Modelling L3 and L2 edges for LNO Cathode Batteries

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Project Background

- Ni rich cathodes have tendencies to undergo degradation due to oxygen loss within batteries. In this case of LNO it oxidises into NiO_2.
- This project will be attempting to find the exact structure that appears during this process
- X-ray absorption near edge structure (XANES) is an x-ray spectroscopy method which has a sensitivity to oxidation state. Using this we can investigate different martials related to LNO and NiO_2.
- The martials that were investigated for LNO are a high temperature Rhombohedral (Rhom), low temperature Yung-Teller distorted Monoclinic (Mono), Colinear (c2m) and non-colinear (p21c).
- The martials that were investigated for NiO_2 are a high state NiO_2, Ni_3O_4, Triagonal (P3M1) , *NiO* (Rock Salt) and a Rhom-NiO_2.

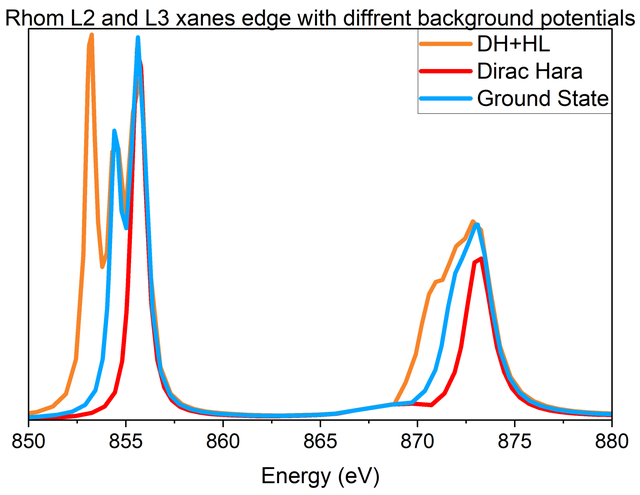
Feff Variable Details

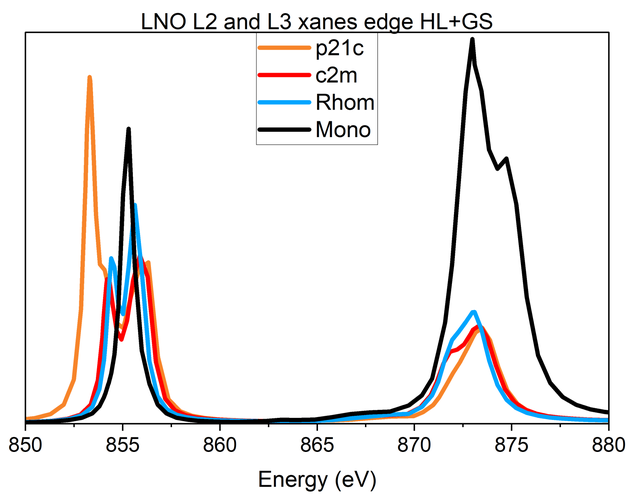
- To find which material structure was most suitable, variables in Feff were kept the same throughout the process, with our FMS = 11, SCF =5 and our COREHOLE as RPA.
- There are 5 Exchange Potentials and 6 Background Potentials.
- Initially for the Rhom-LNO we tested each combination this was to find which gave the best results.
- After the initial investigation into the Rhom-LNO only the HL exchange potential was measured.

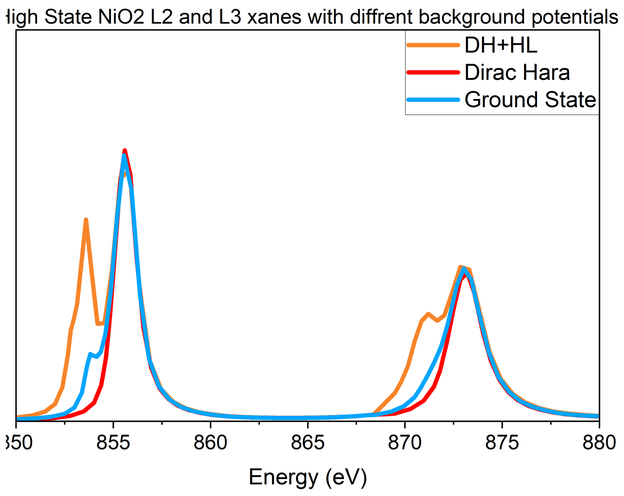
Exchange Potentials	Background Potentials
Hedin-Lundqvist (HL)	Empty
Dirac Hara (DH)	Hedin-Lundqvist
Ground State (GS)	Dirac Hara
Dirac Hara + Hedin-Lundqvist (DH+HL)	Dirac Hara
Partially Non-local (PNL)	Dirac Hara + Hedin-Lundqvist
	Partially Non-local

Results

- Initial investigation of the Rhom-LNO L3 and L2 edge using XANES with HL exchange.
- The expected shape was a double peak for L3 and a shouldered peak for L2, which is shown from our GS background potential.
- To confirm if any similar structures produce the intended shape, we looked at 3 other structures.
- c2m produced a double peak for L3 and a shouldered peak for L2, whereas the Mono and the p21c did not.

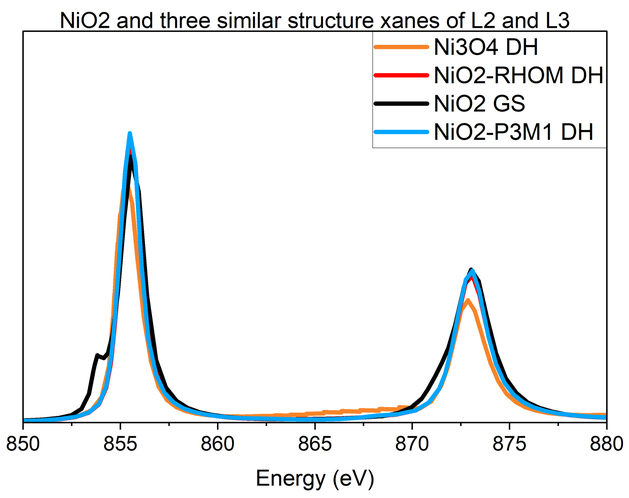


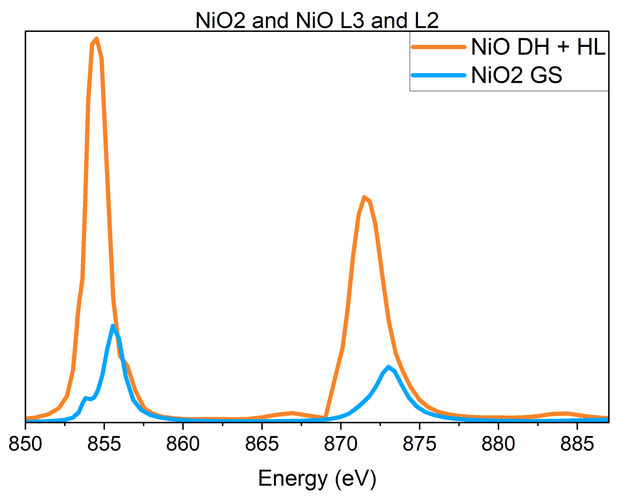


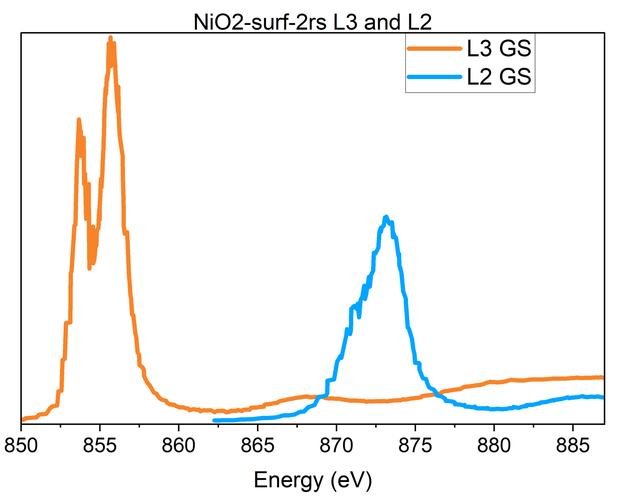


- Following this the same investigation was done on the high state NiO_2 structure, this again should that a HL exchange potential with a GS background potential produces the expected shape
- However, what is also expected is a bump that would appear at the 865 and 881 eV energy range.

- To attempt to produce these bumps this method was repeated on similar structures.
- This only produce similar results to high state NiO_2.
- The next structure was a *NiO* which was then measured this produced the required bumps.
- Next an appropriate combination of the two materials had to be made to find the correct spectrum







- The final structure measured was a NiO_2 with an *NiO* layer which was 2 atoms thick (NiO_2-surf-2rs)
- Using this we were able to get a double peak L3 and a left shouldered L2 with the bumps needed.
- By using a running averaging with a larger bin, the double peak can be reduced to the left-shouldered peak which is the desired shape.
- This also makes the bumps slowly vanish with a larger bin value.

Conclusion

- The initial investigation of the LNO structures gave appropriate insights into what could be expected from the NiO_2 and its similar structures.
- Following that the measurements for some of the structures produced a close match to the shape we would expect however, missing the bumps.
- By fine tuning this with a combination of NiO_2 and *NiO* the results have gotten even closer and has confirmed that this is the correct direction

From here the next steps would be to fine tune the structure even more to create the perfect balance of NiO_2 and *NiO*.

References

- Genreith-Schriever, A. R., Banerjee, H., Menon, A. S., Bassey, E. N., Piper, L. F., Grey, C. P., & Morris, A. J. (2022). Oxygen Hole Formation Controls Stability in LiNiO\(_2\) Cathodes: DFT Studies of Oxygen Loss and Singlet Oxygen Formation in Li-Ion Batteries. *arXiv.Org*. https://doi.org/10.48550/arxiv.2205.10462