Spatially resolved X-Ray characterization of Ni-rich cathode materials

Investigating physico-chemical properties of Ni-rich cathode materials

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Abstract

Rechargeable Li-ion batteries (LiBs) are used for a wide range of applications including power tools, medical devices, smart watches, short-term energy storage and more.

- Next-generation LiBs are crucial for use in high discharge rate applications such as electric vehicles and long-term energy storage. LiBs using Ni-rich $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) cathodes are favoured due to enhanced properties such as increased energy density and higher specific capacity.

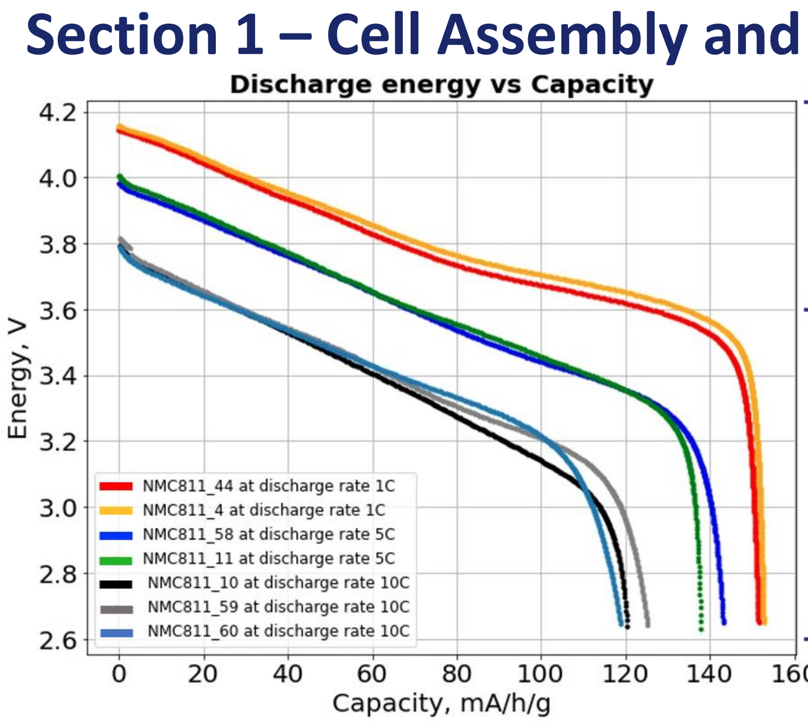
Synchrotron X-Ray Absorption and Diffraction imaging studies are used for NMC chemical characterization and microstructure modelling.

- Mapping trends between different Li-NMC particles and electrodes can identify the effect of different discharge rates on cathode structure, effectively linking the energy release mechanisms to structural changes which may limit performance.

Aims and Motivations

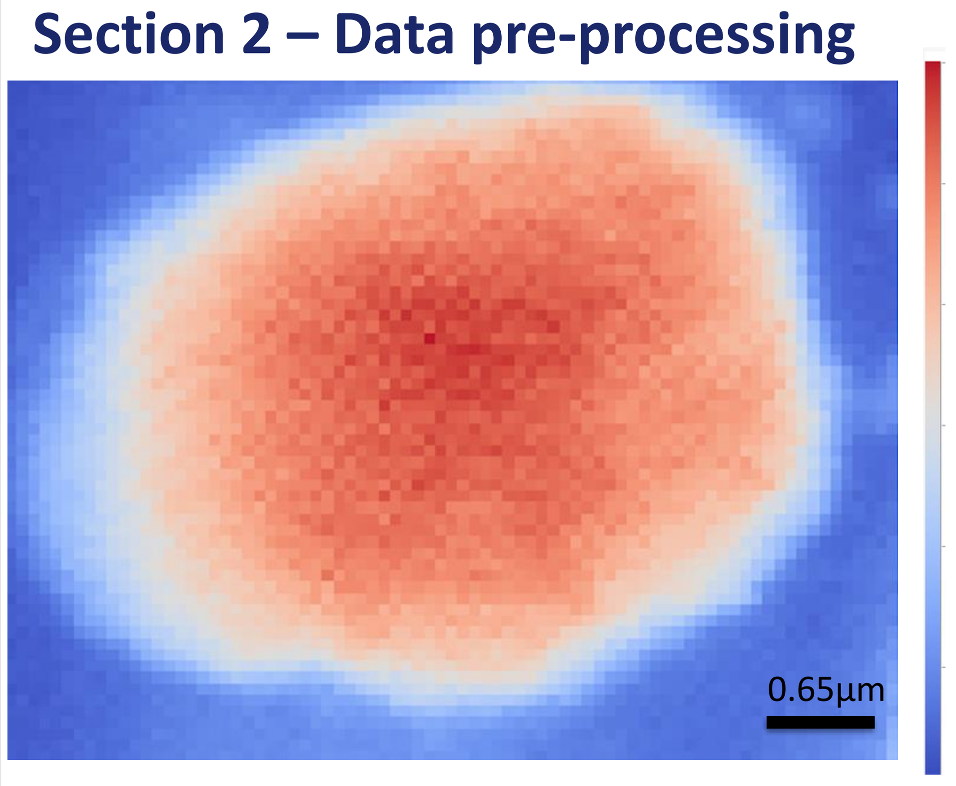
- The aim of this project is to investigate physico-chemical changes in the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) cathode material induced after one discharge cycle at various discharge rates.
- Changes in the Ni oxidation state of discharged NMC811 materials induced by different discharge rates relates to lithiation mechanisms.
- Changes in the NMC811 hexagonal phase lattice parameters and electrode thickness gradients can point towards the structural mechanisms occurring during different discharge rates.

Section 1 – Cell Assembly and Cycling

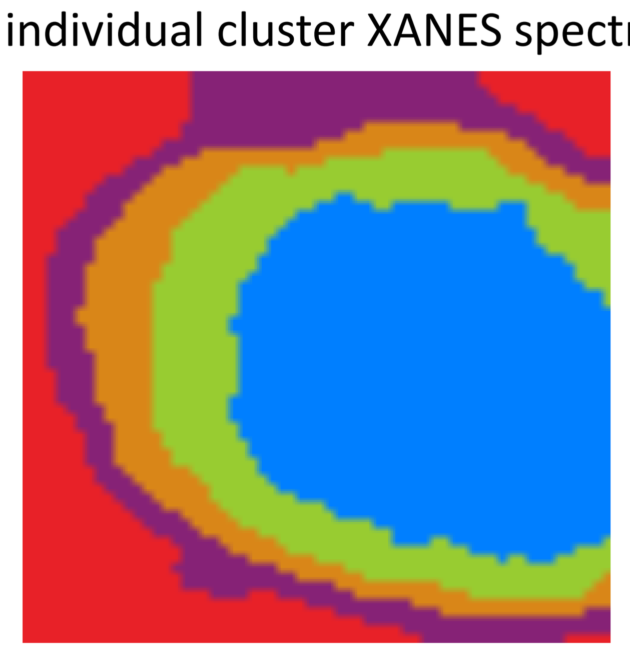


- NMC811 coin cells were assembled and disassembled in the glove box using a hydraulic crimper.
- Formation cycling took place at a rate of C/20 (based on 185 mAh g^{-1}_{NMC}) using CC-CV charge (C/40 current cutoff) and discharge between 4.2-2.65 V. Next, slow charging to 4.2 V at a rate of C/20 CC-CV.
- Lastly, discharge at 3 different discharge rates of 1C, 5C and 10C was conducted.

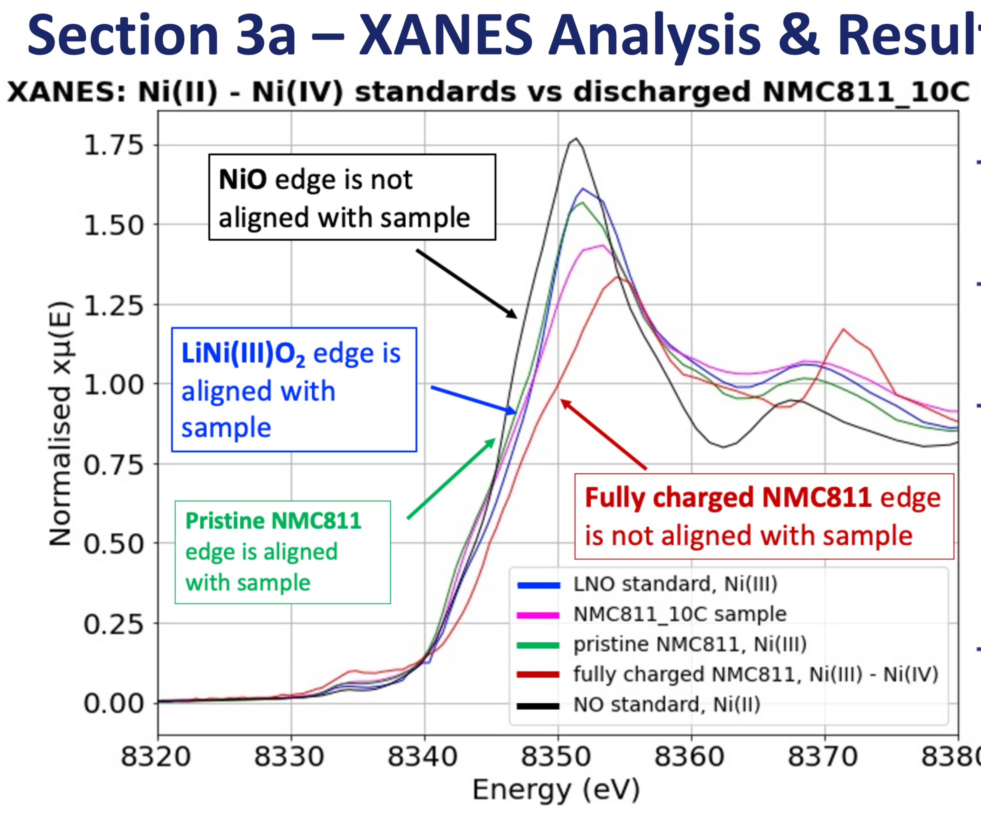
Section 2 – Data pre-processing



- Particle image size is 61 × 81 pixels, and each pixel size is 60 × 60 nm.
- Each pixel produces one XANES spectrum.
- Principal Component & Cluster Analyses are performed to simplify raw data, improve signal-to-noise ratio and produce individual cluster XANES spectra.



Section 3a – XANES Analysis & Results



- Individual particle spectra showed no discrepancies.
- The particles showed no heterogeneities.
- Discharged NMC811 has a Ni oxidation state comparable to that of pristine NMC811 & $LiNi(III)O_2$ standards.
- Ni exhibits reversible redox activity despite applying different discharge rates.

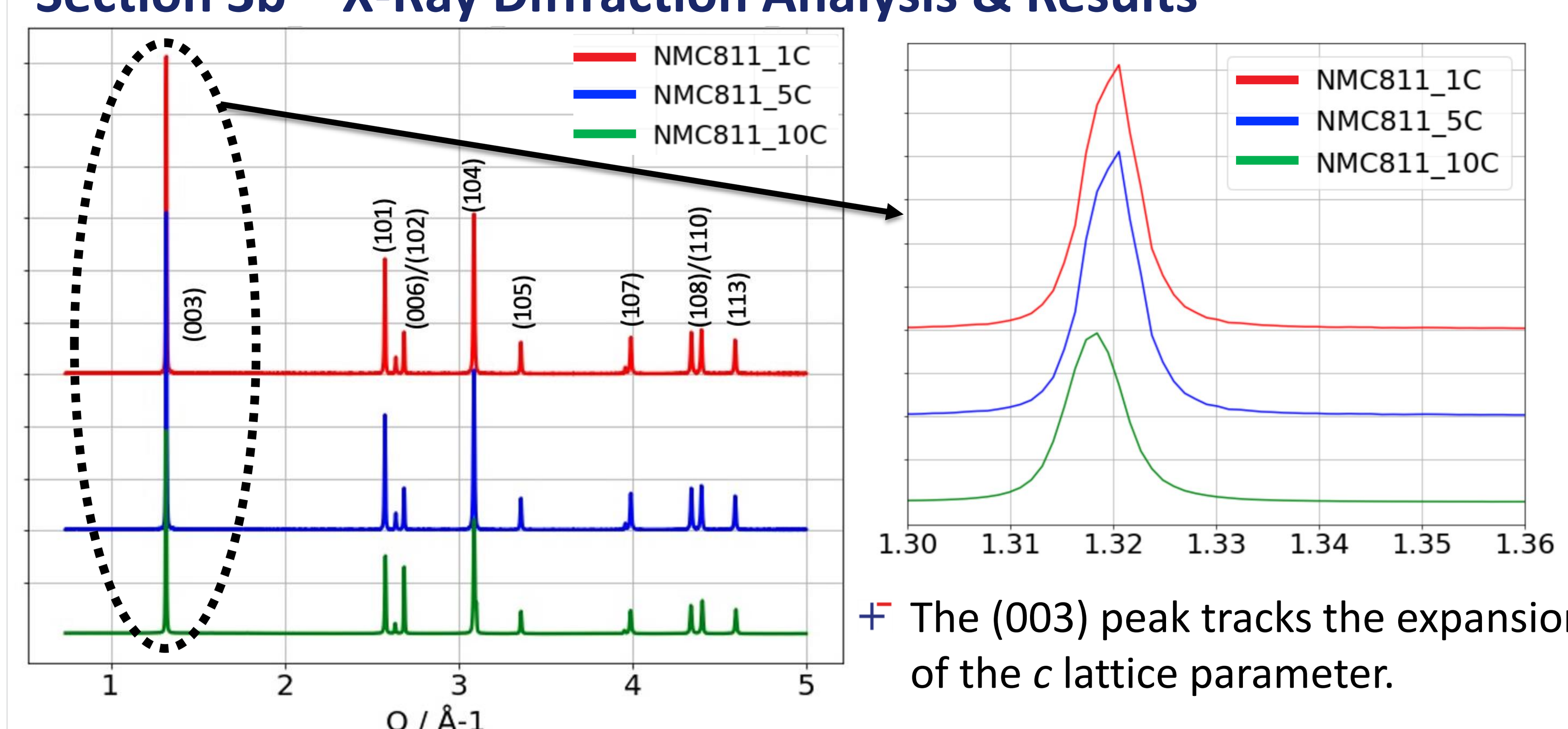
Methods

NMC811 coin cell assembly, formation cycling, slow charging, discharging at different rates and disassembly

Single particle isolation by a) a micromanipulator or b) solvent dispersion → Sparse X-Ray Absorption Near-Edge Spectroscopy (XANES) at the I14 Beamline → Data stacking, cluster analysis in MANTIS and spectra analysis in ATHENA

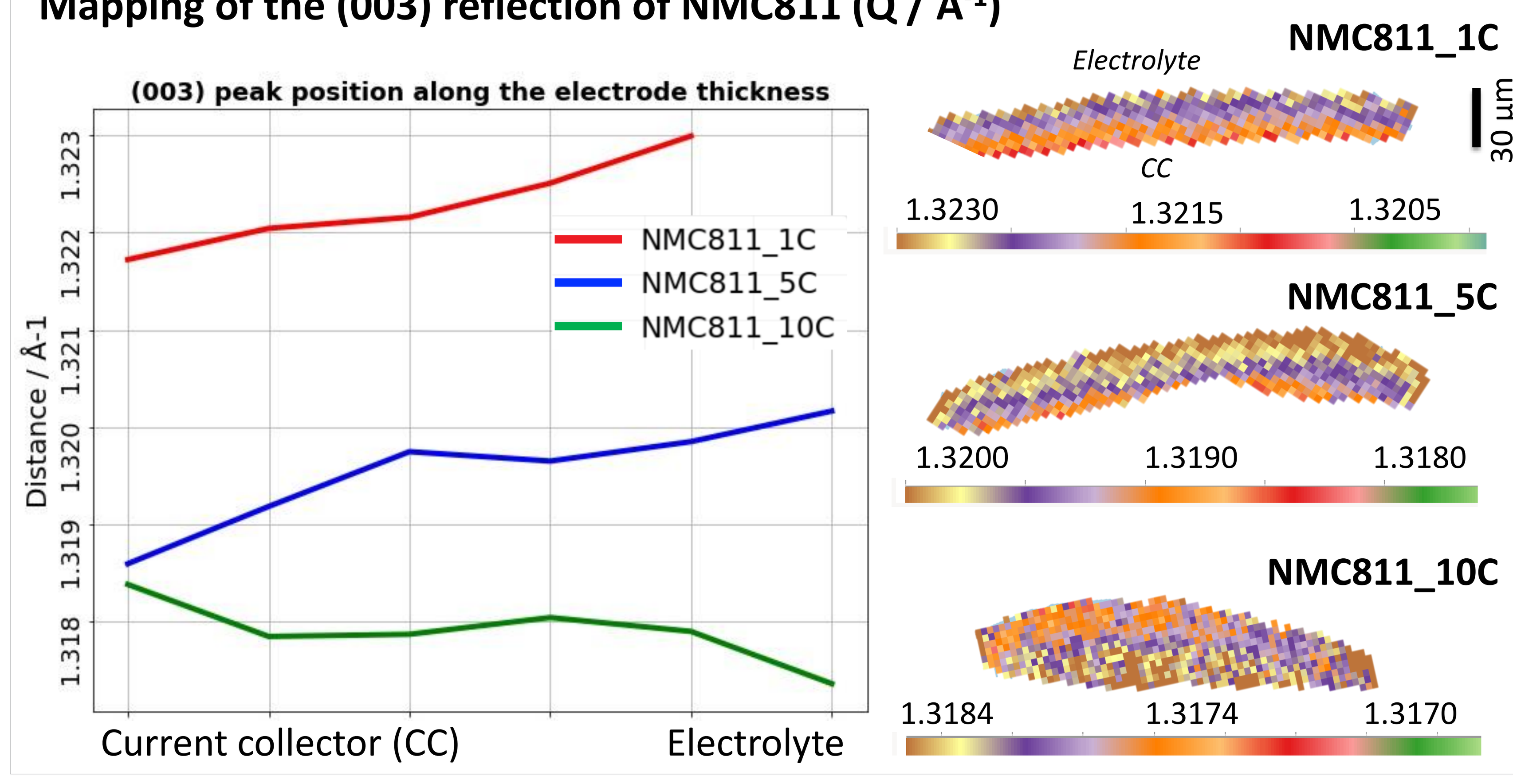
1 mm electrode disc cut-out using a laser → Dual Imaging and Diffraction (DIAD) for tomography and mapping → X-Ray Diffraction map generation, and tomography data visualisation

Section 3b – X-Ray Diffraction Analysis & Results



- The (003) peak tracks the expansion of the *c* lattice parameter.
- The 10C electrode shows the (003) reflection peak shifting towards a lower q space (i.e., larger *c* parameter) and thus contains **less Li in its structure** relative to the 1C and 5C electrodes.

Mapping of the (003) reflection of NMC811 (Q / Å^{-1})



Conclusions / Next steps

- ✓ No heterogeneities in the particles with respect to the Ni oxidation state.
- ✓ The final Ni oxidation state of a discharged NMC811 cathode is similar to the Ni oxidation states of a pristine NMC811 cathode and $LiNi(III)O_2$.
- ✓ The NMC811 electrode discharged at 10C contains less Li in its hexagonal structure when compared to electrodes discharged at 1C and 5C.
- ✓ At 10C discharge, the (003) peak position through the electrode thickness (CC towards electrolyte) shows a negative gradient, as opposed to 1C and 5C.
- ↳ Use longer and repetitive cycling (charging until 50 – 80% capacity loss) to explore long-term capacity fade and the formation of fatigued NMC811.

Intern bio

Christina is studying MSc Chemistry at Imperial College London. She is entering her 4th and final year, about to begin her project in bioinorganic chemistry on novel electron paramagnetic resonance (EPR) techniques for single spin limits. Main interests include inorganic synthesis, analytical chemistry, imaging and materials science in the biochemistry, energy and bioinorganic sectors. Aspiring to advance my scientific career by pursuing a PhD in one of these fields.

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