Operando X-ray Absorption Spectroscopy Studies of Oxidation State: Improving Energy Density
Cathode: Moving from LiFePO₄ to LiMn₀.₆Fe₀.₄PO₄

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Abstract
Operando X-ray absorption spectroscopy (XAS) K-edge measurements of LiFePO₄ (LFP)/Graphite and LiMn₀.₆Fe₀.₄PO₄ (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
- 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
- LFP and LMP have similar theoretical specific capacity: 170 mAh/g
  - 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
- 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

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

- 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

Method
- 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, I₀) for normalisation
  - Pre-edge, edge, and post-edge regions set along with scan rate:
    - Smaller intervals taken in XANES (pre-edge and edge) region

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

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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