Chemical Imaging of Cathode Materials

The effect of W on the inner workings of a $LiNiO_2$ Cathode

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Abstract

This project aims to develop **data analysis procedures** for X-ray diffraction/fluorescence CT (XRD-CT/XRF-CT) data from cathode materials using ***Python*** as to **quickly and reliably perform data processing to facilitate analysis.** The processing steps include:

- Selecting the **optimal algorithm** to construct an image of the different components of the battery using the projections obtained from the experiment.
- Selecting the **ideal data clustering technique** to segment the reconstructed image into the different components of the battery.

The developed data analysis procedure was then applied to datasets obtained from **LNO** ($LiNiO_2$) and **LNO-W** (*W* doped LNO) based cathode materials charged to 4.7 V to analyse the **effect of *W* doping on the structural stability** of such materials.

Motivation

- **Reduce the time** spent on data processing.
- **Quickly generate accurate images** of the distribution of the different phases in the cathode.
- Apply the developed data processing procedure to **map the distribution of *W*** in LNO cathodes to better understand their structural changes.
- Deepen our **understanding of LNO cathodes** as to one-day replace unsustainable LCO ($LiCoO_2$) cathodes.

Methods

1. A simulated sinogram of the Shepp-Logan image was generated where the effect of **Poisson-Noise** and **reduced number of projections** were tested to benchmark the accuracy of each reconstruction algorithm.
2. Several clustering algorithms were run on a simulated dataset of XRD-CT and that **best able to deconvolute the signal into the constituent chemical elements was selected**.
3. Rietveld Refinement was then used as a reference to **quantify the performance of the selected clustering algorithm** on a real dataset.

XRF-CT for Elemental Mapping

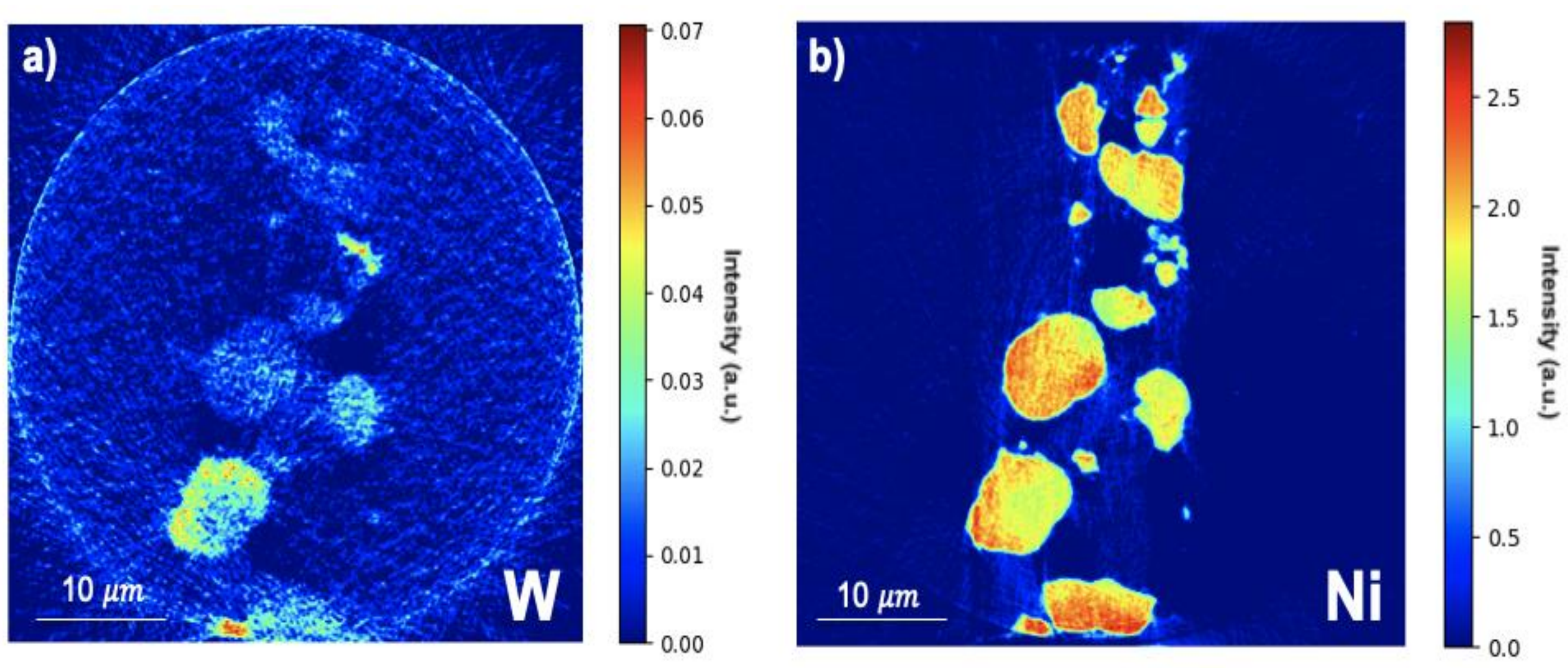


Figure 1. XRF-CT image of cycled LNO-W cathode particles reconstructed using SIRT, a) *W* signal and b) *Ni* signal. From a) it can be seen *W* segregates to the surface [1]. From b) the particles have a broad size distribution with homogeneously distributed *Ni*, which has *x40 the intensity of the W, as W* is a doping element.

NMF for Phase Identification

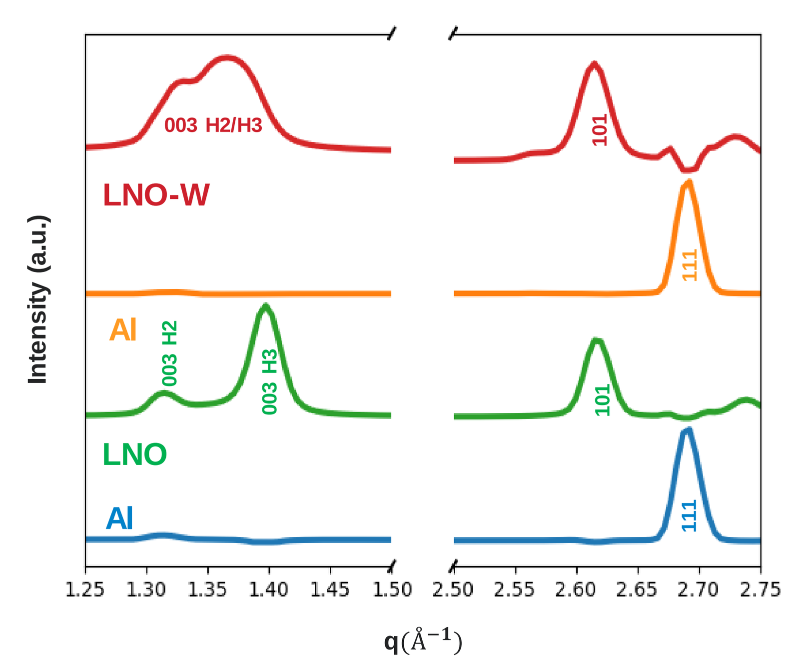
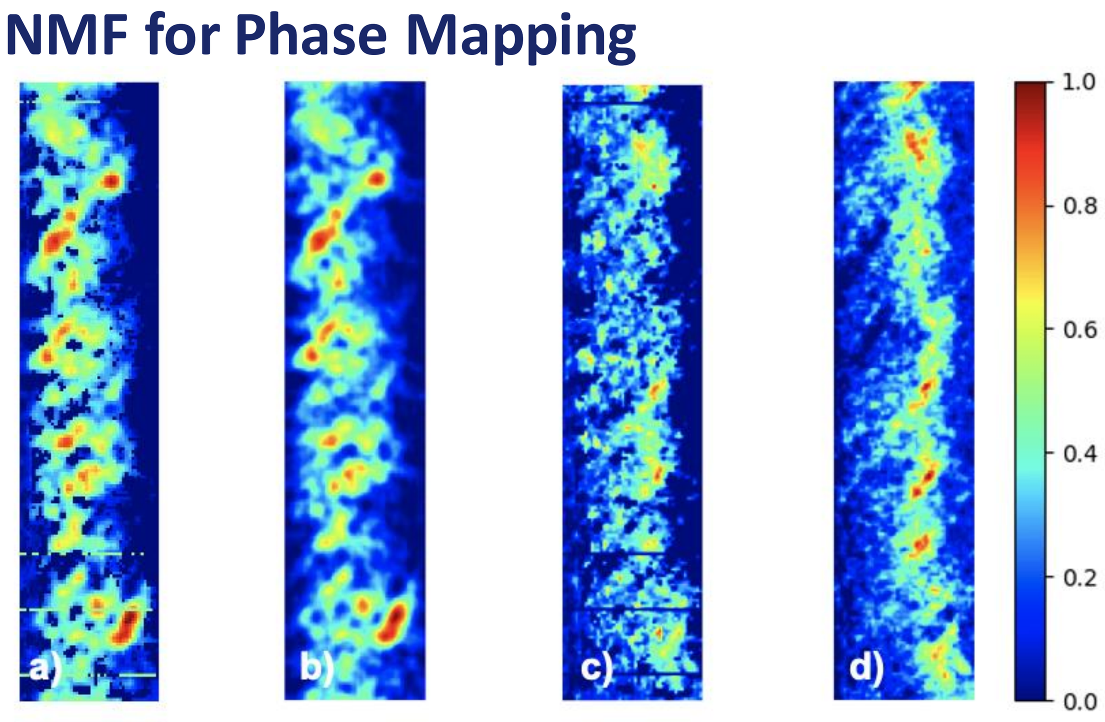


Figure 2. NMF clustering applied to the spectral domains of LNO and LNO-W cathode datasets. For each dataset two XRD patterns were fitted; one for the current collector (identified to be *Al)* and one for the cathode material (identified to be LNO) [2].

- The intensity of the H2 peak in LNO-W is much greater than that in LNO, signalling ***W* inhibits the formation of the detrimental H3 phase which causes high strain** [1],[3].
- The H2 and H3 peaks of the LNO-W spectra superpose, suggesting the **high c-axis strain reduces upon *W* doping**.
- Hence, by segregating to the surface, **W forms an amorphous $W_xLi_yO_z$ phase,** leading to a **Ni-rich lattice and an increased c-axis** [1].

NMF for Phase Mapping



45 μm

Figure 3. NMF clustering and Rietveld Refinement applied to the image domain of the LNO cathode dataset. Distribution of a) the H3 phase and c) the H2 phase derived from Rietveld Refinement. Distribution of b) the H3 phase and d) the H2 phase derived from NMF clustering.

- Figure 3a) and b) are similar, suggesting like Rietveld Refinement, **NMF can precisely locate the H3 phase** as it is the major component of the signal.
- Figure 3c) and d) show it is more **difficult for NMF to detect the H2 phase as it is the minor phase**.

Rietveld Refinement for c-axis Mapping

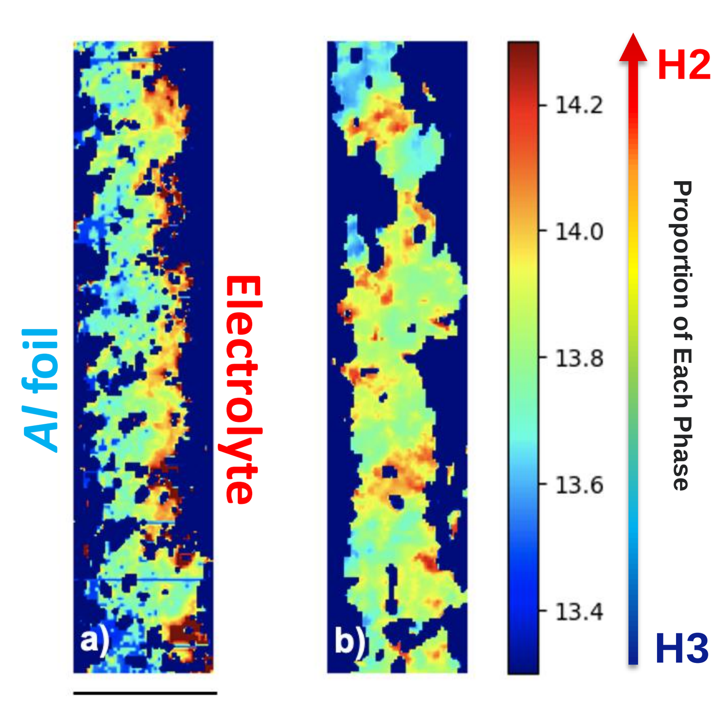


Figure 4. c-axis distribution derived from Rietveld Refinement for a) the LNO and b) the LNO-W datasets.

- Using the c-axis length as an indicator of the proportion of each phase, figure 4 shows there is **more H2 in LNO-W compared to LNO**.
- Figure 4 indicates the **H2 phase segregates towards the electrolyte** on the right hand side in LNO, whereas the **H2 and H3 phases distribute more uniformly in LNO-W**.
- Given the H2 phase is concentrated at the electrolyte, this suggests the **cathode was not fully delithiated**.

Impact / Next steps

- We were able to demonstrate the power of SIRT and NMF in generating **quick images of the phase distribution** inside cathode materials **up to x1000 faster than Rietveld Refinement**.
- As a next step, **improving the NMF clustering technique** as to be able to detect minority components, could lead to better imaging.
- XRF-CT shows ***W* segregates to the surface inhibiting the collapse of the c-axis and detrimental transformation to the H3 phase** [1].
- **Improving the resolution of the XRD-CT scan** could help to precisely locate each phase at the secondary particle level providing greater insight.

References/Acknowledgment

[1] Geng, C. et al., 2021. Mechanism of action of the tungsten dopant in $LiNiO_2$ positive electrode materials. *Advanced Energy Materials*, 12(6), p.2103067.

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Intern bio

Kenan is studying Materials Science and Engineering (MEng) at Imperial College London. During his studies Kenan developed a deep interest for the art of XRD characterisation, understanding materials using simulations, and battery chemistry and design. Having finished this internship, that was able to combine all his interests, Kenan hopes to be able to help shape a more sustainable future through innovative battery designs using simulations.

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