Degradation 8-Month Review Summary

Paul Shearing and Rhodri Jervis

WP2 Leader and PL
Institution: UCL

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Overview

- Intro to the project
- Materials and protocols
- Scientific Highlights
- Engagement with Large Scale Facilities
- Future Plans
- Engagement with Industry

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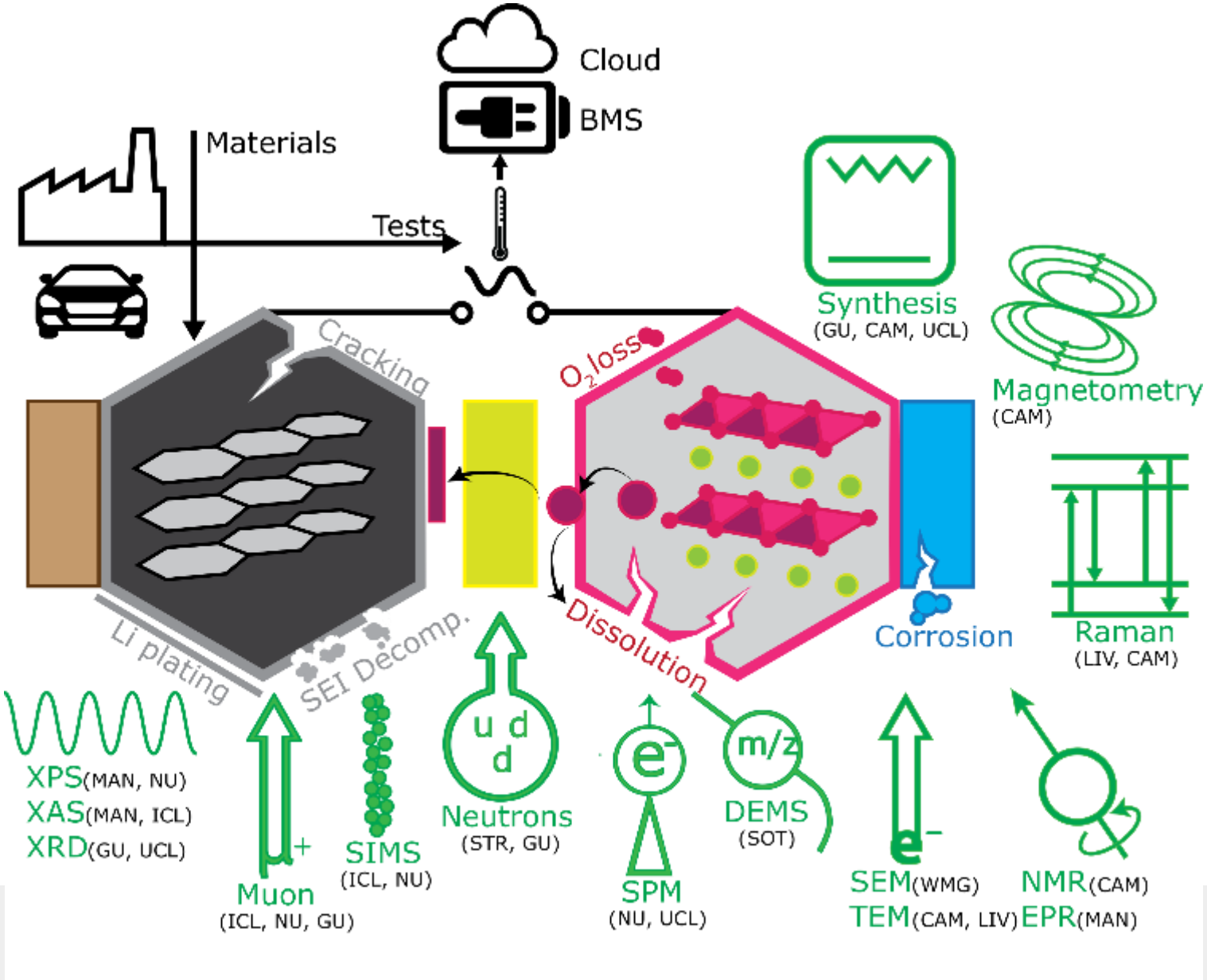
Degradation



Suite of characterisation techniques to study battery degradation across multiple time and length scales

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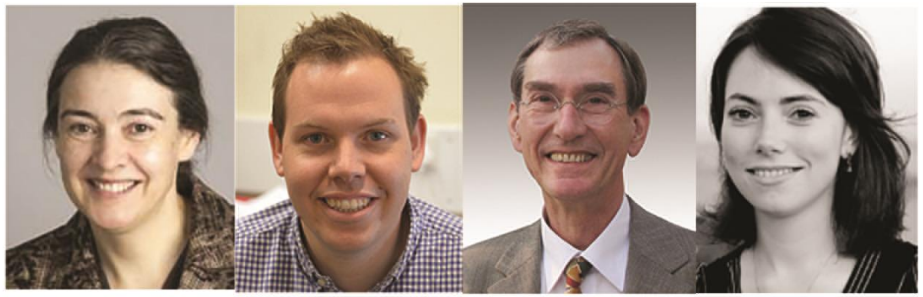

Clare Grey, Cambridge PI WP1 Lead | Paul Shearing UCL WP2 Lead | Ulrich Stimming Newcastle WP3 Lead | Serena Corr Sheffield WP4 Lead

Ainara Aguadero ICL | Jeremy Baumberg CAM | Dan Brett UCL | Peter Cumpson NEW | Eddie Cussen SHE | Jawwad Darr UCL

Michael De Volder CAM | Robert Dryfe MAN | Caterina Ducati CAM | Siân Dutton CAM | Andrea Ferrari CAM | Norman Fleck CAM | Nuria Garcia-Araez SOT | Laurence Hardwick UoL | Lee Johnson NOT | Alpha Lee CAM

Mel Loveridge WMG | Mohamed Mamlouk NEW | Eric McInnes MAN | Layla Mehdi UoL | Volker Pickert NEW | Mary Ryan ICL | Ifan Stephens ICL | Robert Weatherup MAN | Dominic Wright CAM | Rhodri Jervis PL UCL

The overarching goals of this programme are to:

- Identify **stress-induced degradation processes**
- Study **synergistic effects in full cells**
- Obtain **correlative signatures** for degradation
- Determine how **cycling programs and materials solutions**, mitigate degradation
- Feedback **fundamental understanding** and provide insights into how they can be improved.

Structure of the Project

WP1: Chemical Degradation (Clare Grey)

WP2: Materials Degradation (Paul Shearing)

WP3: Electrochemical Degradation (Ulrich Stimming)

WP4: Materials Design & Supply (Serena Corr)

Project Leader: Rhod Jervis

Materials Selection and Protocols

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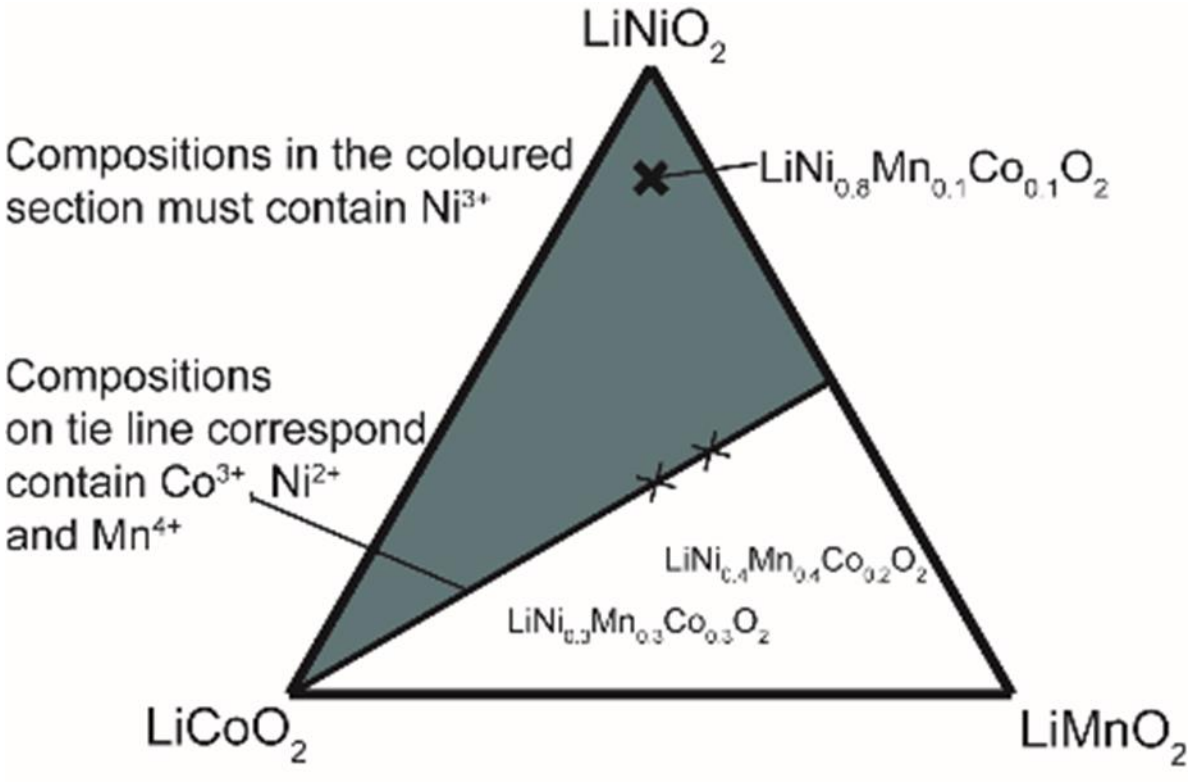
Materials Selection

- NMC 811
- Graphite (natural and synthetic)
- 1 M LiPF6, EC/EMC 3/7 weight ratio, 1-2% VC additive

Suppliers

- 811 – Targray, NEI, consortium
- Graphite – Elcora, SGL, Hitachi



Protocols

- Detailed cycling and cell assembly protocols have been produced in consultation with WMG and JLR to ensure consistency across the consortium
- 811 half cells cycled from 2.5 V to 4.2 V vs Li
- 4.3 V and 4.4 V for ‘stressed’ cycling
- Graphite cycled from 0.01 V to 1.0 V
- Full cells: 2.5 V – 4.2 V, CCCV charge, CC discharge

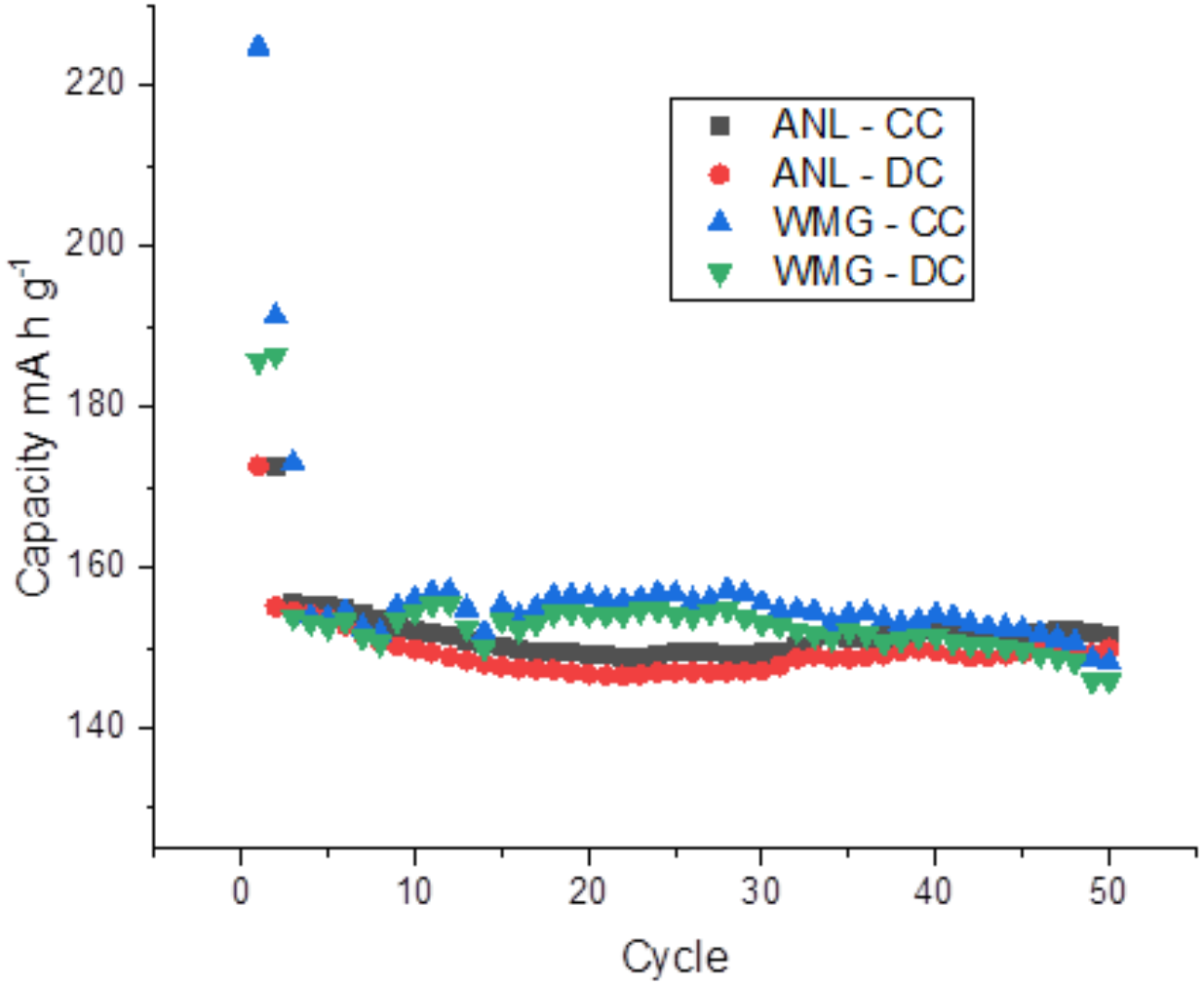
Objectives Last 4 months

- Developing a portfolio of characterisation methods
- First stage characterisation for real (pristine) electrodes
- Securing a materials supply chain
- Championing in situ and operando approaches

Scientific Highlights

Cycle Performance

- Initial cycling performance of 811 comparisons of electrodes coated at Argonne vs WMG



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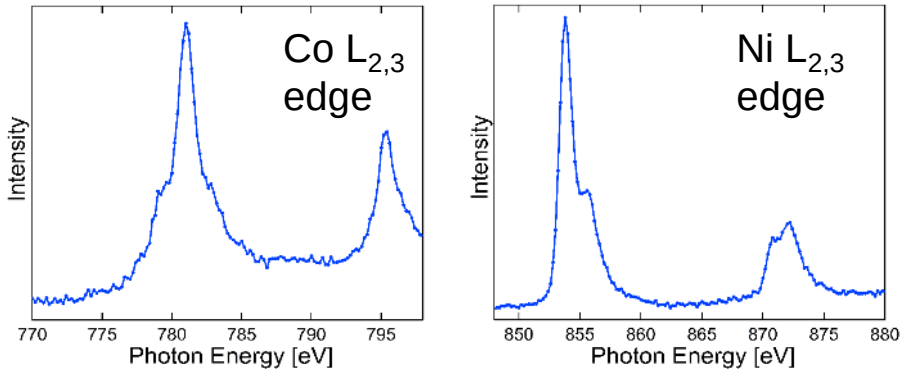
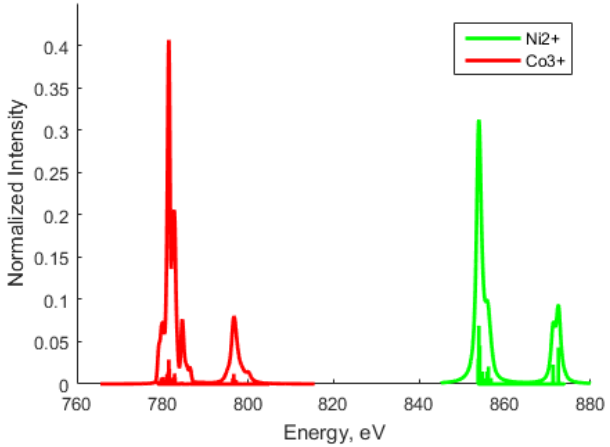
Results: XPS & XAS

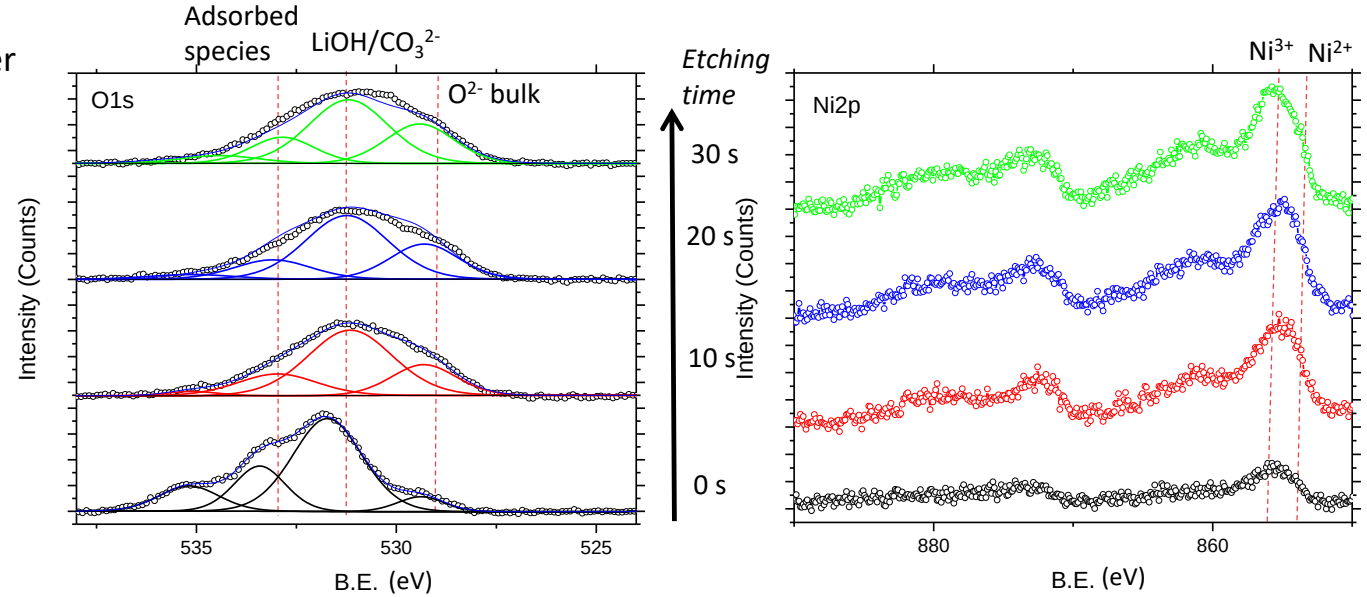


Experimental NMC 811 Co and Ni L-edge absorption spectra (Auger electron yield mode) for electrodes provided by Warwick



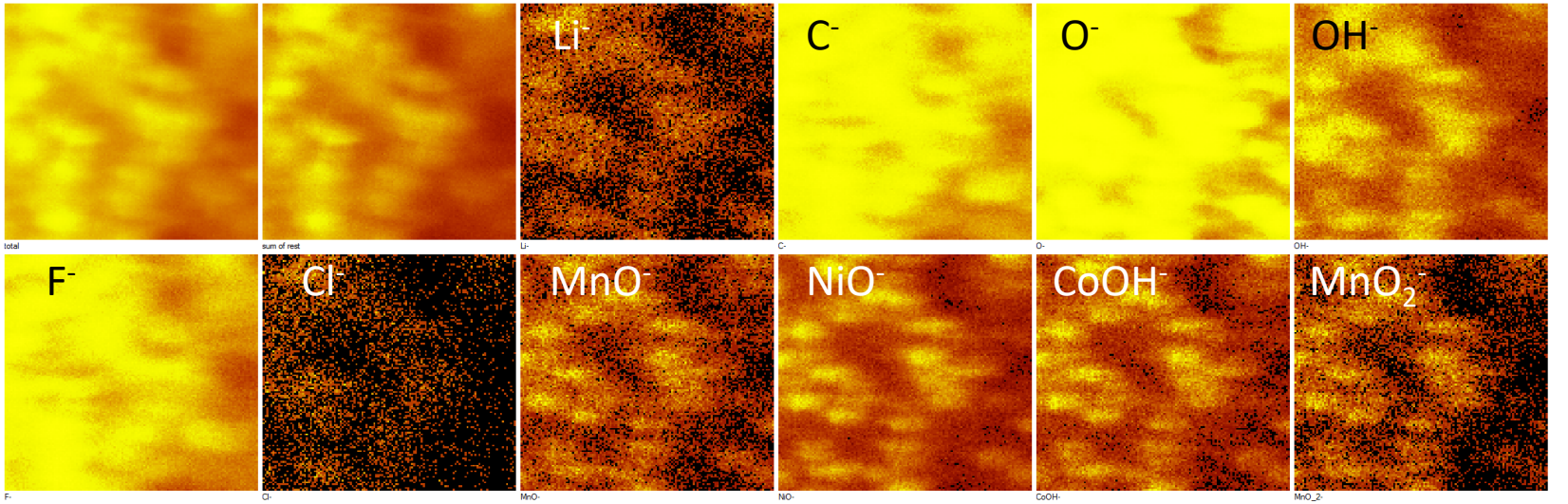
Simulated L-edge absorption spectra for Ni^{2+} and Co^{3+}.

- Surface characterisation of pristine and ambient treated NMC particles with XPS and XAS
- Confirmation that real electrodes give good signal without requiring model system.
- Initial simulation of XAS spectra using CTM4XAS



XPS depth profiling (cluster etching) removes surface carbonate and increases Ni^{3+}/Ni^{2+} ratio

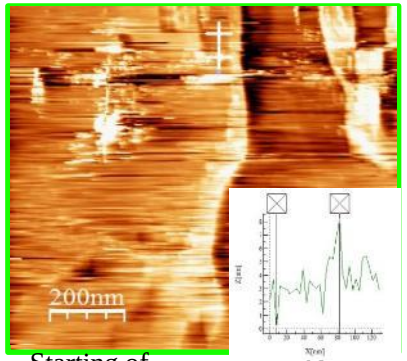
Results: TOF SIMS O_2 sputtering of NMC material



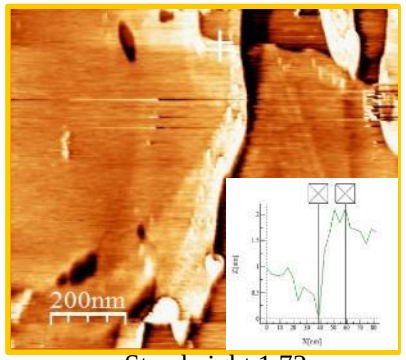
150 x 150 μm maps

- Ni, Mn and Co distribution highly inhomogeneous
- Depth profile reveals surface enrichment of OH, due to air transfer (need improved transfer)
- TOF-SIMS instrument cannot resolve elemental distribution within individual particles

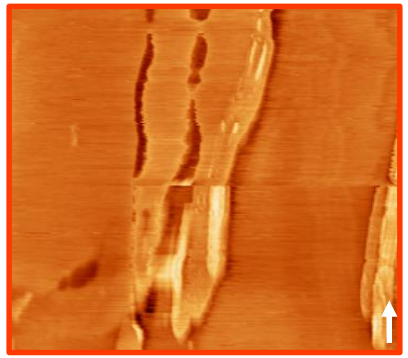
Results: EC-STM in Glove Box

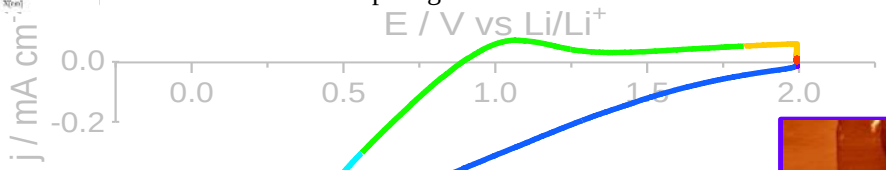


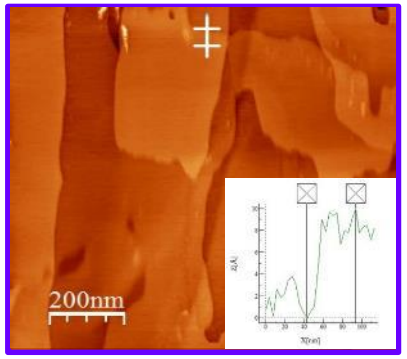
Starting of deintercalation.
Step Height 3.13nm



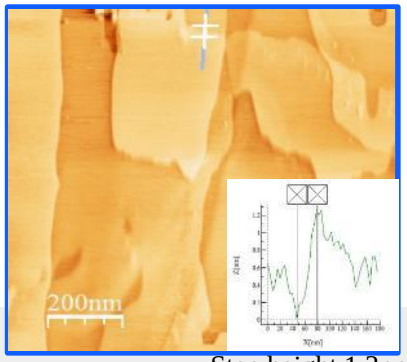
Step height 1.72nm



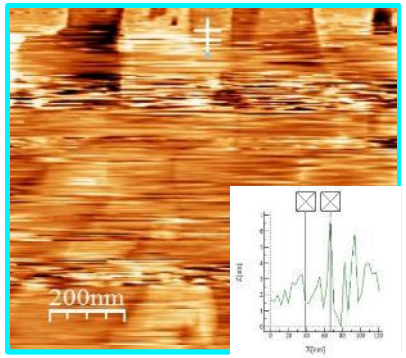




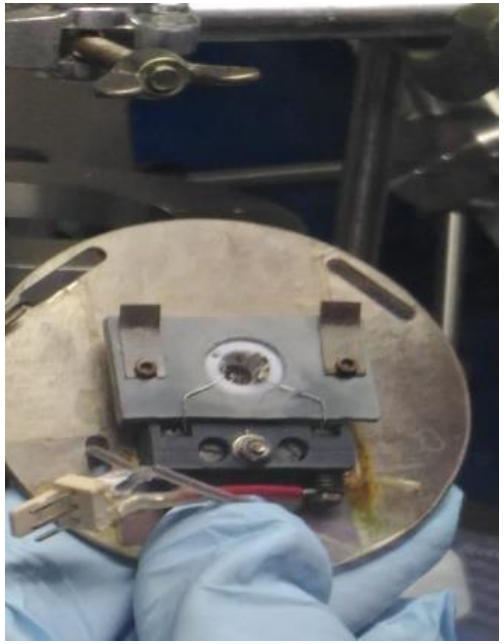
Pristine HOPG
Step Height 1nm



Step height 1.3nm



Roughening of the surface and noisy STM images at lower potentials due to the swelling of graphene layers with a Step height 3.38nm. SEI formation during Li intercalation



Standard commercial electrolyte:

1M LiPF6 in EC:DMC 1:1 v/v

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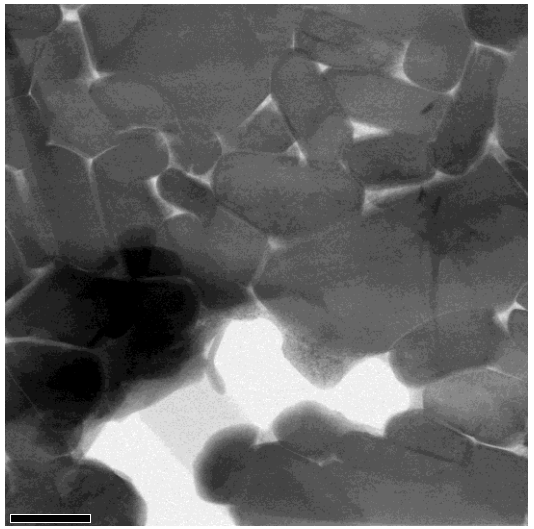
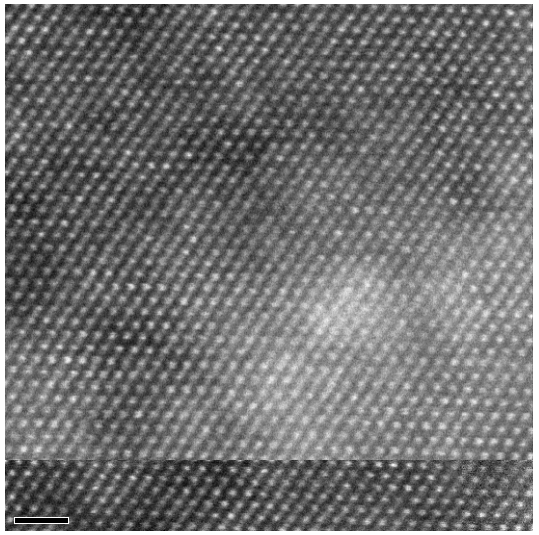
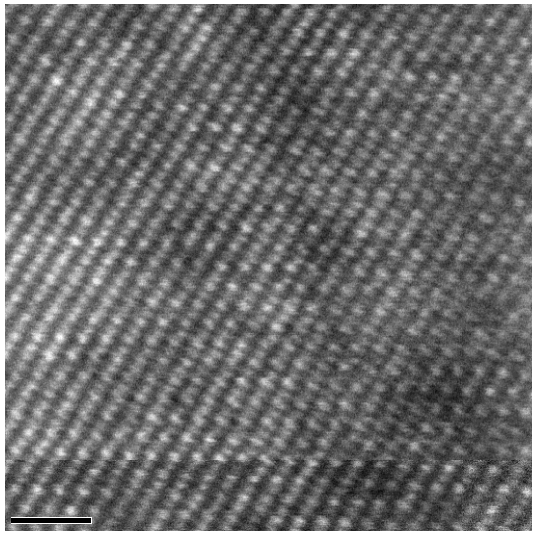
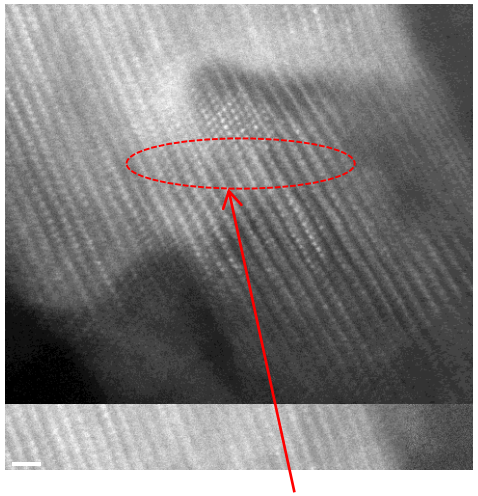
Results: Preliminary STEM

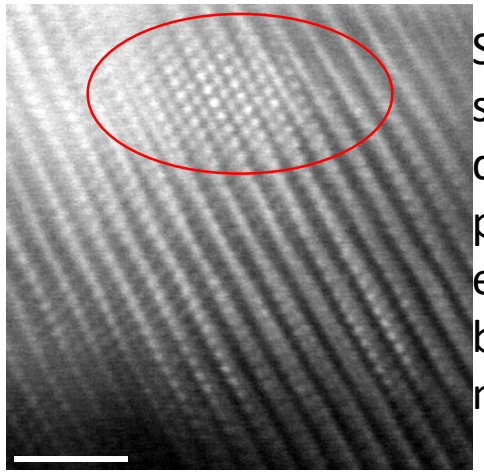
Pristine NCM 811 FIB



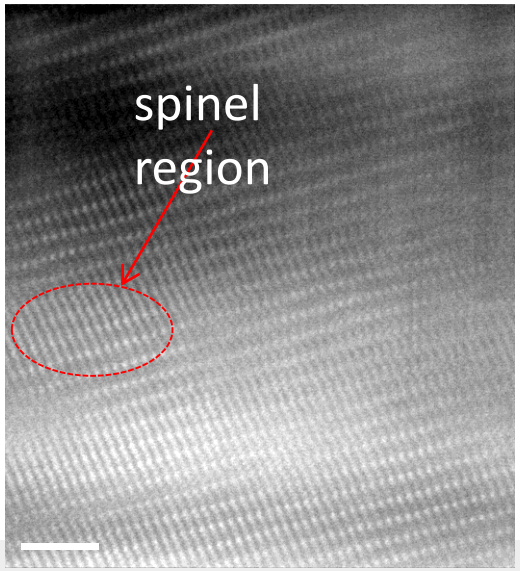








Sample showing some dislocations, possibly screw, edge mixed… but we need more data



HiRes Spatailly resolved EELs possible

We can distinguish some of the termination of plane of atoms in the middle of a crystal.

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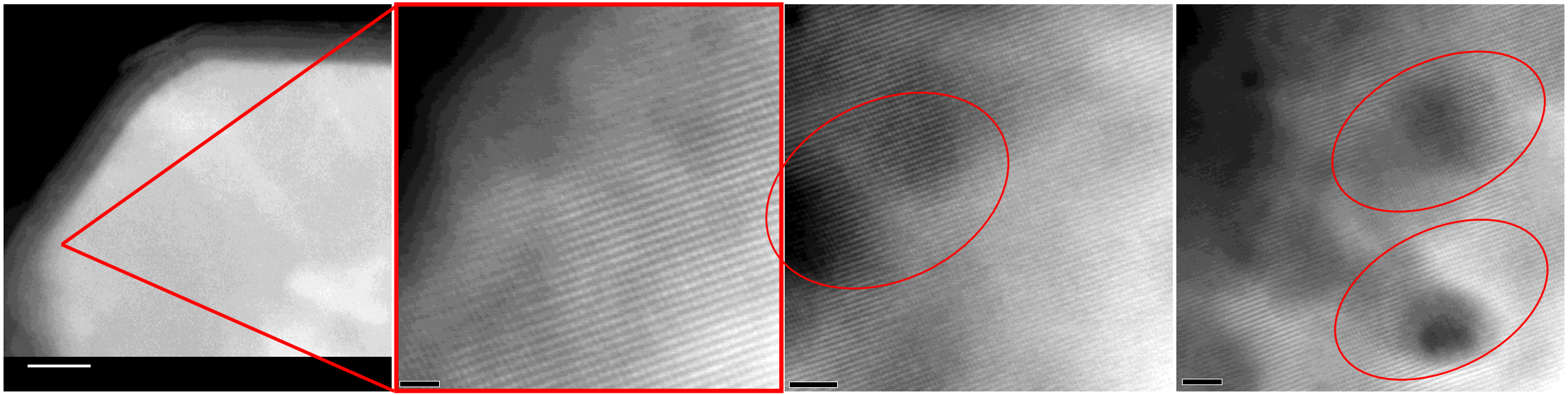
Targray 811- cycled 4.3V



Clear phase separation region, sample more susceptible to e-beam damage then pristine 811.

Results: In-situ TEM Development

Trials of deposition of NMC powder on electrochemical in-situ TEM chips were done.

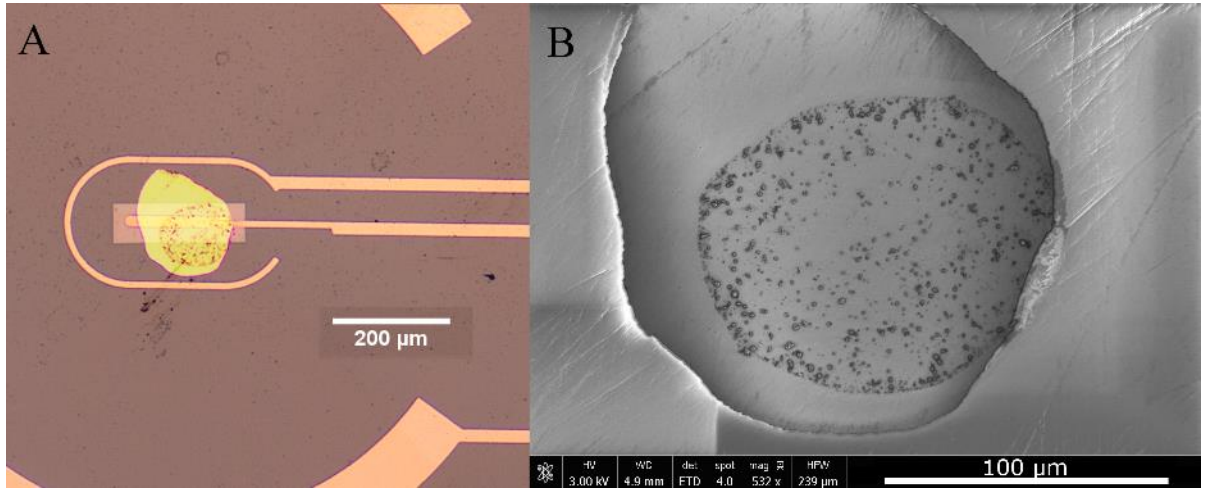


Figure 1. (A) Optical microscope image of an electrochemistry chip with an overlaid image of deposited layer of NMC811. The yellow area is a gold layer that acted as a target for selected area deposition. (B) SEM image of the same deposit.

Further materials' structure investigations have been done, especially EDX/STEM mapping of NMC811 particles from Targray and Dr Serena Corr's group. Non-uniform distribution of the transition metals has been found.

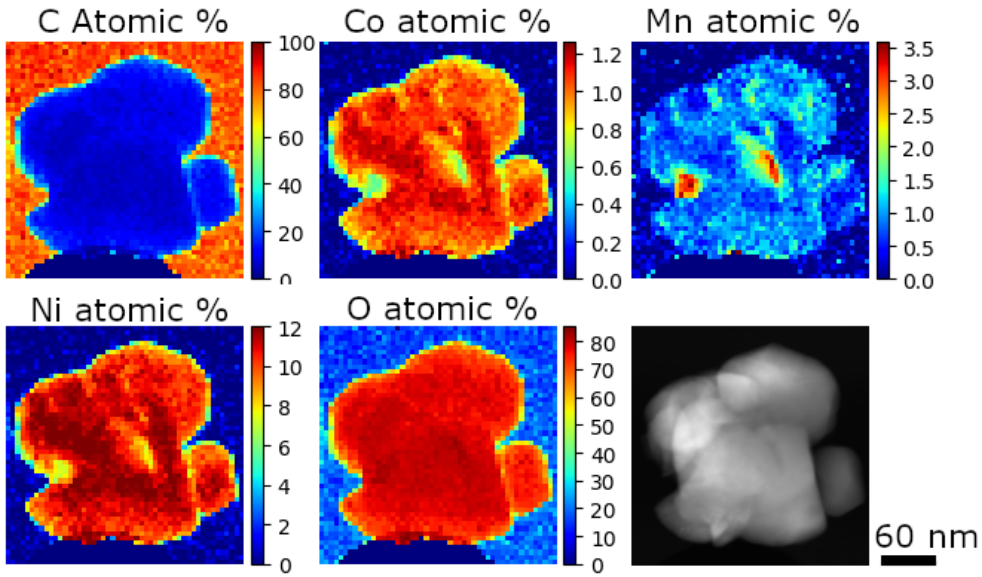


Figure 2. EDX/STEM maps of NMC811 particles from Glasgow.

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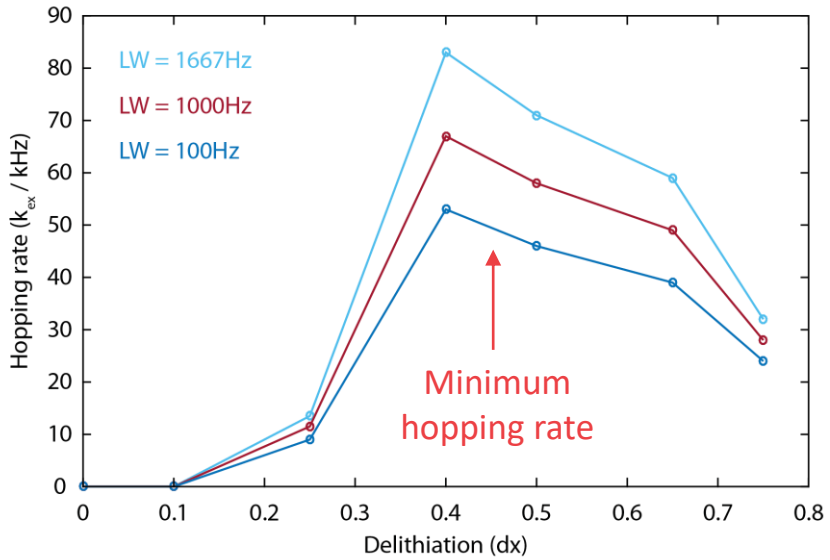
Li ion hopping: Hopping rates calculated from NMR spectra

Hopping rates at different SOC



Assumptions:

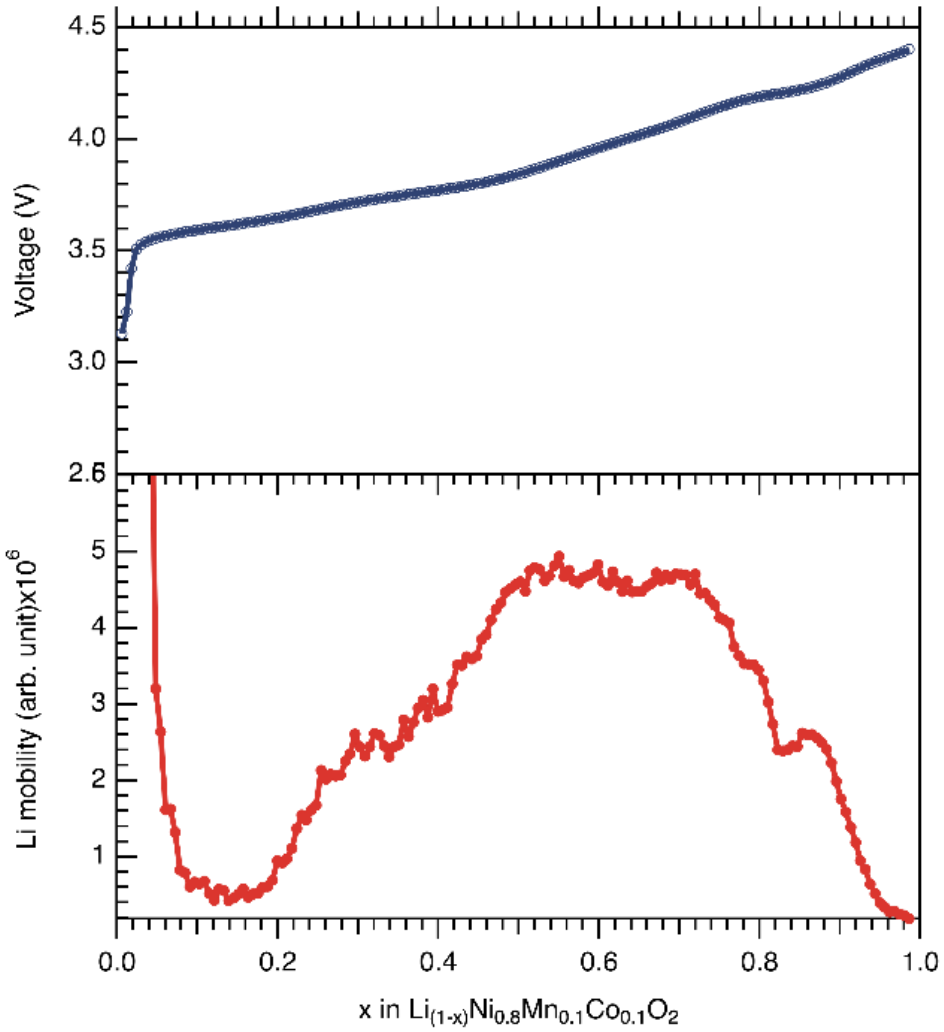
- All sites participate in hopping process
- Same rate for all hops
- Random distribution of TM ions

Challenge:

- Model depends on linewidths of the peaks involved in the hopping process (difficult to determine)

→ Hopping rates calculated for reasonable estimates

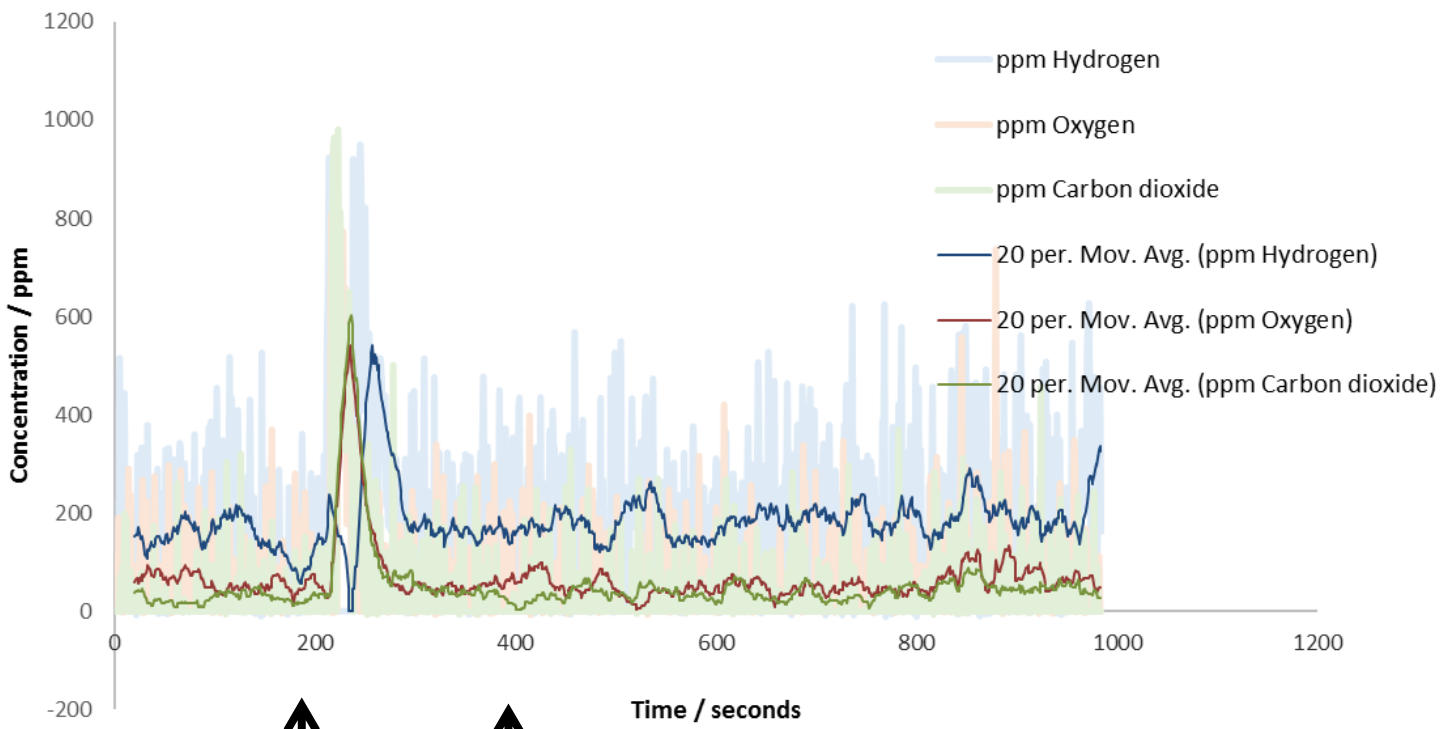
Galvanostatic Intermittent Titration Technique (GITT)



Overall trend agrees well with GITT data!

Results: Gas analysis of cycled cells

- NMC811 half cell cycled in 1.5M $LiPF_6$ in EC for 10 cycles at C/2
- **O_2, H_2 and CO_2 detected** once the cell is connected to mass spectrometer
- Formation of gases during subsequent cycling at C/2 or 1C is not detectable



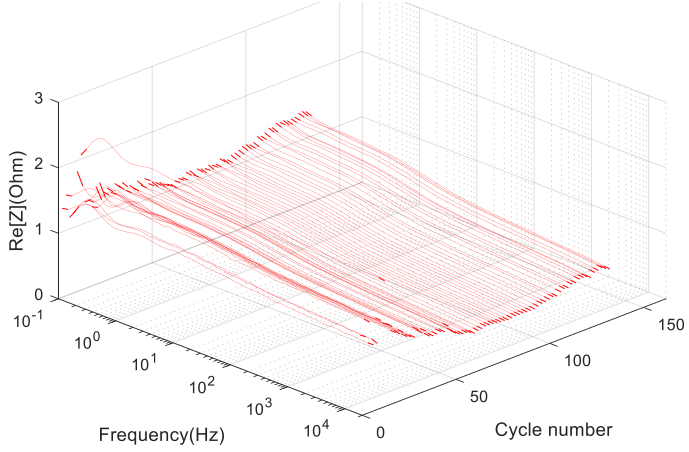
Connection to mass spectrometer

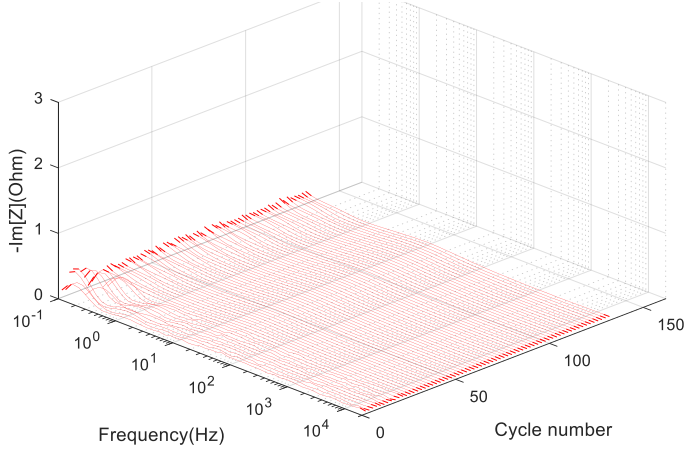
Start of subsequent cycling

Results: Machine Learning Using EIS Data

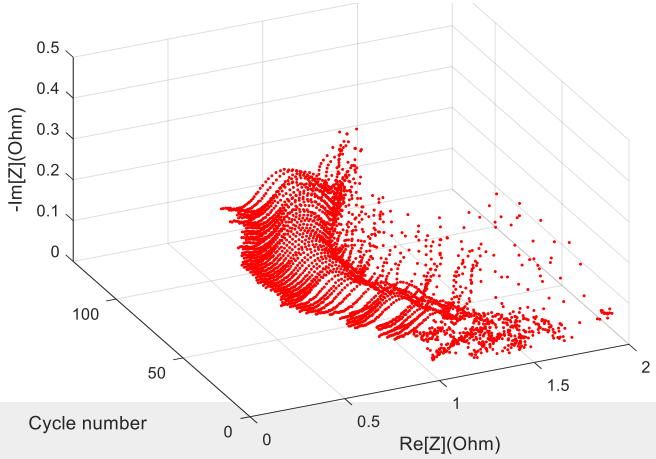
EIS measurement on coin cells during cycling and a machine learning model to predict SoH are experimented preliminarily

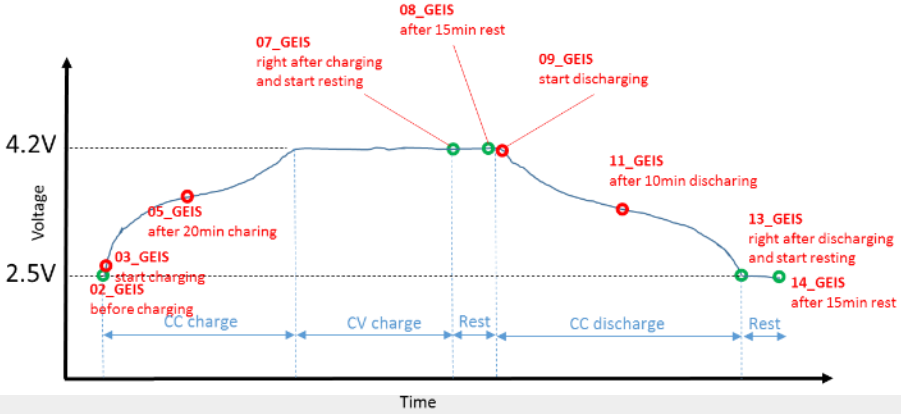
EIS of commercial coin cell during cycling: bode plot





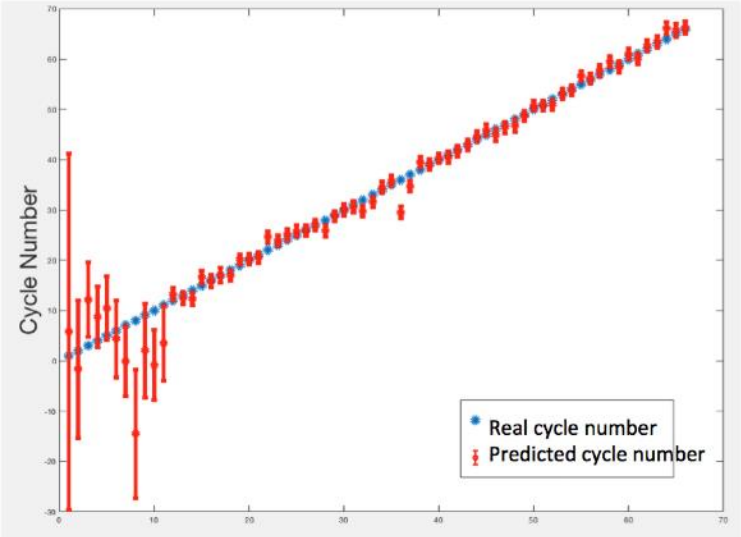
EIS of commercial coin cell during cycling: Nyquist plot





Temperature: 60°C; Charge: 1C, 4.2V cut;
Discharge 2C, 2.5V cut; 1C=45mA; Chemistry: LCO/Gr

A preliminary "prediction" of cycle number using machine learning



EIS is measured in different phases of charge/discharge during cycling.

Using the machine learning model trained with EIS data, cycle number can be inferred with another set of EIS data measured under similar condition.

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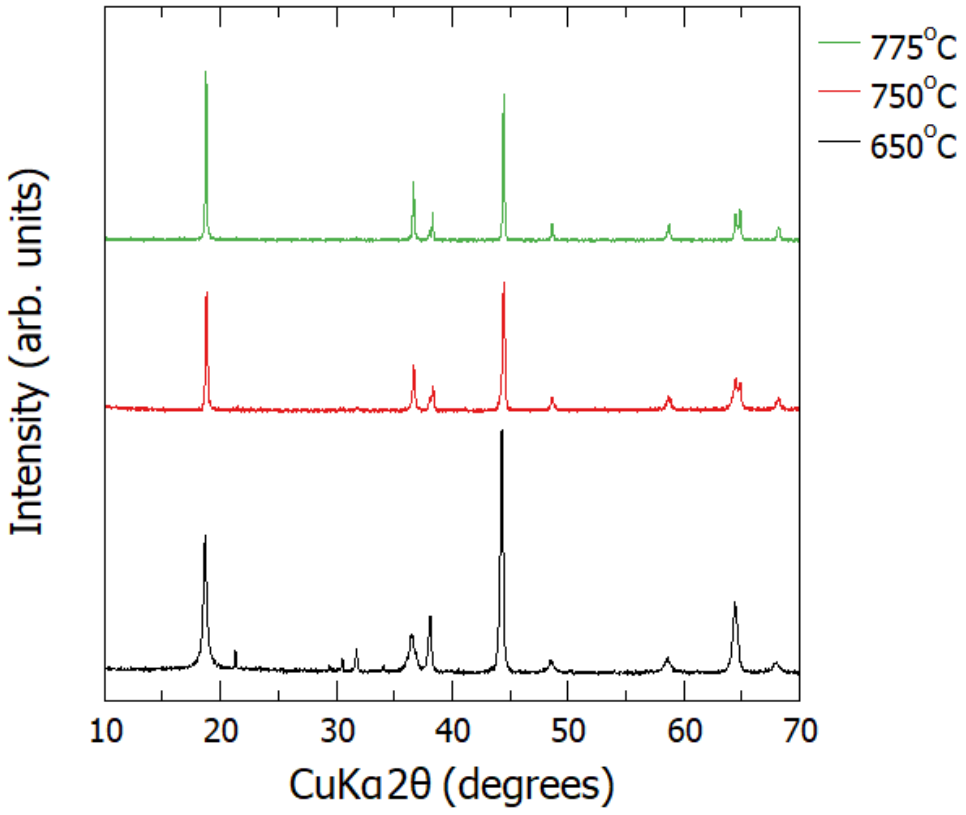
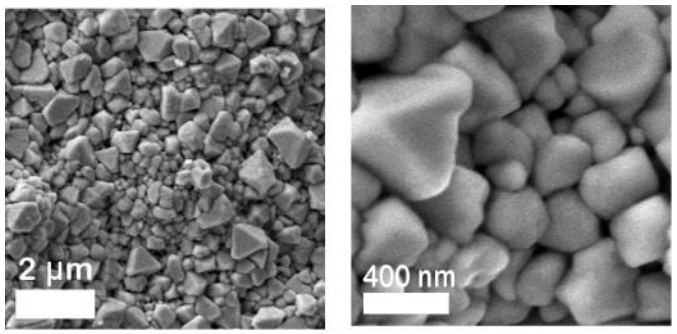
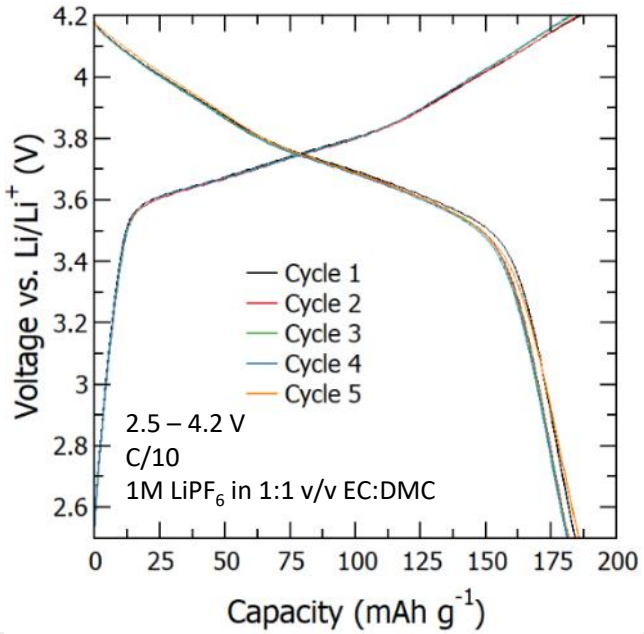
Results: Nanostructured NMC synthesis

Microwave synthesis affords clean products at 775°C after only 3 hours





Polydisperse particles with sizes typically around 250 nm obtained



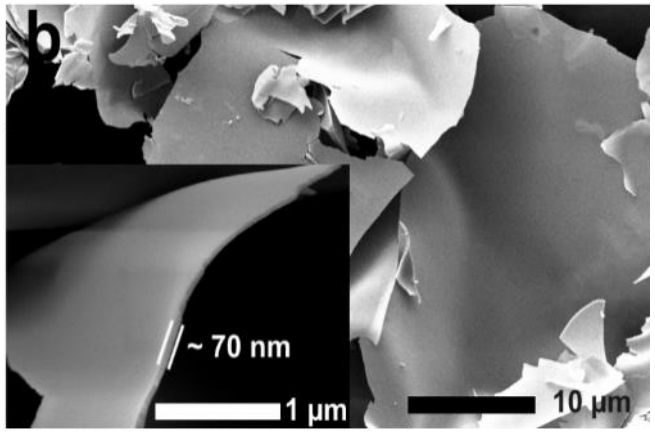
Results: Al_2O_3 coating of NMC-811

- Coating with Al_2O_3 can provide protective layer surrounding NMC to avoid breakdown by HF formed through electrolyte decomposition
- Two proposed initial strategies : Al_2O_3 coating via nitrate precursor and use of nanostructured Al_2O_3

1. Pristine NMC-811 mixed with aluminium nitrate
2. Evaporation of solvent
3. Calcination at 450°C

Coating via precursor

Sol-gel synthesis of Al_2O_3 nanosheets



Coating via nanostructures

Degradation 8-Month Review Summary

Engagement with large scale facilities

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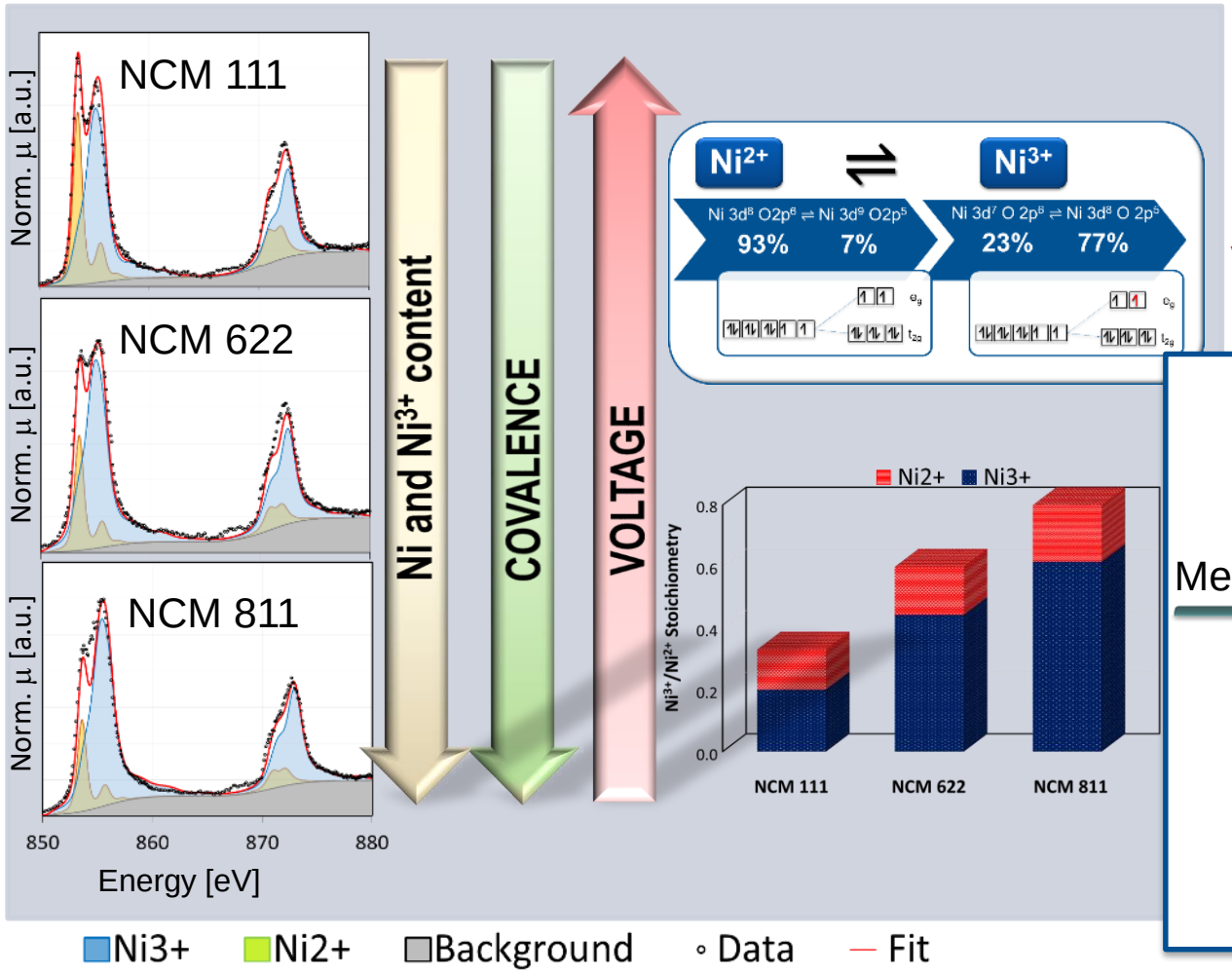
Voltage limits in Li-ion batteries: XAS @ DLS

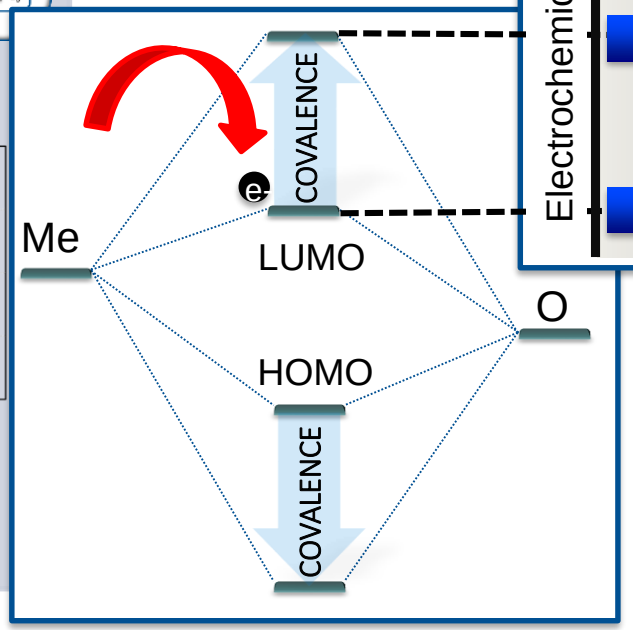


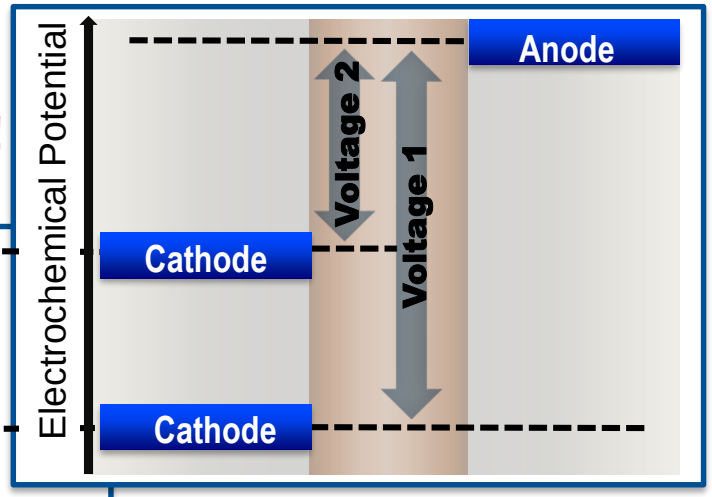
Charge

$LiMe^{III}O_2 \rightleftharpoons (1\text{-}x)\ Li^+ + x\ e^- + Li_xMe^{IV}_xMe^{III}_{1\text{-}x}O_2$

Discharge

Voluntary reaction!





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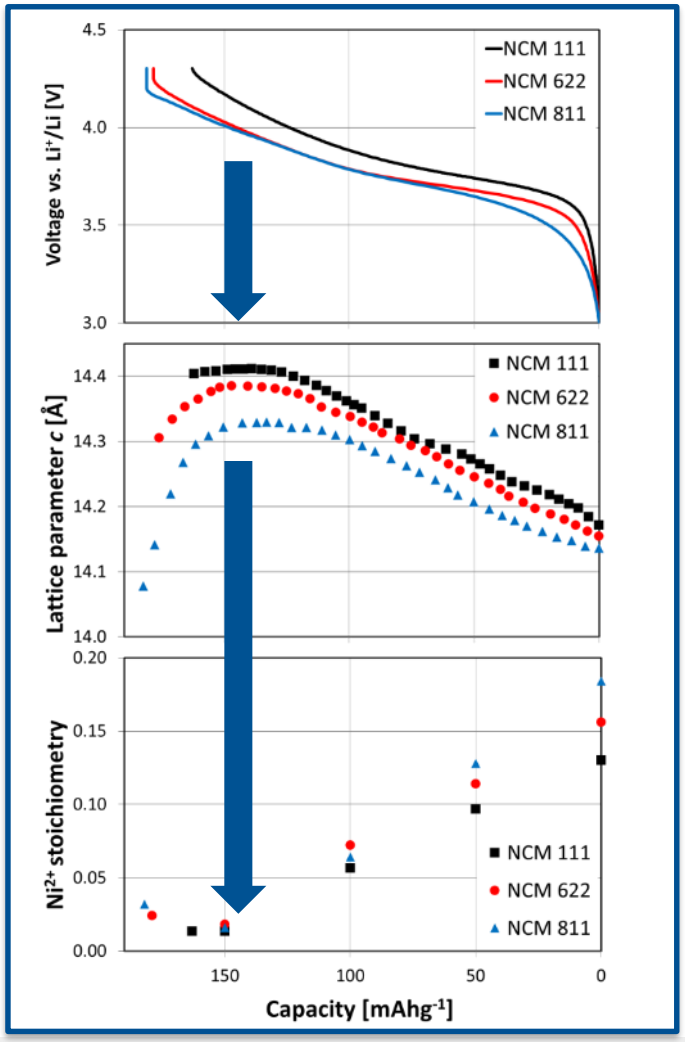
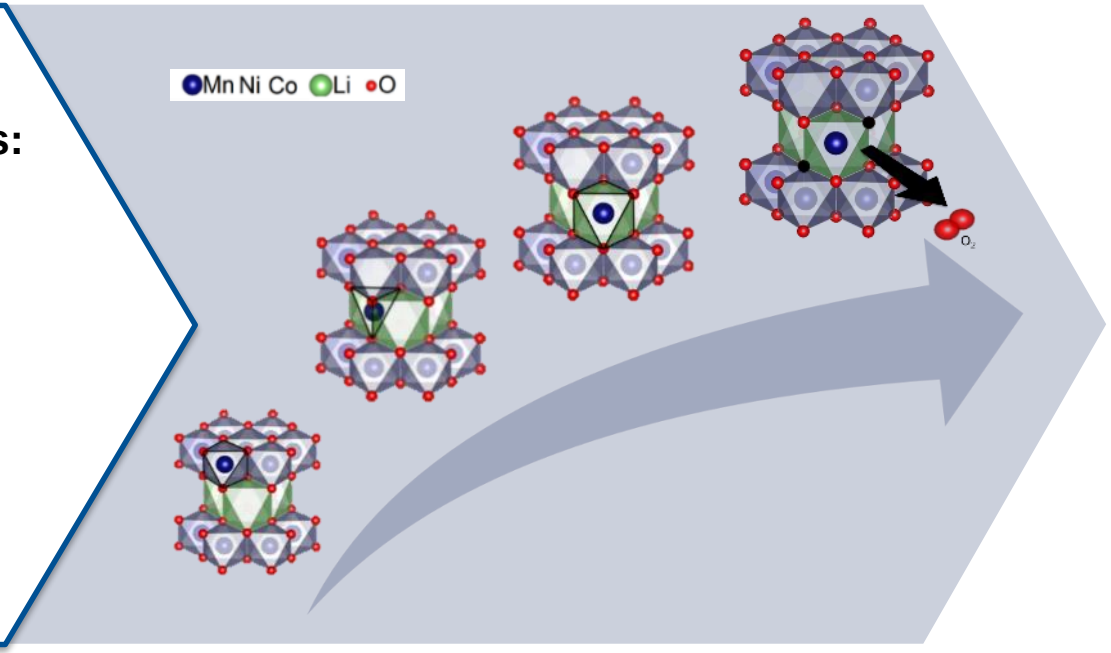
Capacity Limits in Li-ion batteries: In-situ XRD @ DLS



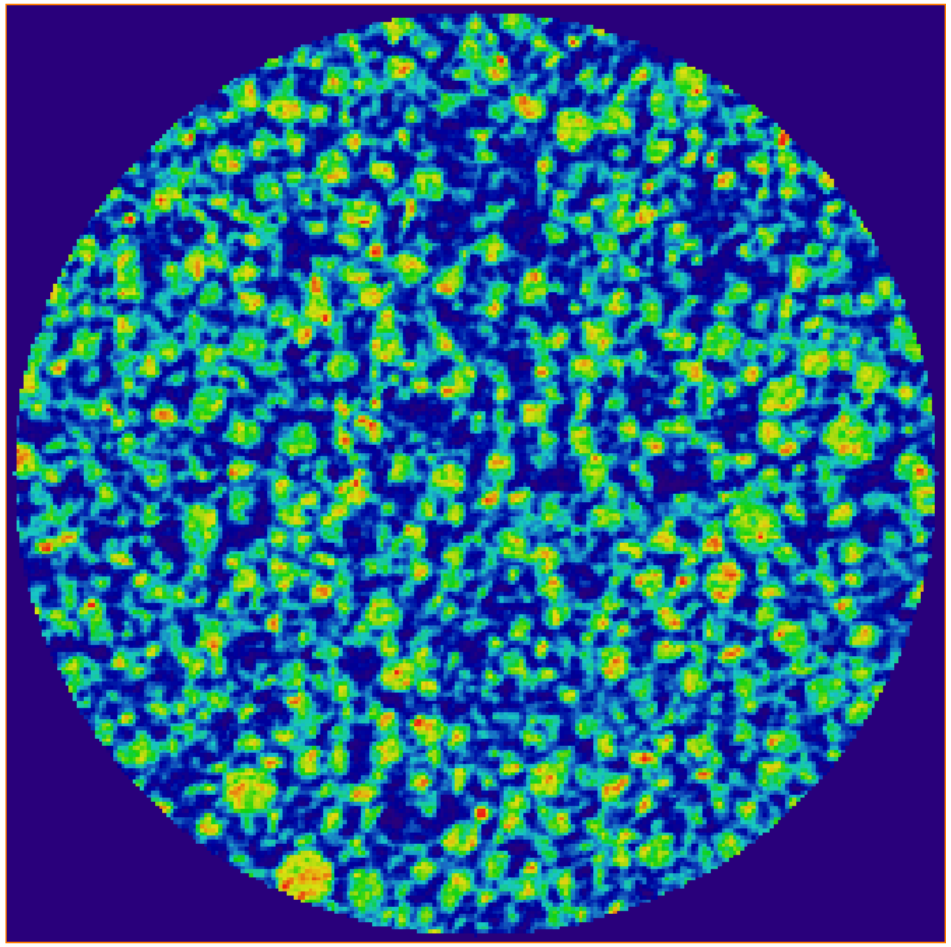
Change from reversible to irreversible reactions:

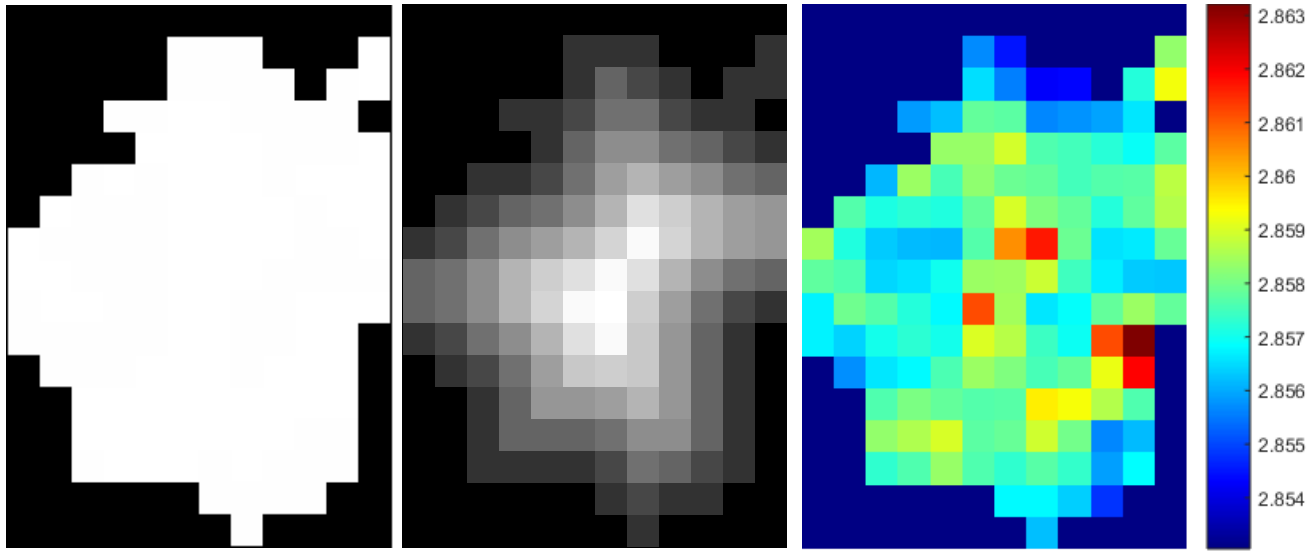
- **Collapse in *c-lattice parameter***
- **Minimum in Ni^{2+}**
- **Ni^{2+} content close to zero**



Oxygen release

3D XRD Understanding Heterogeneities @ ESRF





Single particle → Dist. Map → Sub-particle lp. mapping

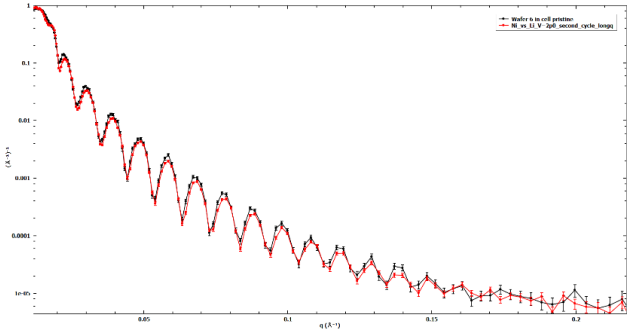
Future Engagement: Synchrotron

- *Manchester/Diamond/Cambridge – in situ XAS/XPS – B07 and ALBA, ex situ NMC I09*
- *Imperial – Cu/Graphite interface XANES I20*
- *UCL/Diamond – operando XRD – I11, nanoprobe I14*
- *Diamond/UCL/Cambridge – Long duration experiments – I11*
- *UCL/NREL – XRD CT – ESRF*
- *Liverpool – Kerr Gated Raman - Central laser facility*

Large Scale Facilities: Neutron

- SEI Formation from Neutron Reflectometry (*Manchester)*

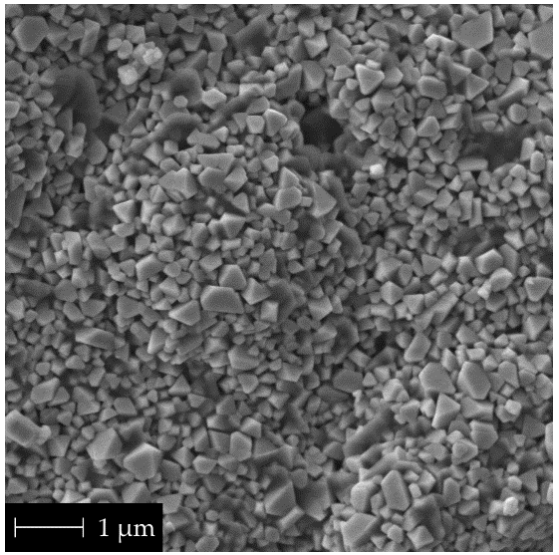
- *Weatherup* group using Offspec reflectometer to characterise the SEI formation and growth for electrolytes on nickel, graphene and silicon surfaces.



Neutron Reflectometry

- Nanostructured 811 NMC (*Sheffield*)

- Nanostructured NMC-811 shows enhanced cycling and improved stability when coated with Al_2O_3
- Proposed total scattering on POLARIS to examine pristine & coated materials, characterise nanostructure and alumina surface structure (*Cussen, Sheffield*)
- *Grey group, Cambridge* has neutron diffraction structure of commercial NMC-811 material (Munich reactor source) to share and contrast with nano-PDF.



Nanostructured NMC-811 from *Corr* group for PDF analysis by *Cussen (Sheffield)*

- Sian Dutton – Spin polarised neutrons on d7 at ILL

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Degradation 8-Month Review Summary

Science Plans

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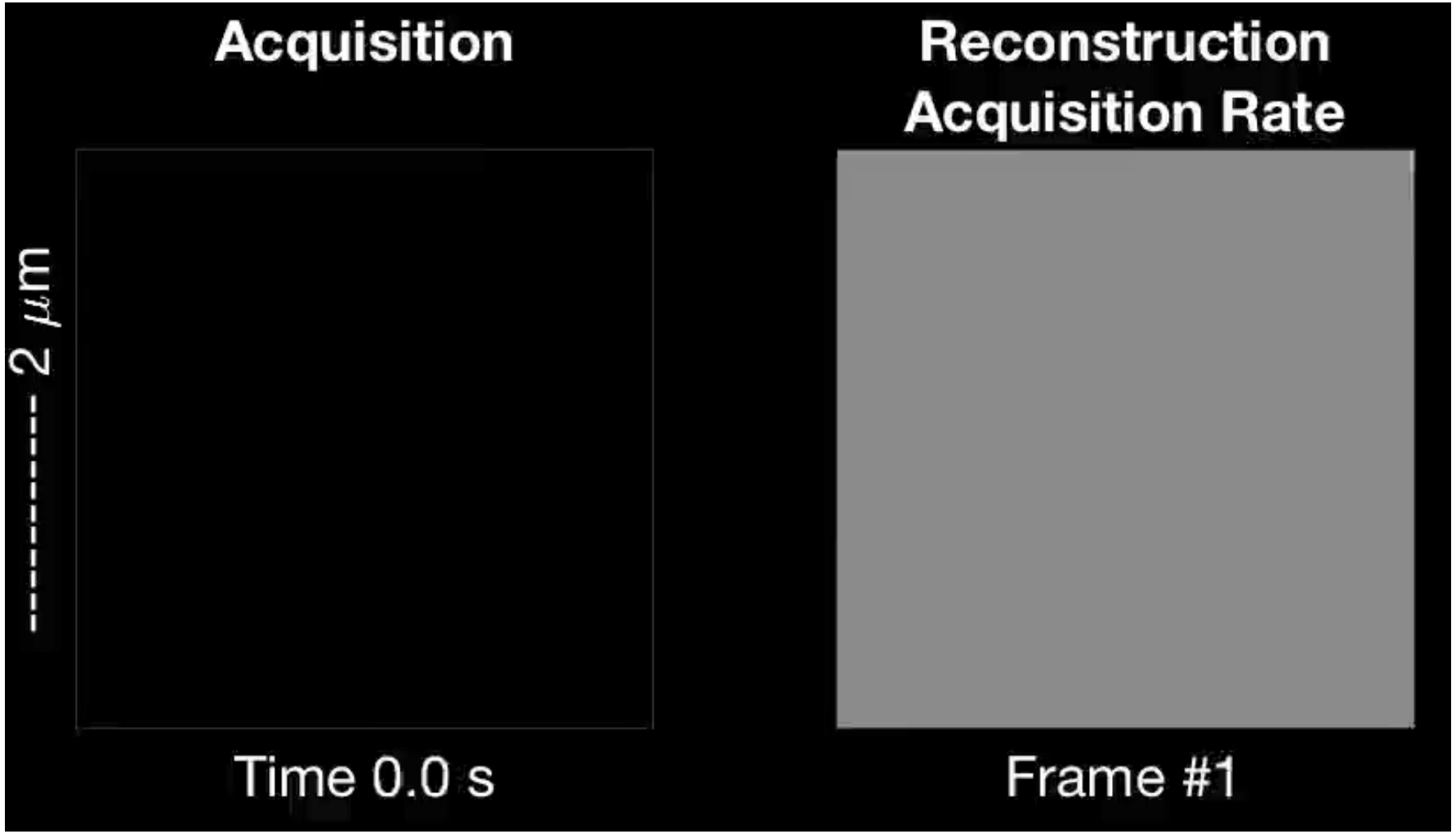
Plans: Observing Growth Dynamics by Inpainting



Even low sub-sampling rates identify all the particles and permit analysis

Mehdi et al, under review

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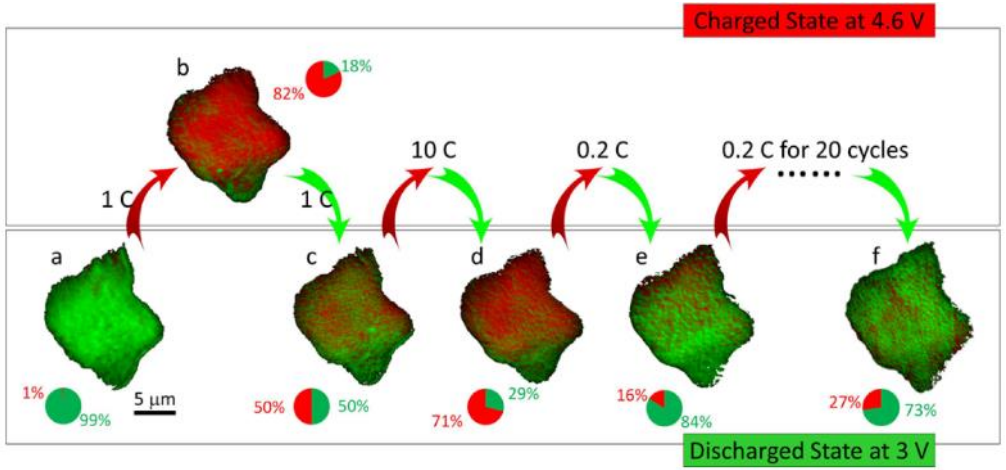
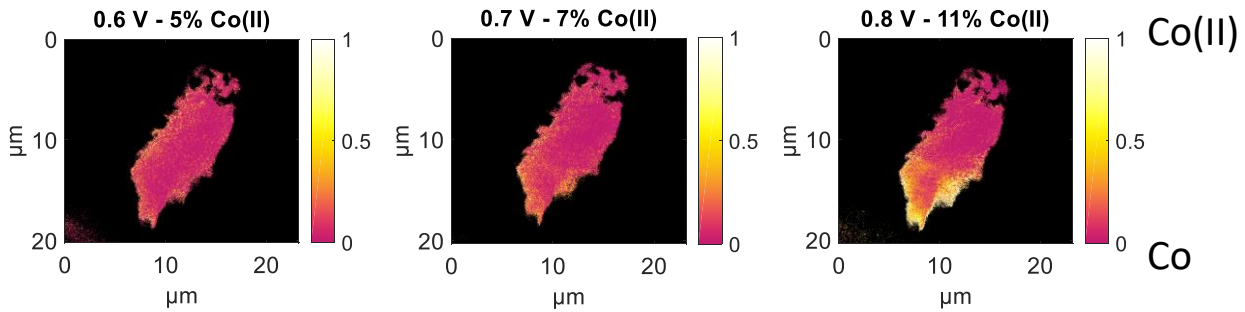
Plans: Spatially resolved dissolution of NMC

- Studying degradation at individual particle/nanoscale level (can resolve effect of elemental inhomogenities)
- *In situ* spectro-microscopy using X-ray Transmission Microscopy (TXM) and X-ray absorption spectroscopy (XAS):
- Spatially resolved chemical information as function of time and cycling conditions on NMC



TXM on $LiCoO_2$ Xu *et al.*, ACS Energy Lett., 2017, 2



TXM of CoCrMo corrosion under simulated conditions of human body

Hi5 has arrived!!!

This week

- Main chamber at 100°C to remove moisture, etc
- Current vacuum level: 10^{-7} / 10^{-8} mbar
- Target vacuum level: 10^{-10} mbar
- Antechamber with probes to be added

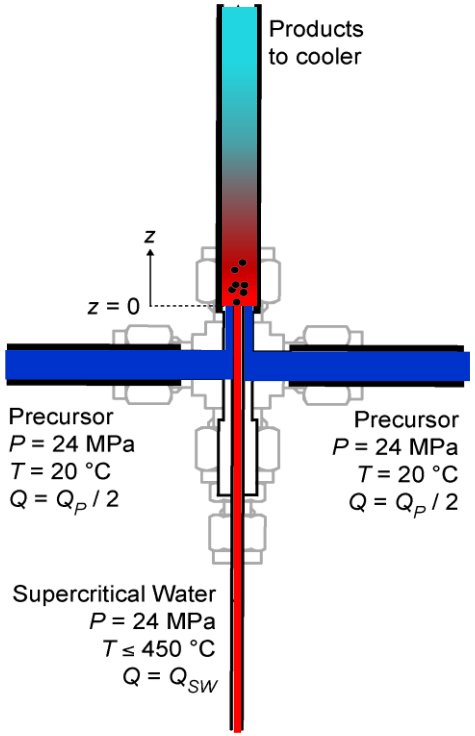
Next three months:

- Initial tests on Hi5

Longer term:

- Binderless-carbon free NMC electrodes

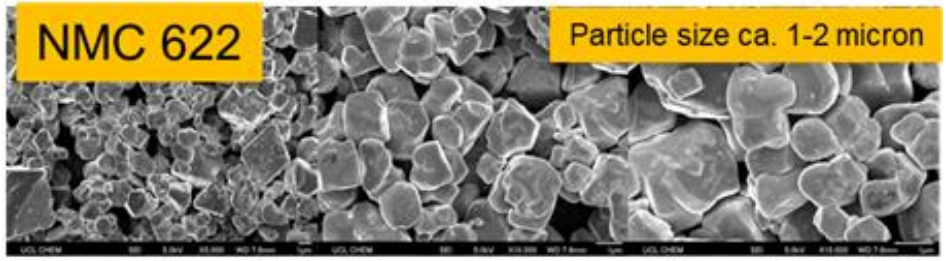
Plans: Scalable synthesis of NMC materials



Step 1: The scalable confined jet mixer makes nanoparticles in flow

Step 2 The precipitates from our process are lithiated via SS reaction to make NMC or doped variants

In year 2 we will scale up leading materials from the project up to 2kg h^{-1}



- Background Materials: 7 High Ni NMCs developed, simple process; all phase pure
- Target: Over 300 Doped NMCs made/tested (Dec18) visitors / flowchart
- Future: Spray dry, Start scale up in early 2019 for **lead materials** from above work

Degradation 8-Month Review Summary

Engagement with Industry Partners

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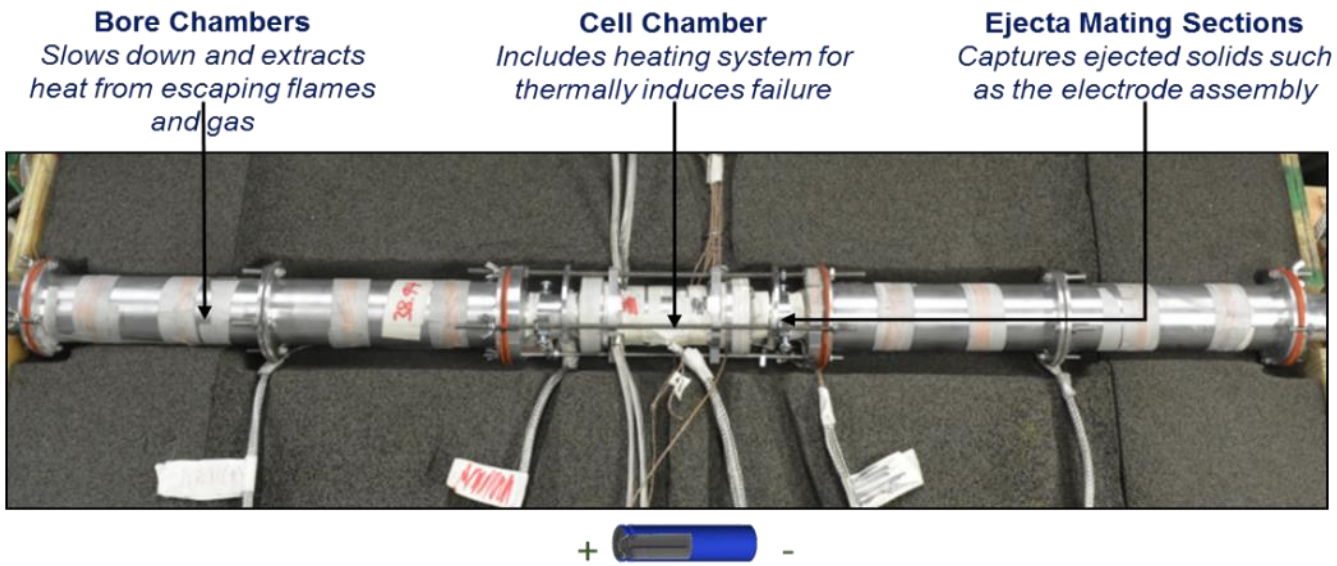
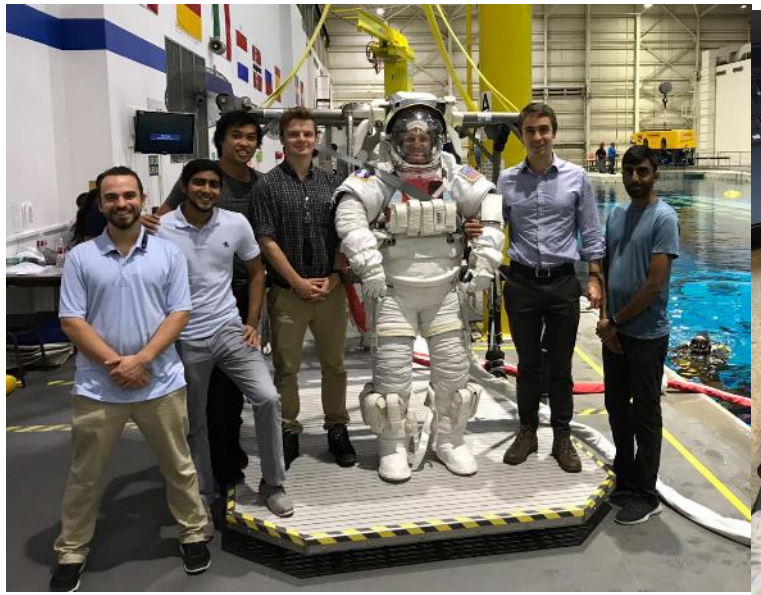
Partner Engagement: UCL/NPL/NREL/NASA Johnston Space Centre, NASA, Texas



Ref - Li-ion battery failure: Linking external risks to internal events, Power Sources Conference Proceedings, Denver, 2018.



Left to right: John Darst (Staff, NASA), Hasan (intern, NASA), Martin Pham (PhD candidate, UCL) Thomas Heenan (Post-Doc, UCL/Faraday), Bob Hines (astronaut candidate, NASA), Donal Finegan (Staff, NREL/NASA), Abhi Raj (PhD candidate, Princeton).

Demonstration of novel cells for safe failure after mechanical abuse.

NPL National Physical Laboratory

NASA

NREL NATIONAL RENEWABLE ENERGY LABORATORY

UCL

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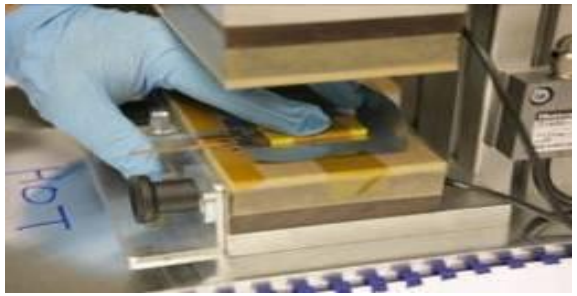
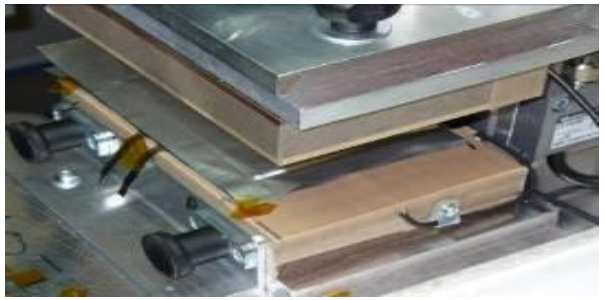
QinetiQ





- Electrode materials supply
- Large scale coating in the dry room
- Input into formulation of electrodes
- Development of new materials from WP4 into full cells

QinetiQ

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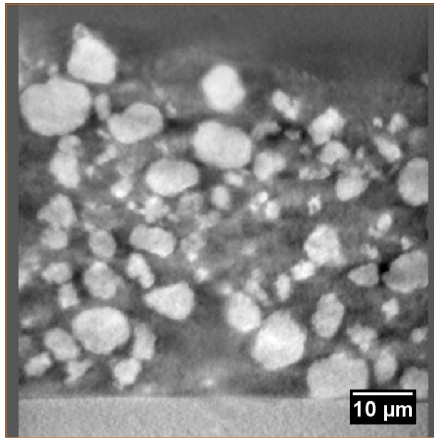
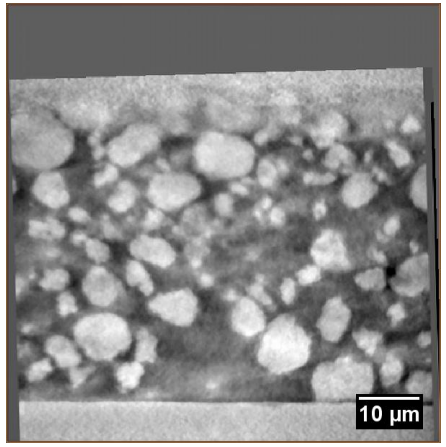
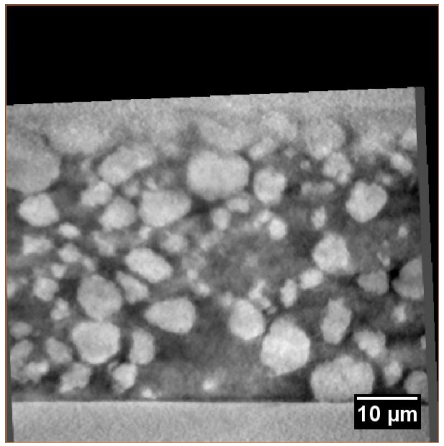
Johnson Matthey



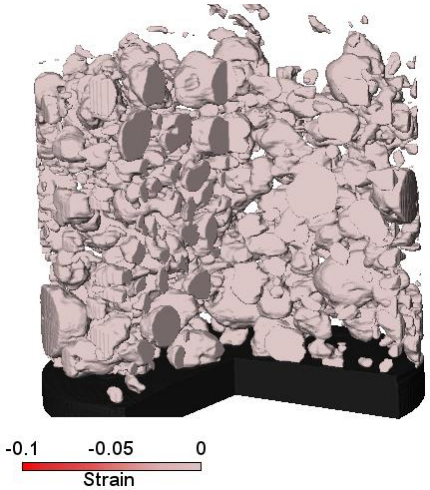
Pre-compression

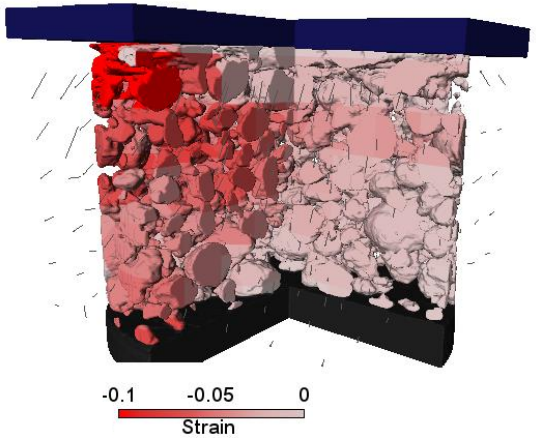


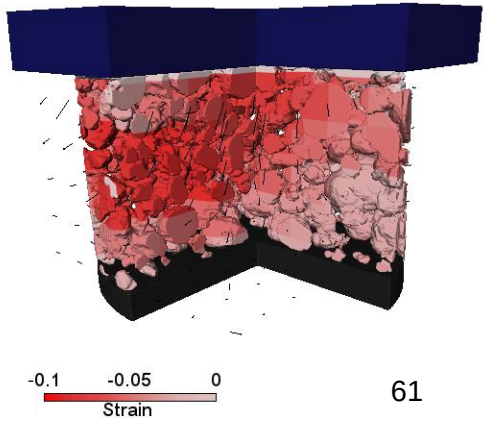
65 µm ind. stage displacement



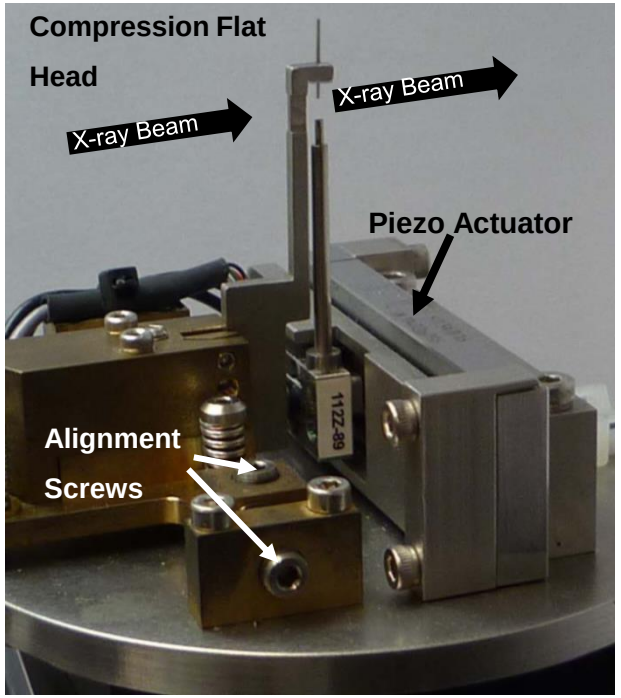
80 µm ind. stage displacement







- '4D Imaging' to mimic calandering process of NMC
- Load stage purchased under FI project to continue work, and extend to degradation studies



Conclusions

- Correlation of a suite of techniques to study battery electrodes
- 811 provides unique challenges in sample preparation and degradation mechanisms
- Coordinated approach to in situ and large scale facilities

<u>Focus for the Next Period</u>

- Continue challenge led research across WPs (metal dissolution, oxygen loss, potential windows)
- Cycled materials
- Correlation across techniques
- Collaboration with other fast starts (identifying ambassadors)

Thanks