Degradation 12-Month Review Summary

Clare Grey (PI)
Rhodri Jervis (PL)
Overview

- Recap of the Project
- Cycling and Materials
- Scientific Highlights
- Year Two Plans
Degradation

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

Connect degradation processes to electrochemical signatures

Learn via AI methods

Integrate into BMS systems

Connect to modelling activities
The Team

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Norman Fleck, CAM
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Layla Mehdi, UoL
Volker Pickert, NEW
Mary Ryan, ICL
Ifan Stephens, ICL
Robert Weatherup, MAN
Dominic Wright, CAM
Rhodri Jervis, PL

THE FARADAY INSTITUTION
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.
- Provide insight into and help provide mitigation strategies for issues and challenges being identified across the UK by various partners
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
Cell Cycling/Materials
Materials: Overall Strategy

- Year 1: 811 + graphite
- Year 2 and Beyond: Coated 811 and Si/SiO

Strategy

1. Purchase materials from recognized suppliers worldwide
   - Targray pristine material, coated electrodes (by ANL initially, then WMG)
   - NEI – pristine material and coated electrodes
   - BTR – pristine materials: graphites and coated 811
   - Small scale testing across the consortium
     - Identified challenge re. moisture sensitivity very early on – cannot scale-up uncoated materials outside dry room
     - Use of dry room in Cambridge
     - Developed protocols for optimal full scale electrode construction at small scale
   - Larger scale electrode fabrication in Warwick
   - Electrode fabrication in QinetiQ – this week!

2. Synthesize materials in-house (WP4) for bespoke experiments, coatings and eventually scale-up

- O1s/C1s NAP XPS => suggest rapid growth of LiOH & slower conversion to Li$_2$CO$_3$

Rob Weatherup, Chris Sole (MAN/Diamond)
Benchmarking and Cell Development

Multiple scales of cells are needed: bespoke in situ cells with in house processing, stable performance from commercial materials, larger scale processing for post-mortem analysis.

3-electrode cells allow separation of anode and cathode polarisation

Improved Formulations and processing lead to stable cycling performance

Commercially sourced electrodes and large scale electrode coating
Susceptibility Measurements: A Simple Method for Screening (Bulk) Variations in Samples

Results (1) – dc magnetometry on 3 separate batches of pristine Li NMC 811

- Targray, ANL
  - $T_{cusp} = T_{irr} = 8$ K
  - spin glass,

- Targray, WMG
  - $T_{irr} = 122$ K
  - cluster glass

- LiFun
  - $T_{irr} = 148$ K
  - cluster glass

- Difference in ZFC and FC is measure of Ni occupancy in Li layers

N. Chernova, M. S. Whittingham et al.
Scientific Highlights
A Summary of Key Year 1 Achievements

• Materials: secured a supply chain, synthesised high performance materials, scaled up, understanding processing, consistency

• Method development: refined in situ and operando techniques, predictive machine learning algorithms, use of large scale facilities

• Advances in mechanistic understanding: Li mobility, gas evolution, spectroscopic understanding metal dissolution, EPR of radicals
Chemical Information

Li Mobility, Raman
In-situ $^7$Li solid-state NMR: Identifies Optimum Window with Highest Li-ion Conductivity

Room temperature

Li metal

Li in NMC811

Li in the electrolyte

Room temperature
In Situ Raman spectroscopy can probe chemical changes during cycling

Goal:
Study of degradation processes in Lithium Ion Batteries (LIBs) using in-situ and in-operando Raman spectroscopy

Li-Ion (pouch) cell

Embedded fibre-optics

Raman

Operando Raman – Cambridge

Interpretation of data – Liverpool and Cambridge

Kerr Gated Raman – Liverpool

New cell designs
Electrochemical Observations

Gas formation, AI EIS
Detecting Volume Changes on Cycling via Pressure Measurements: NMC811 vs. Li cells

- Fast cycling at C/2
- Cyclic volumetric changes due to lithium plating/stripping
- Overall changes due to electrolyte decomposition and gas evolution
- => extremely sensitive set-up

*corrected for temperature fluctuations
Gas evolution from NMC811 vs. graphite cells

- Three electrode cell with a reference electrode
- ca. 3 mmol of gas evolved per mole of Li\(^+\) inserted on graphite in the first cycle due to SEI formation on graphite
- Gases consumed on rest – reaction with cathode?

*: corrected from temperature fluctuations
Can we use machine learning to detect degradation with EIS?

- Experimental EIS spectra do not perfectly fit the classic capacitor-resistor model. We can fit it to more complex equivalent circuits, but the fit can be ill-posed.

- However, the spectrum changes with cycle number, thus it is an indicator of degradation, but why and how?

- Can we use machine learning to detect persistent but subtle features in the EIS that correlate with degradation?
AI×EIS: Subtle but persistent correlation between impedance and cycle number at the “magic frequency”

The bode plots of Im[Z] during cycling

One “magic frequency” in the imaginary part of EIS was identified as the key predictor of cycle number.
Morphological Degradation

Microscopy and Crystallography
Post-mortem analysis reveals substantial particle fracturing

Post-mortem analysis: EIS, XRD, SEM/EDX and ssNMR (K Marker) on cathode and anode, solution NMR on cycled electrolyte (J Allen, C O'Keefe)

How is particle cracking affected by voltage window limits? holding at specific SOCs? shapes and sizes of particles?

C/2 cycling ~ 14.3 % capacity loss

Pristine NMC (by WMG Warwick)

After 201 cycles

1 μm

Operando SEM: Method Development

1. Make “half coin cell”
2. Fill with electrolyte
3. Seal the cell

Precise the full cell

Cross-section of a standard coin cell

Silicon wafer

SiNx film (50-75 nm)
Imaging the cross sectioned coin cell

Wheel polishing

Al
Separator
Cu

Doubled coated commercial electrodes.
NMC 111
**NMC 811: reducing particle size for in- and ex-situ TEM analysis**

Sub-µm particle size and high precision printing are essential for in situ electron microscopy.

<table>
<thead>
<tr>
<th>Targray secondary particles are too large for TEM work so:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball milling in a planetary mill – 60 min, 350 rpm</td>
</tr>
<tr>
<td>Efficient fragmentation of secondary particles, crystallography and composition are preserved</td>
</tr>
</tbody>
</table>

- **Standard electrodes can be studied with SEM and FIB**

<table>
<thead>
<tr>
<th>(a) Ball milling in a planetary mill</th>
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<tr>
<td>10 µm</td>
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<tr>
<th>(b) Aerosol printing</th>
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<tr>
<td>Mass transfer to substrate, compatible with TEM e-chip prep</td>
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</tbody>
</table>

| 80 µm |

**Team:** Cate, Jedrzej, Georgina and Amogh (Cam)
Operando XRD CT Technique Development

Bespoke Cell Housing

Electrochemical cell

In-situ and operando imaging

- Pin
- Li metal
- Separator
- Electrode
- Current Collector

Potentiostat terminal

Radiation

Diffraction

Tom Heenan, Chun Tan, Andy Leach, Rhodri Jervis, Paul Shearing (UCL), ID15 ESRF
Operando XRD CT allows Sub-particle Spatially Resolved XRD

1 µm voxel length
400 µm FOV

1 µm resolution

FOV 400 µm x 400 µm

Tom Heenan, Chun Tan, Andy Leach, Rhodri Jervis, Paul Shearing (UCL), ID15 ESRF
XRDCT – Sub-particle analysis

• Distance map approach to plot radial distance from centre of particle

• Pixel lattice parameter / mean particle lattice parameter plot vs depth within particle (surface to core)

Sohrab Daemi, Tom Heenan, Chun Tan, Andy Leach, Rhodri Jervis, Paul Shearing (UCL), ID15 ESRF
Materials Synthesis and Supply

Phase pure NMC, Bespoke Materials, Coatings
Results: NMC-811 synthesis

XRD indicates reduced Ni/Li cation site mixing in temperature regime 750-850°C. Electrochemical testing reveal materials display similar performance to initial benchmarking ANL electrodes.

XRD of sol-gel precursor and NMC-811

First five charge/discharge cycles for microwave NMC-811 (C/10; up to 4.2 V)

Morphology control via long-chain alkyl surfactant addition

Preferred orientation \( I_{(003)}/I_{(104)} \) peak intensities?

Increasing surfactant concentration

Increasing particle size and size heterogeneity
What role do protective (particle) coatings play?

• Novel routes to coatings involving new precursors (e.g., Al(O\text{Pr})_3)
• Synthesis of [(tBuO)_2Al(μ-OH)]_3 and use as a precursor for coating synthesis
• Preliminary SEM and EDX results
  • Very strong coating agent and tendency to aggregation (type 2)
• Al(O\text{Pr})_3 thicker coating (type 1)– too thick coating reduces particle contact and reduces capacity.

Conformal coating – prevent metal dissolution?
- protect surface from electrolyte “attack”

vs. patchy cover – scavenge electrolyte decomposition products?

Strategy:
synthesise in house coatings and test commercial samples

Victor Riesgo Gonzalez, Dominic Wright, Cambridge
Year Two Focus
Year 2 Plans

• Correlative understanding of degradation mechanisms from operando and in situ experiments – technique development and significant initial experiments have already taken place on XAS, NMR, XRD, XPS, X-ray CT, XRD CT, Raman. Results from these experiments will be processed and inform mechanistic understanding

• Full cell testing as a priority

• Key parameters from initial degradation experiments to be fed into MSM. Discussions already under way as to the required information/format of information

• More ‘top down’ input from industry on key questions or challenges regarding degradation to investigate specific problems
Year 2 Plans

• Iterative post mortem analysis to run along side operando fundamental understanding, at a ‘prototype’ cell level (WMG/QinetiQ)

• Understanding how environmental conditions can influence physico-chemical stability of 811

• Commercial 18650/21700 cells (pre-formed) to be added to a second layer of post mortem analysis to understand what degradation mechanisms are key for industrially relevant ‘large scale’ cells (and which are not)

• Scale up and coated materials from WP4