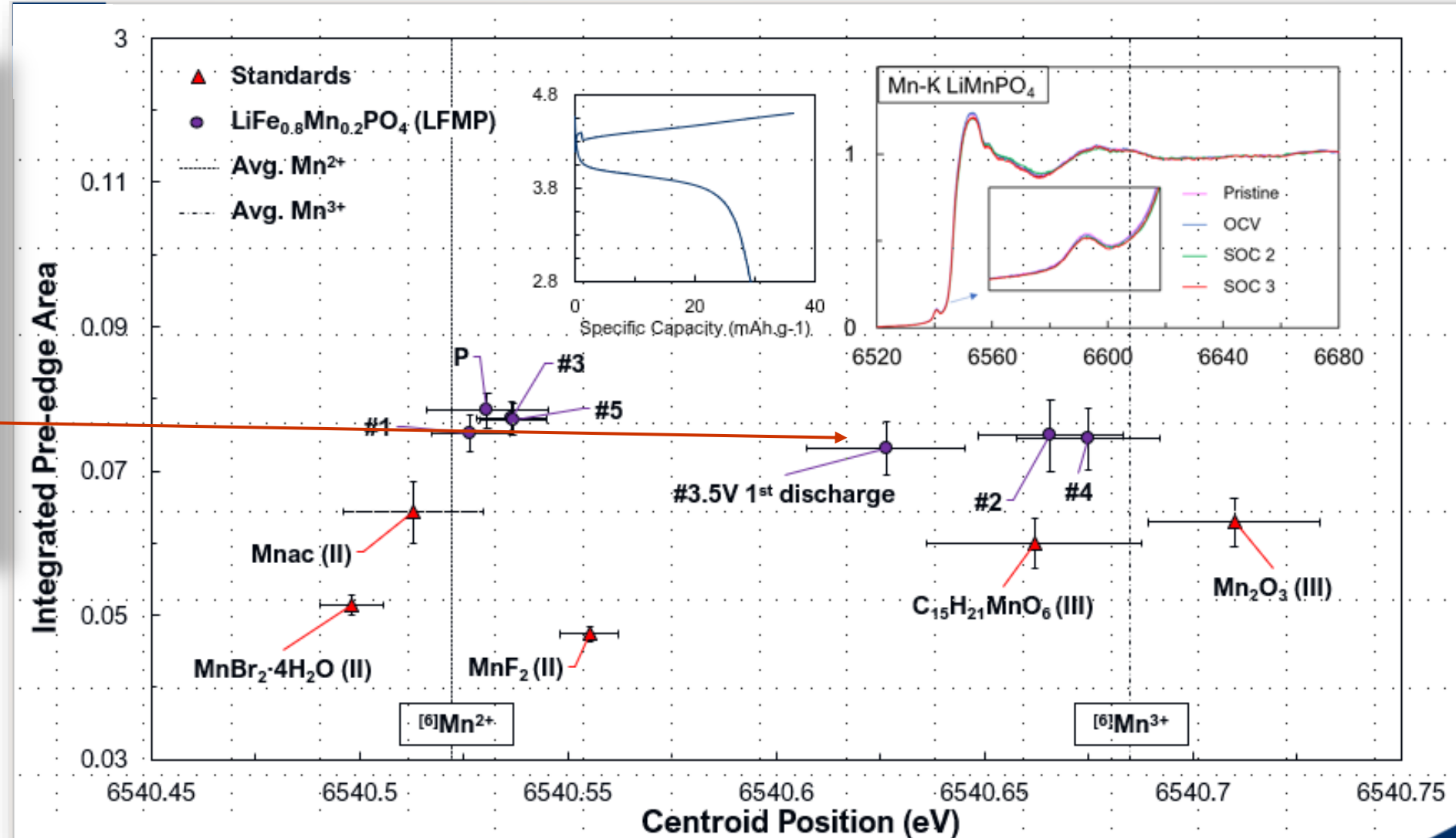
Fe K-edge and correlation XANES



- Higher symmetry
lower XANES
intensity
- Groups in
different oxidation
states
- LFP higher
intensity than
LFMP
- **LFMP higher
ordering than LFP**
- Increased
intensities as
battery cycles
- **Atomic structure
is ordering during
batter cycling**

Mn K-edge and correlation XANES

- Differences between standards due to different local environments
- **Charged states shows similarities with Mn(III)**



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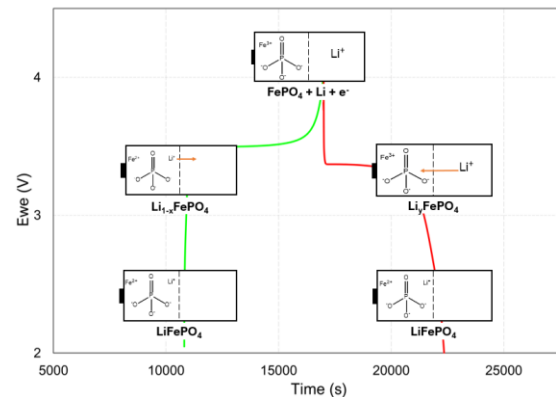
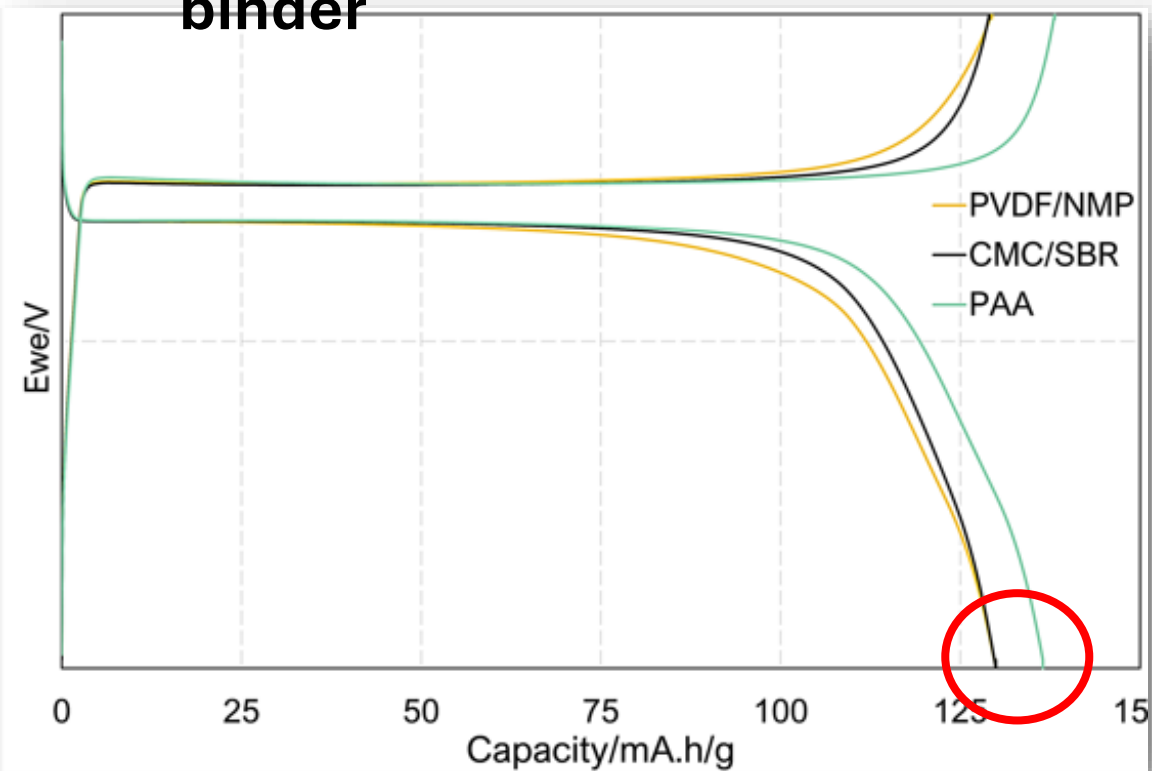
DSTL and EPSRC for CASE
Award

Alistore-ERI

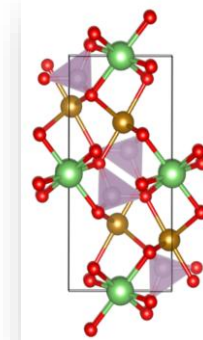
LiFePO_4 (soft-XAS)



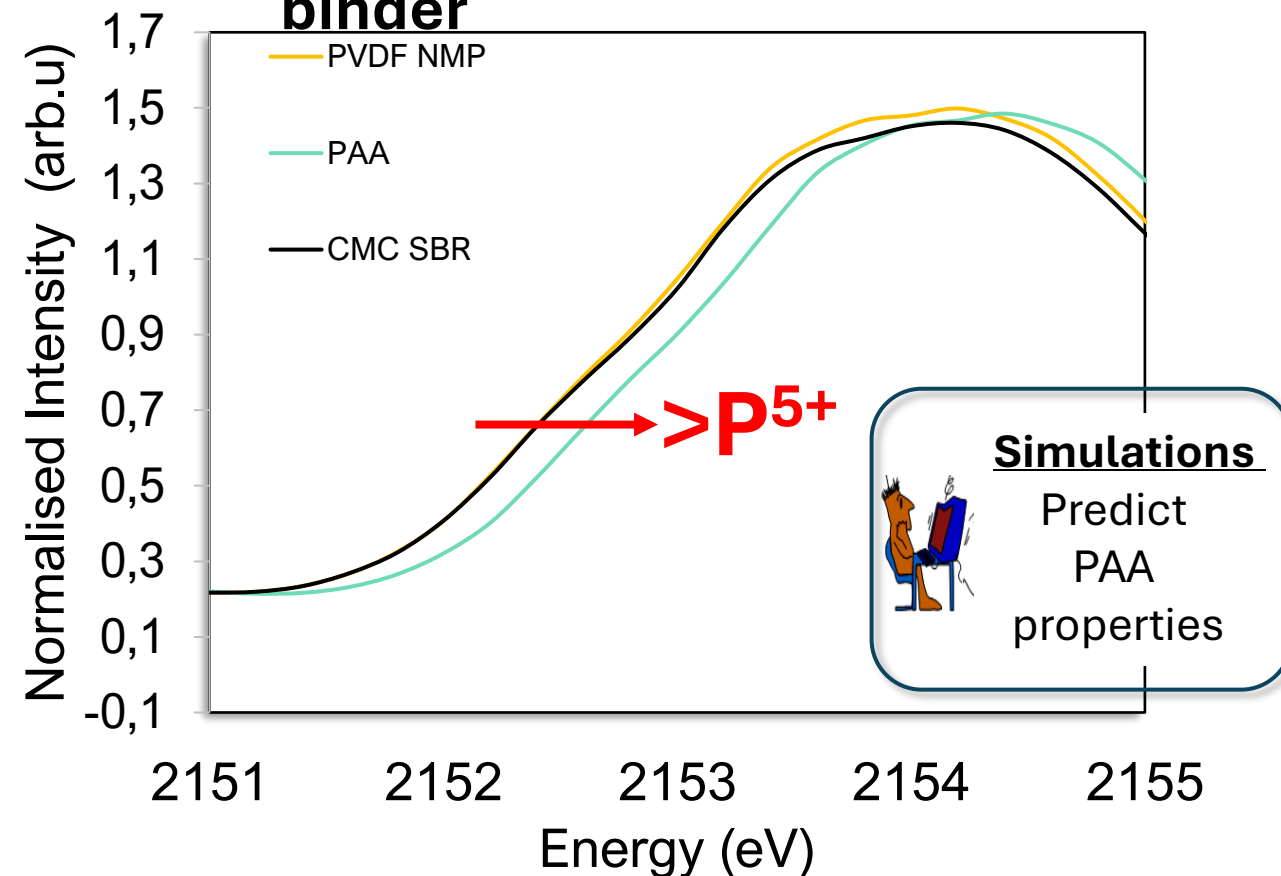
Capacity as function of binder



Batteries cycled BM28
@ ESRF
Special cell designed for
operando measurements



P K-edge as function of binder

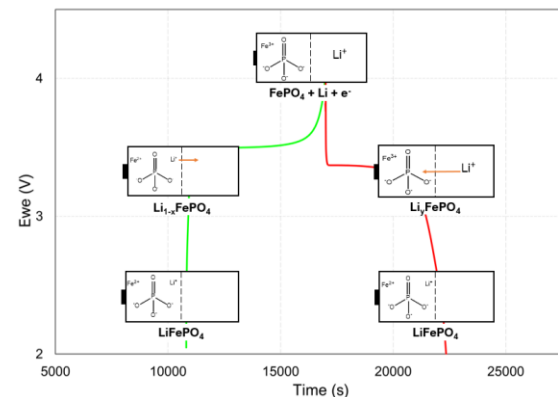
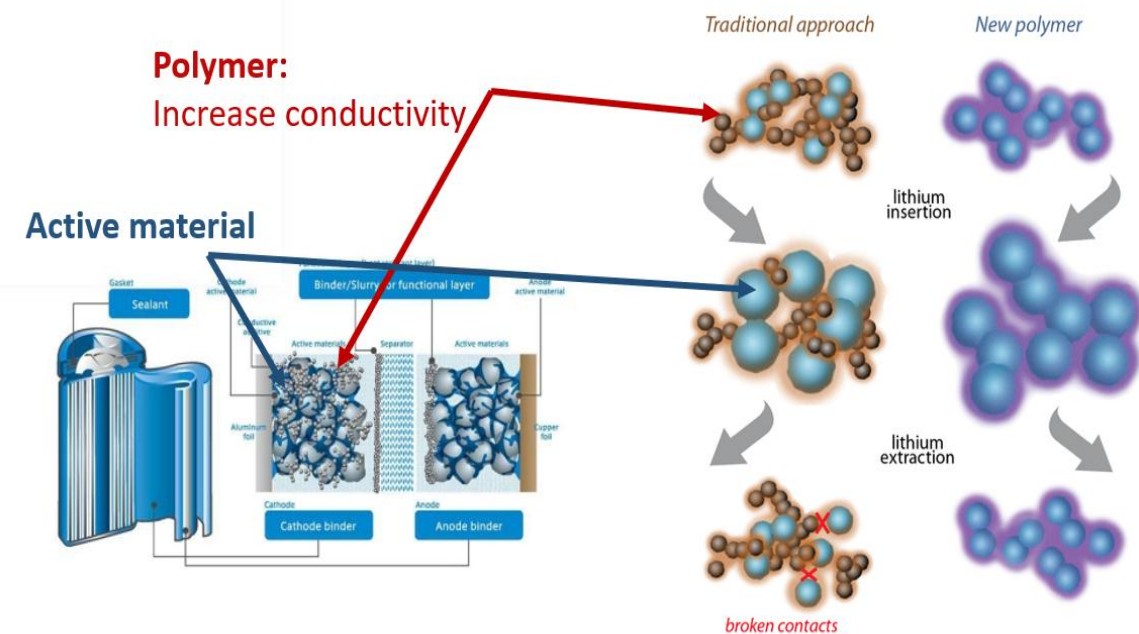


LiFePO₄ (soft-XAS)

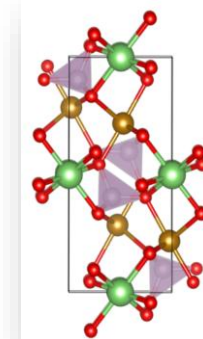


Binder function

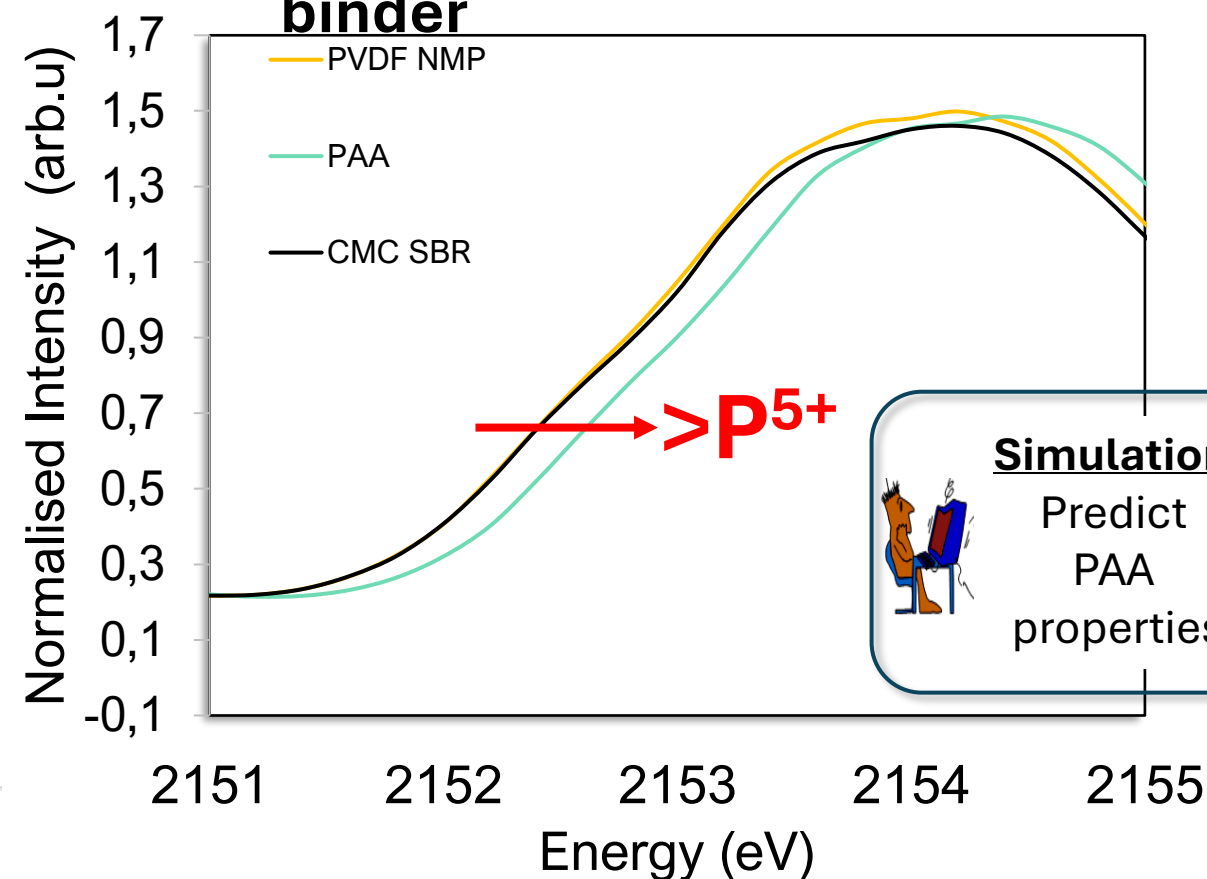
Electrode Components



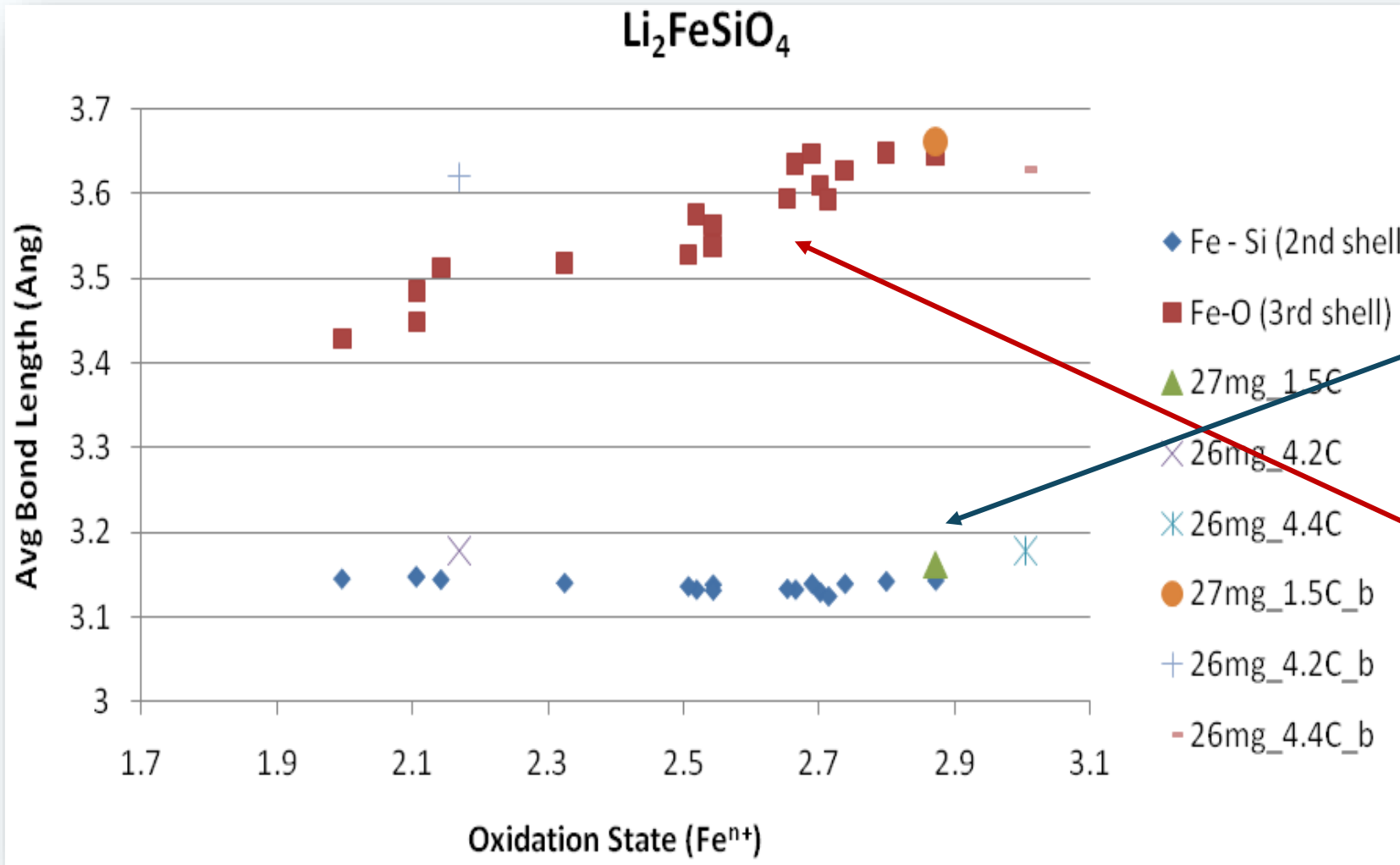
**Batteries cycled BM28
@ ESRF**
Special cell designed for
operando measurements



P K-edge as function of binder



Li₂FeSiO₄ (EXAFS) – Structural stability



• **Si – Fe constant as oxidation state change**

• **Fe – O distance increase with oxidation state**

LiFeSO₄F - PEDOT (XAS)

- **S K-edge** in the SO₄²⁻ anion is sensitive to **changes** in electron distribution
- **Electron distribution changes with battery cycling**

