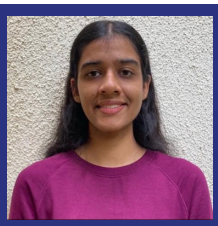
Operando X-ray Absorption Spectroscopy Studies of Oxidation State: Improving Energy Density

Cathode: Moving from $LiFePO_4$ to $LiMn_{0.6}Fe_{0.4}PO_4$?



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Abstract

Operando X-ray absorption spectroscopy (XAS) K-edge measurements of **$LiFePO_4$ (LFP)//Graphite** and **$LiMn_{0.6}Fe_{0.4}PO_4$ (LMFP)//Graphite single crystal pouch cells** were taken while cycling the cell between **2.5 V to 4.4 V** at **C/3**.

- Grain boundary free **single crystalline** cathodes **avoid cracking**[1]
- LMFP reaches **20.4%** higher plateau voltage compared to LFP
  - Suggesting possible higher specific energy density
- Coexistence of LMFP Fe and Mn oxidation states between **3.45 V and 3.67 V**
- Agreement of Python with Athena within **7×10^{-3} % error margin**

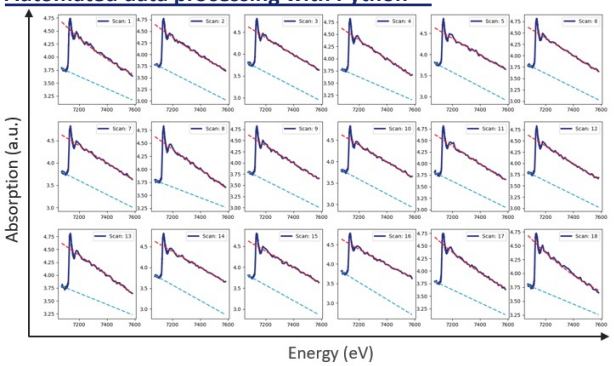
Motivation[2]

- LFP and LMP have **similar theoretical specific capacity**: **170 mAh/g**

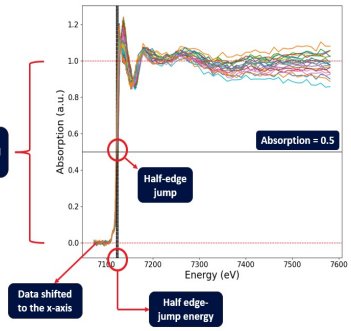
LFP	LMP
▪ Better kinetics ▪ Lower plateau voltage = lower energy density	▪ Sluggish kinetics ▪ Higher plateau voltage (Mn ions have a higher redox potential than Fe ions) = higher energy density

Could LMFP make the best of both?

Automated data processing with Python[3]



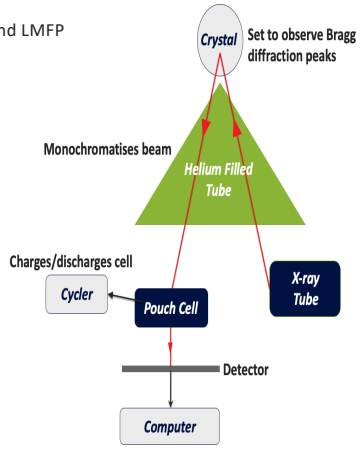
- **Pre and post-edge lines** simultaneously fit for all scans using **chi-squared analysis** (for normalisation)
- **Edge-region** identified by **first peak** in the first **derivative spectrum**
- Normalised edge fit with a straight line to obtain **half-edge jump energies**
- Data processed on **Athena** (XAS processing software) and compared



Method[3]

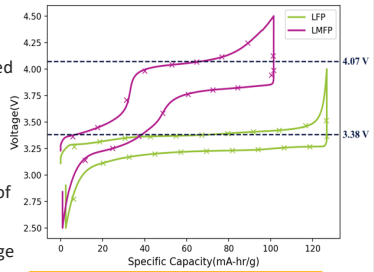
XAS on pouch cell cathode - LFP and LMFP

- **Quick scan** over full spectrum to adjust x-ray tube voltage and current settings for **detector dead time**
- **Metal foil reference** data taken to account for **instrumental systematic error** and **calibrate** data with a known value
- Empty slit data taken (**incident intensity, I_0**) for **normalisation**
- Pre-edge, edge, and post-edge regions set along with scan rate
  - **Smaller intervals** taken in **XANES** (pre-edge and edge) region



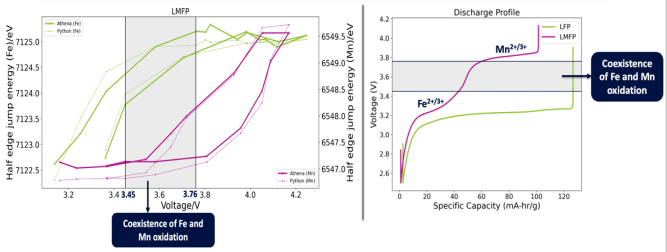
Results and Conclusions

- LMFP reached a **20.4% higher plateau voltage** of 4.07 V compared to 3.38 V for LFP, suggesting possible higher specific energy density
- **Specific capacity** of LMFP was found to be **24.6% less** than that of LFP
- Crosses on graph represent average measurement of each scan



$Energy = Cell\ Capacity \times Avg.\ Discharge\ Voltage$

LMFP could potentially have higher specific energy density than LFP



- Fe ion oxidation: **3.10 V – 3.76 V**
- Mn ion oxidation: **3.45 V – 4.20 V**
- Python processed half-edge jump energies within **7×10^{-3} %** of Athena results

Coexisting environment with Mn and Fe oxidation: 3.45 V – 3.76 V

Impact / Next steps

- First step towards understanding **charge interactions**, **local structural changes**, and **improving diffusivity**
- Potential next steps:
  - **EXAFS** (post-edge) region analysis to obtain **bond lengths**
  - **Electrochemical diffusion** testing

Progress through the internship

- Lab book record through the internship
- Presentations given to highlight results

References

- [1] S. Menon, A. *et al.* (2023) *Operando X-ray and post-mortem investigations of electrochemical degradation in single-crystalline lini0.8mn0.1co0.1o2–graphite pouch cells* [Preprint]. doi:10.26434/chemrxiv-2023-zs9kp.
- [2] Piper, L.F. *et al.* (2013) 'Elucidating the nature of pseudo jahn–teller distortions in lixmnpo4: Combining density functional theory with soft and hard X-ray spectroscopy', *The Journal of Physical Chemistry C*, 117(20), pp. 10383–10396. doi:10.1021/jp3122374.
- [3] Calvin, S. (2013) in *Xafs for everyone*. Boca Raton, FL: CRC Press.

Intern bio

I am an incoming third year undergraduate studying Msci Physics at Imperial College London. I am particularly motivated to contribute towards tackling climate change and advancing renewable energy solutions. The area of battery development offers a range of exciting opportunities, and I look forward to learning about the underpinning science and applying my skills to create efficient battery designs for a sustainable future.

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