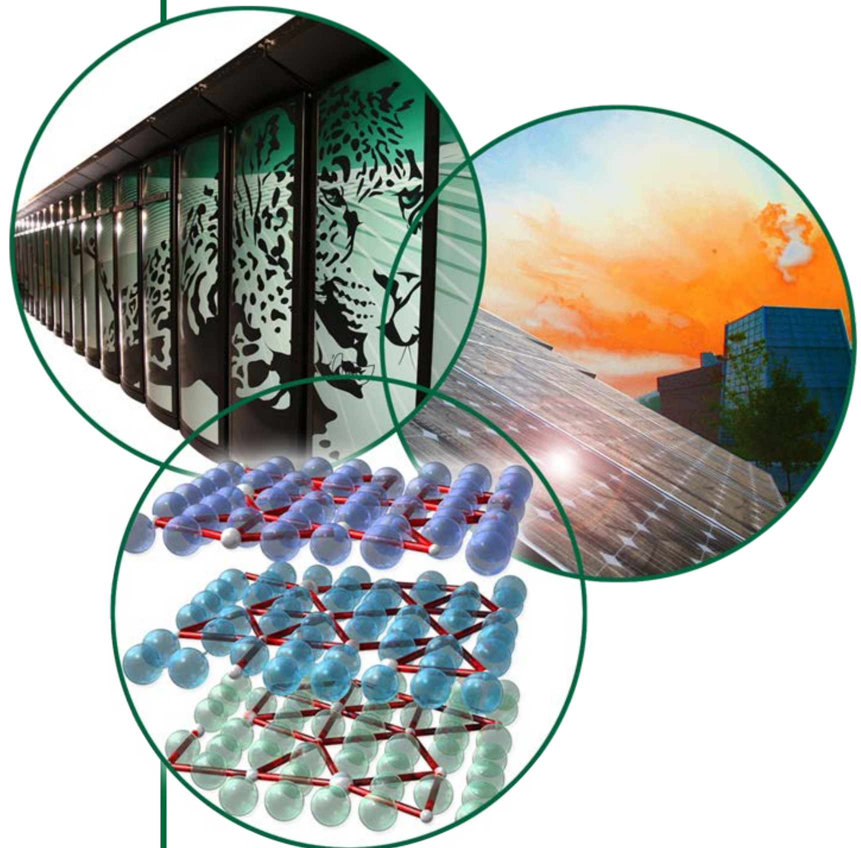
Roll-to-Roll Electrode Processing and Materials NDE for Advanced Lithium Secondary Batteries



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ES165

U.S. DEPARTMENT OF ENERGY

Overview

Timeline

- Start: October 1, 2011
- End: September 30, 2014
- Percent complete: 15%

Budget

- Total project funding
  - DOE: $900k
- FY11 Funding: NA
- FY12 Funding: $300k

Barriers

- **Electrode and material NDE**
  - **By 2014, reduce PHEV battery costs to $300/kWh.**
  - **Materials processing cost and electrode quality control (QC) enhancement.**
  - **Achieve deep discharge cycling target of 3000-5000 cycles for PHEVs (2015) and 750 cycles for EVs (2020).**

Partners

- Collaborations:
  - Keyence
  - Solar Metrology
- Project lead: Oak Ridge National Laboratory

Project Objectives

- <u>Main Objective</u>: To raise the production yield of lithium secondary battery electrodes from 80-90% to 99% and correlate in-situ materials diagnostics (XRD) with ex-situ structural characterization.
  - Reduce associated system cost by implementing in-line NDE and QC.
  - In-line laser sensing for thickness monitoring and in-line XRF for composition and thickness uniformity.
  - IR imaging for electrode coating defects (agglomerates, pinholes, blisters, etc.).
  - Correlation of in-situ XRD with TEM and SQUID for microstructural analysis.
- Relevance to Barriers and Targets
  - Implementation of critical QC methods to reduce scrap rate by an order of magnitude (to meet $300/kWh VTP storage goal for PHEVs).
  - Correlation of cathode microstructural parameters to performance to meet calendar life and long-term performance needs.
  - Integrate material diagnostics findings with electrode NDE development pathway to advance lithium secondary battery manufacturing science.

Project Milestones

Due Date	Milestone
3/2012	Go/no-go: demonstrate ability to meaningfully correlate in-situ XRD with ex-situ SQUID data.
6/2012	A method of correlating wet and dry thickness using in-line laser thickness measurement (wet) and ex-situ XRF (dry).
6/2012	Obtain in-situ XRD results through 200 cycles with Toda HE5050 and NCM 523.
9/2012	An in-line XRF prototype demonstration by Solar Metrology that measures electrode component uniformity, metal contaminant position, and dry electrode thickness.
9/2012	Identification of a Keyence laser thickness sensor(s) designed for lithium secondary battery electrode dispersion deposition.
9/2012	Go/no-go: determine feasibility of in-line XRF method of QC with respect to line speed.

Project Approach

- Problems to be addressed:
  - Excessive scrap rates of electrode coatings and lack of ability to detect defects prior to formation cycling.
  - Thickness measurement: foil vibration and different constituent optical properties.
  - Need to correlate materials diagnostics with in-line QC methods.
- Overall technical approach and strategy:
  - Demonstrate efficacy of in-line QC techniques utilized in other industries (plastics, textiles, ceramics, photovoltaics, etc.) on ORNL pilot coating equipment.
  - In-line laser thickness monitoring (with Keyence equipment) and in-house IR imaging technology will be demonstrated on ORNL slot-die coating line.
  - In-line XRF will be demonstrated using a Solar Metrology bench-top unit and the ORNL tape casting line.
  - Establish materials diagnostics such as in-situ XRD, TEM, and SQUID to quantify effect of microstructural changes on capacity fade.
- Link electrode NDE and materials diagnostics
  - Are electrode QC issues related to capacity fade mechanisms?
  - Correlate in-line XRF and agglomerate detection with in-situ XRD to determine if microstructural changes correlate to electrode architecture.
- New project for FY12: all milestones are on schedule.

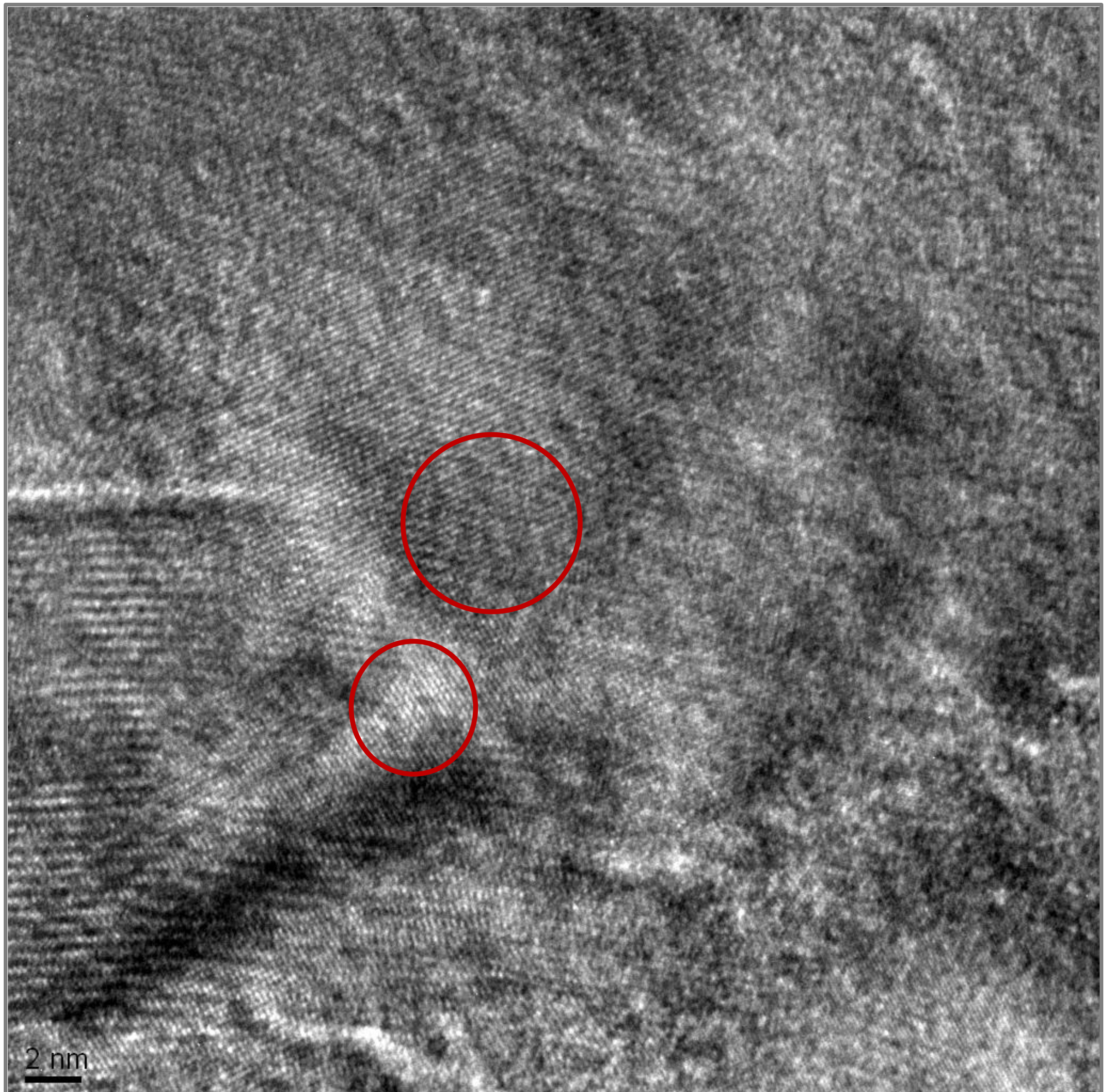
Technical Accomplishments – Executive Summary

- Both TEM and superconducting quantum interference device (SQUID) magnetometry data have been correlated with in-situ XRD results for Toda HE5050.
- SQUID results confirmed long-range superlattice ordering observed with XRD, and an overall composition of $Li_{1.2}Ni^{+2(HS/LS)}{}_{0.15}Mn^{+4(HS/LS)}{}_{0.55}Co^{+3(LS)}{}_{0.1}O_2$.
- In-situ XRD allowed for quantification of both HE5050 hexagonal and monoclinic phases with respect to state of charge, and allowed for prediction of a self diffusion mechanism during prolonged voltage hold.
- Preliminary off-line IR imaging has demonstrated that electrode coatings that have good visual quality may still suffer from thickness inhomogeneities and deposition defects.
- Off-line XRF results have been obtained for slot-die coated electrodes showing excellent transition metal composition and areal loading uniformity.
- In-line laser thickness results show benefits of tracking electrode coating thickness; initial uniformity results of ± 13% have been obtained.

Material Diagnostics on Toda HE5050

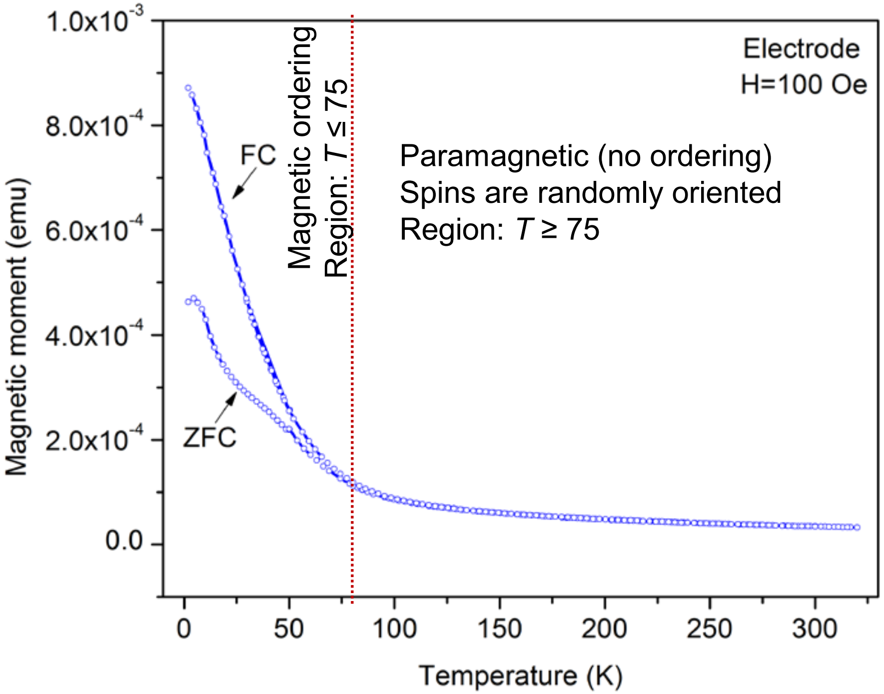
- 50%/50% lithium-rich monoclinic phase and layered NMC hexagonal phase.
- Active Material Composition = $0.5Li_2MnO_3$ – $0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$
- Electrode Composition = 86%wt Toda HE5050 – 8%wt PVDF binder – 4%wt Timcal SFG-6 Graphite – 2%wt Timcal Super P
- Half Cell Configuration:
  - Lithium counter electrode
  - 1.2M $LiPF_6$ in EC/DMC (3:7 volume ratio)
  - Celgard 2500 separator
- HRTEM, SQUID, In-Situ XRD

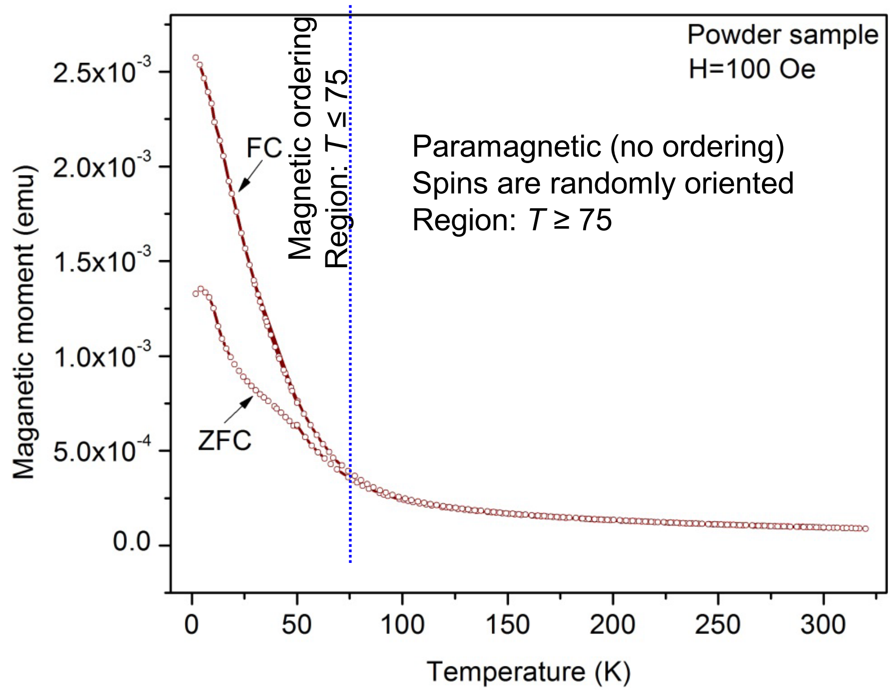
HRTEM of HE5050 Starting Material



- Lattice fringes oriented in different direction within a single particle.
- Likely due to precipitates or cluster having monoclinic phase.

Magnetic Data of HE5050 Starting Material





The data were collected using field cooling (FC) and zero field cooling (ZFC) methods.

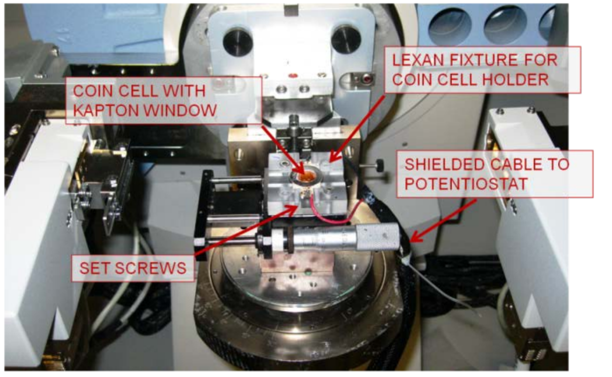
Similar trend in magnetic signal is observed for both the powder and electrode (the magnitude of signal from the electrode is less than the powder because, electrode has less active mass as compared to the powder).

The divergence of FC and ZFC curve at lower temperature ($T \leq 75$) indicates the short-range / long-range magnetic (structural) ordering.

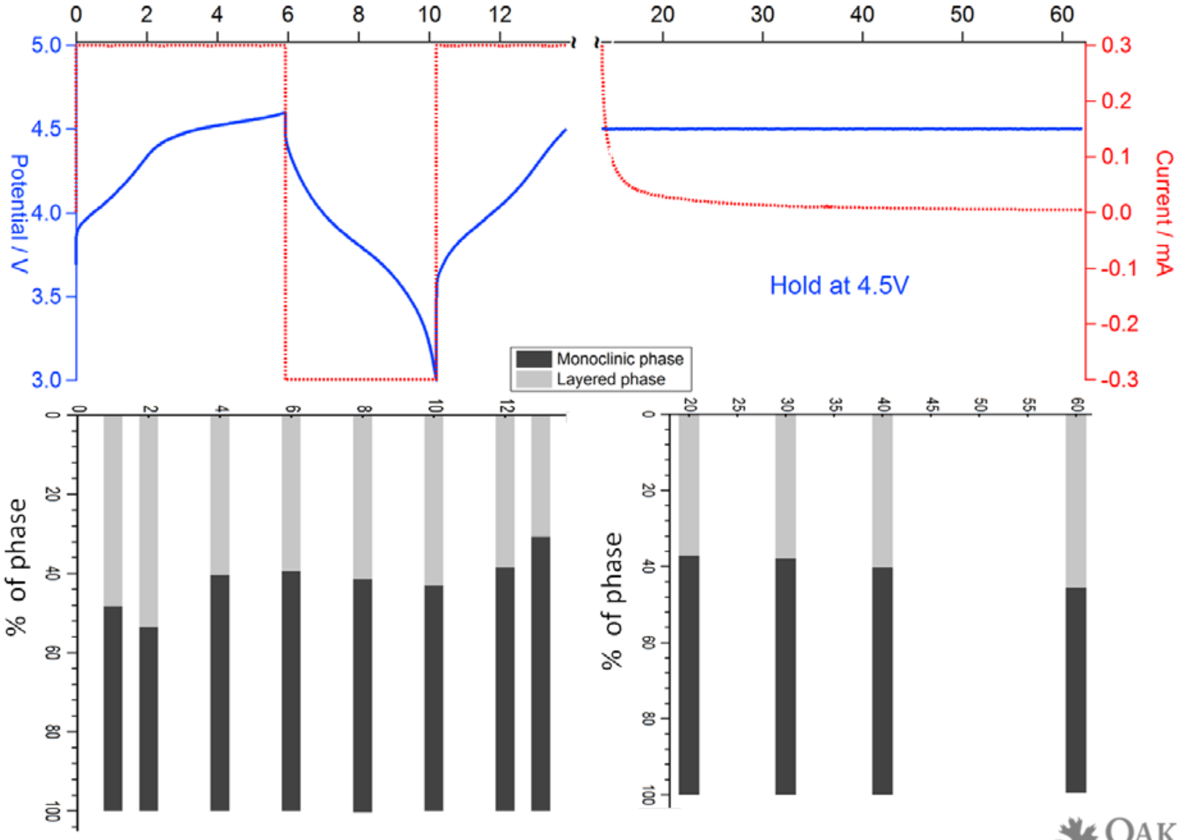
At higher temperature ($T \geq 75$) this is paramagnetic.

Percentage of Monoclinic and Layered Hexagonal Phases

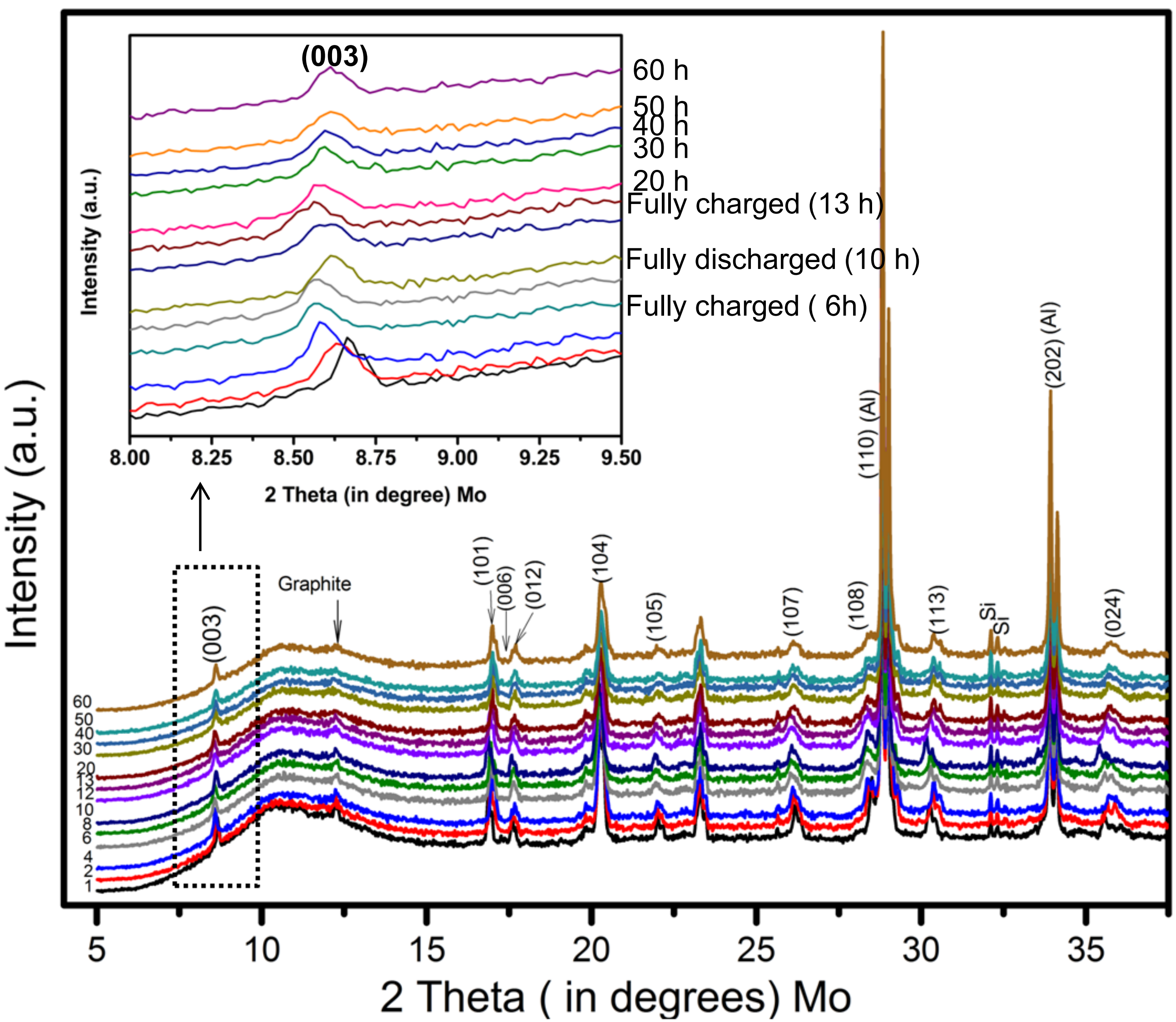
- In-situ XRD experimental setup:



- At the end of the hold, composition returns to nearly original 50:50 state
- Change in composition during hold likely results from the diffusion of ions within the cathode material from the monoclinic to hexagonal layered phase.

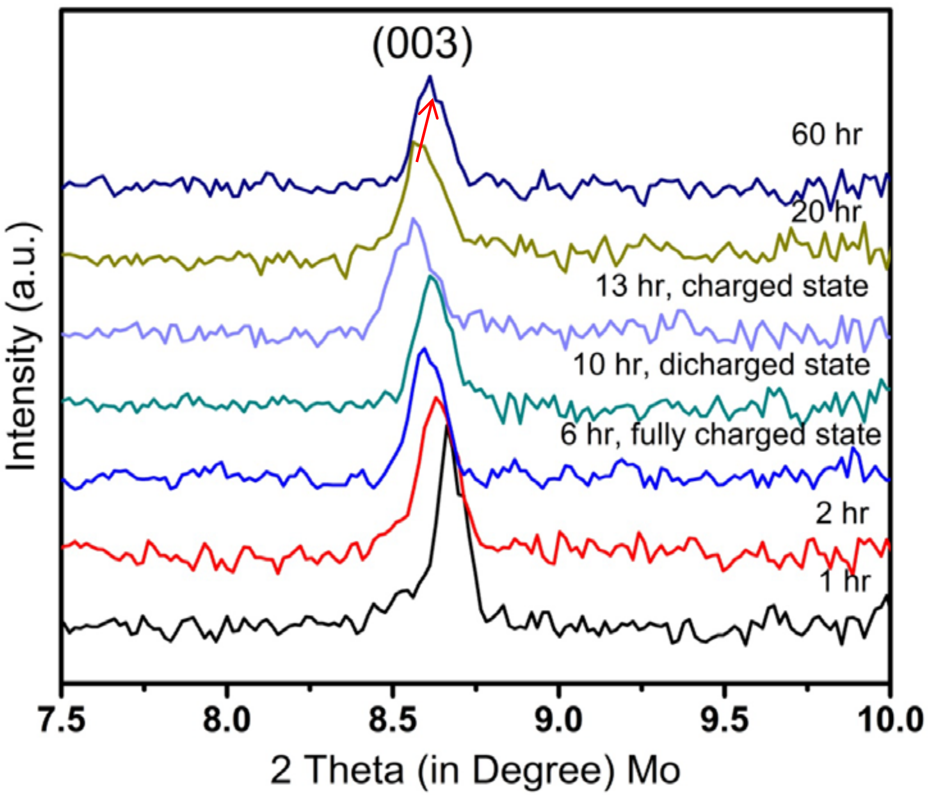


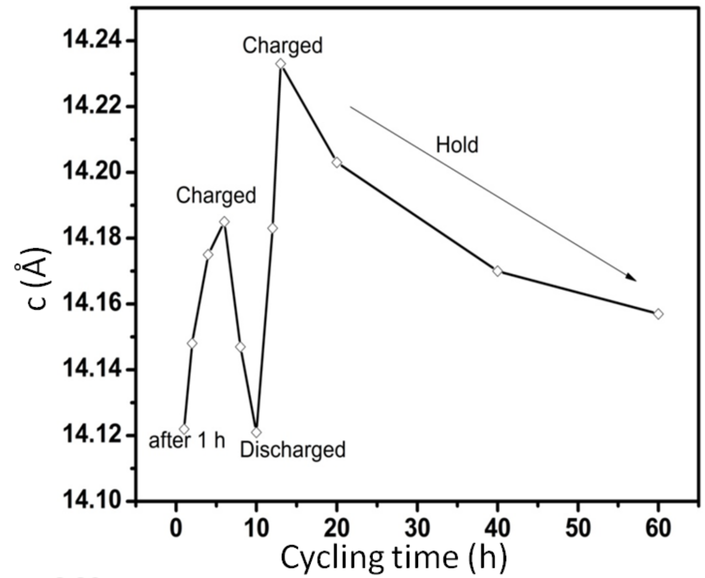
In-Situ XRD Pattern of HE5050 Cathode

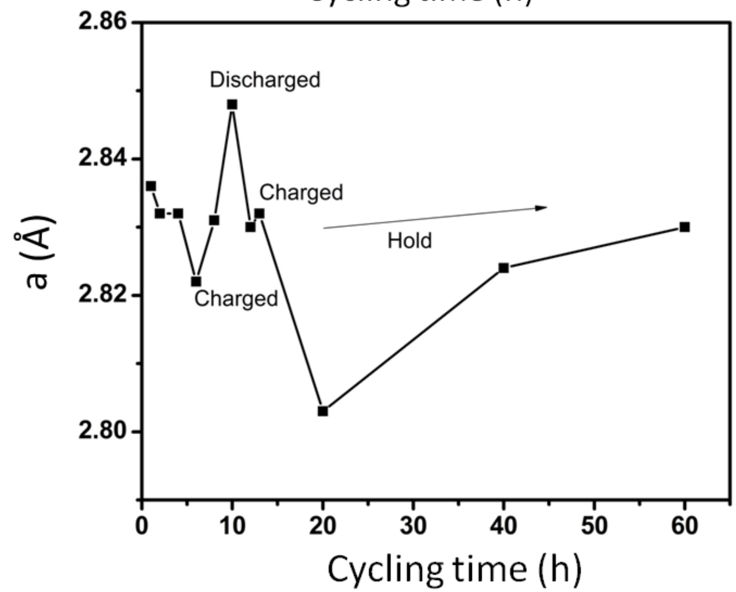


- (003) peaks are highlighted showing the change in position during charging, discharging, and voltage holding.
- (003) peak shifts towards higher 2-theta angle during voltage holding period indicating the unit cell contraction (similar to discharge process).
- Indicates diffusion of Li ions within cathode material.

(003) Peak Positions at Different Time Intervals



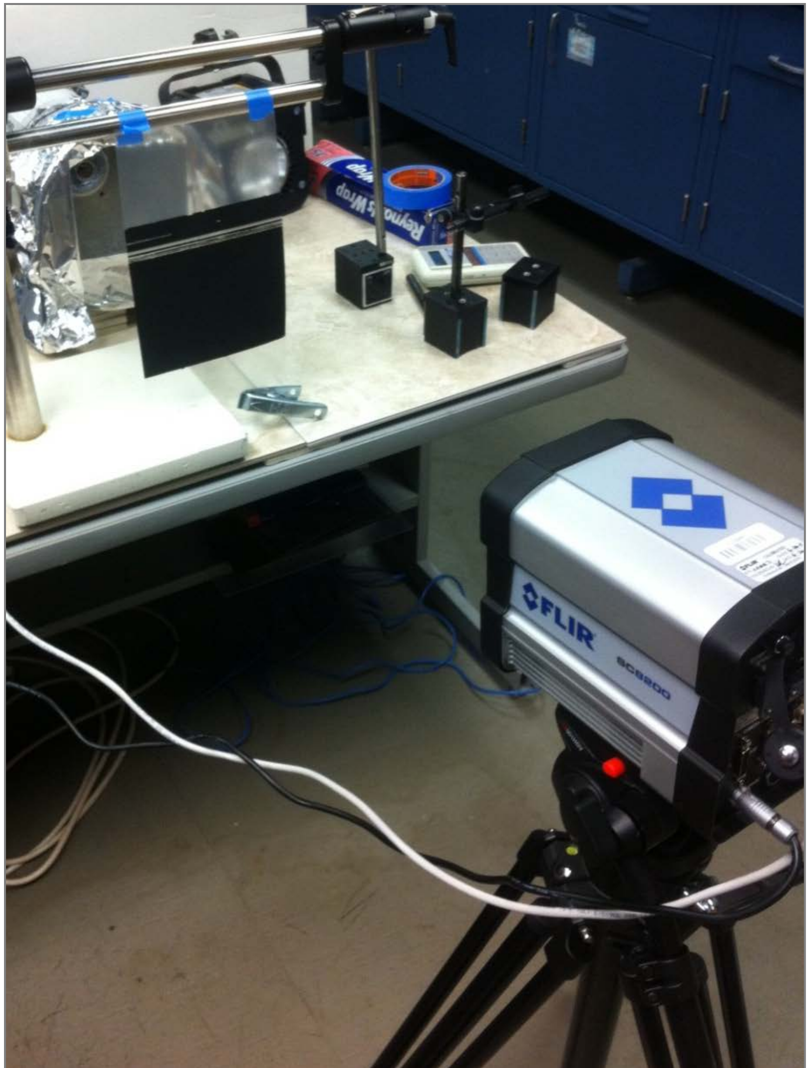




*The arrow shows that shifting of (003) peak to the higher 2 theta angle confirming the shrinkage of unit cell while the voltage remained constant for 40 hours.

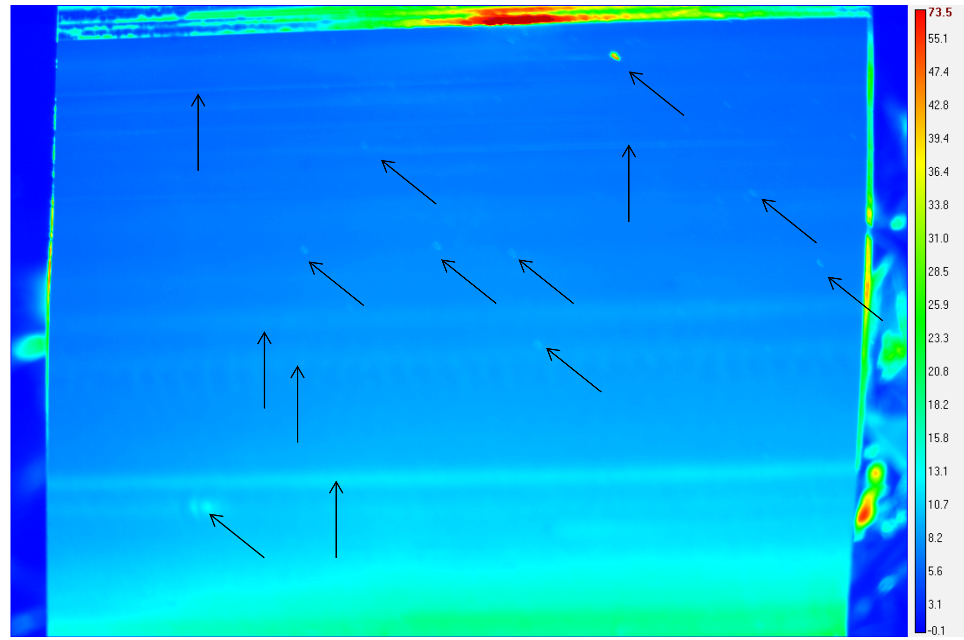
* The data were plotted after background correction.

IR Imaging Results of Tape Cast LIB Cathode: Experimental Setup



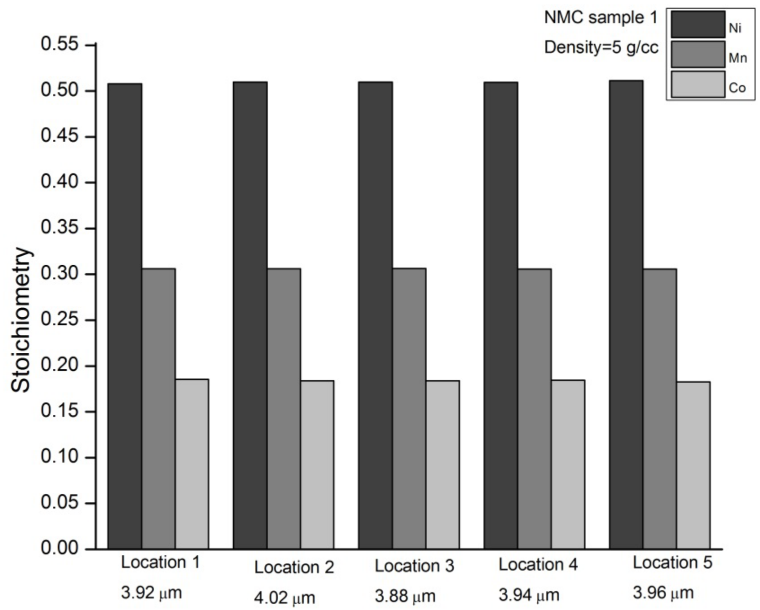
- IR Camera: FLIR SC-8200
- Lens: 25 mm, no filters or extender rings
- Flash System: Hensel 6000 Joules
- Flash Power: 60%
- Lens to target distance = 19 inches
- Flashlamp reflector to target distance = 10.5 inches

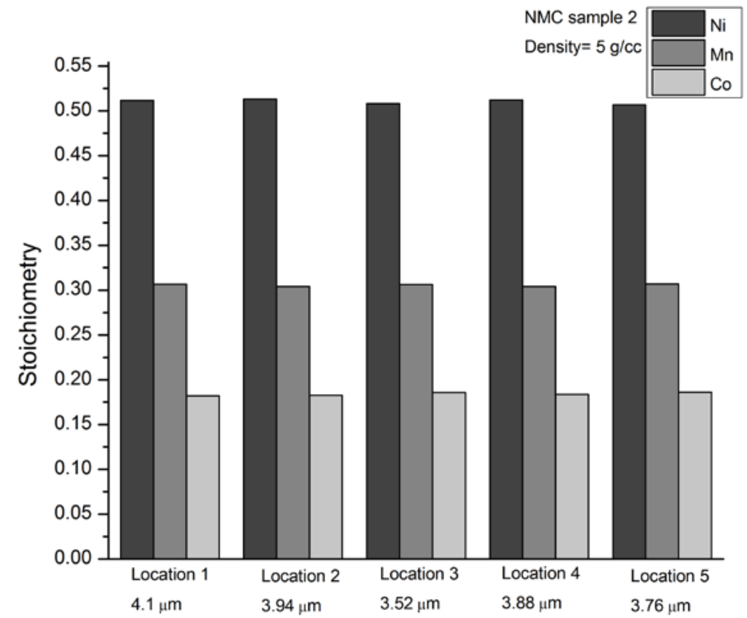
Visual Inspection Shows Little Detail, But IR Imaging Reveals Many Inhomogeneities

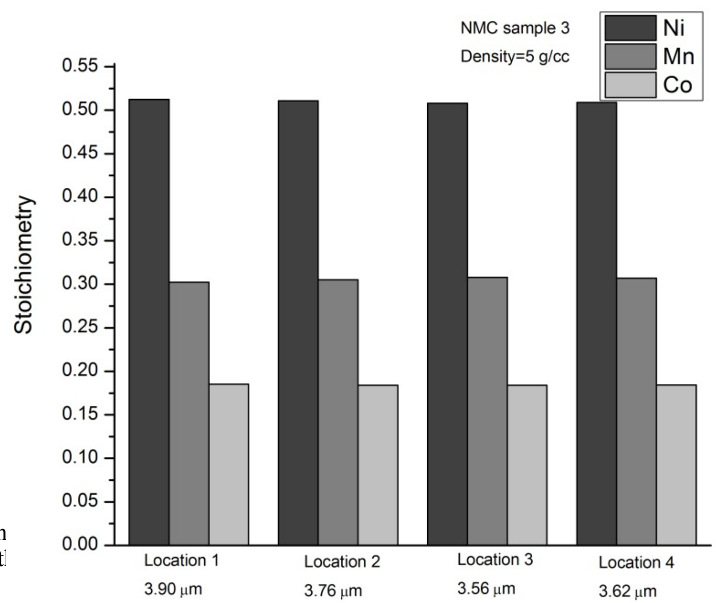


- **During the flash some very thin spots and several thin lines across the width of the specimen are seen (darker blue regions are thicker coating areas).**

XRF: Stoichiometry of Ni, Mn, and Co at Different Locations of Cathode



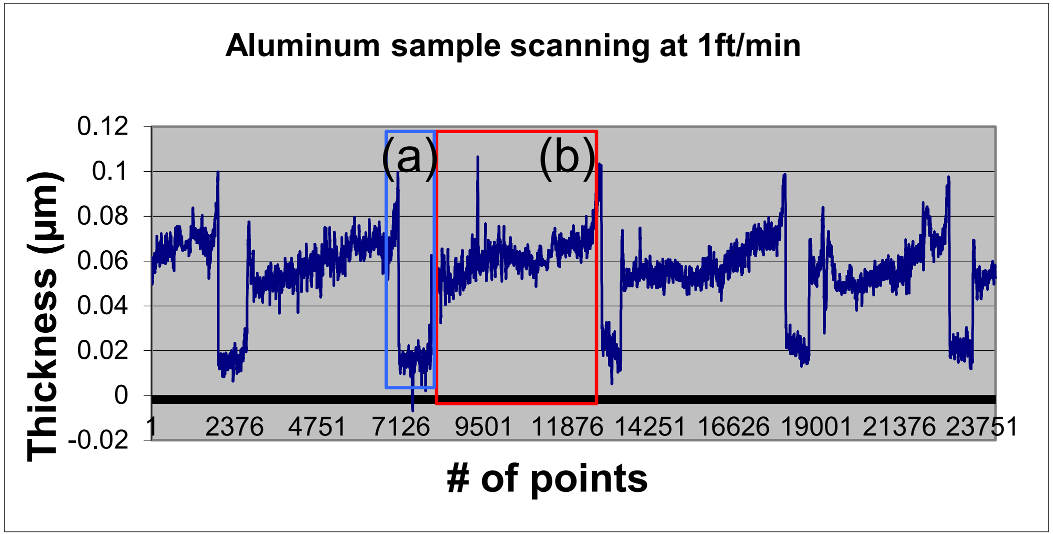


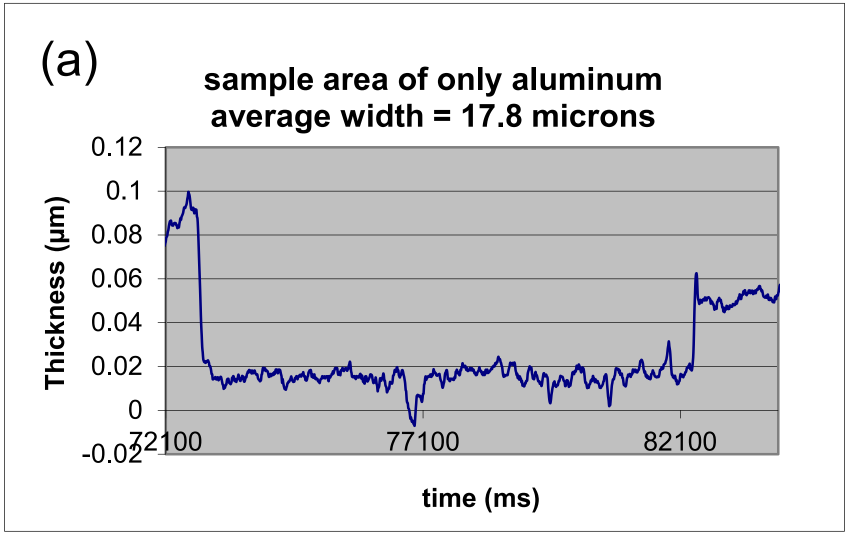


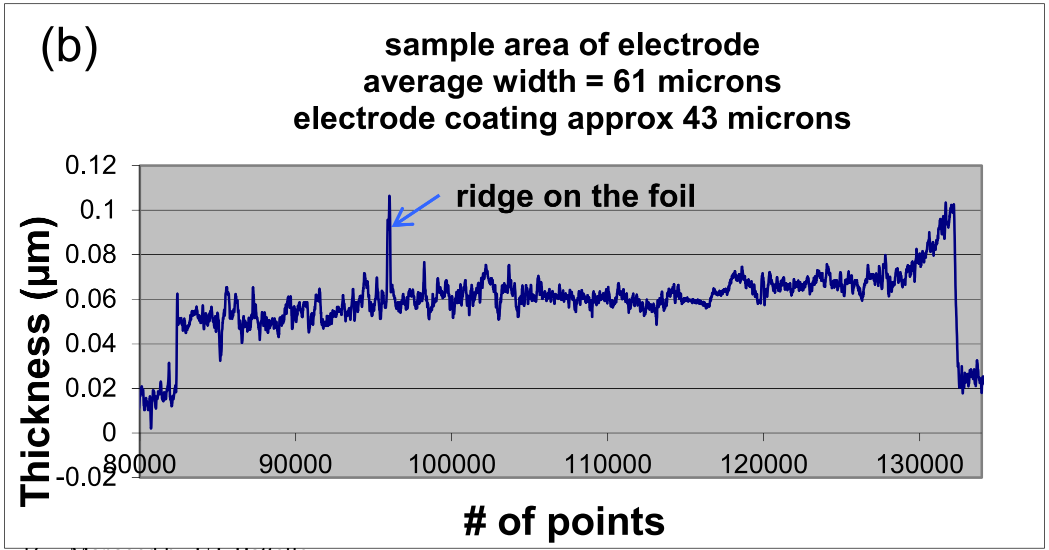
The stoichiometry was the same at all the locations. Ni:Mn:Co ratio was 0.5 : 0.3 : 0.2.

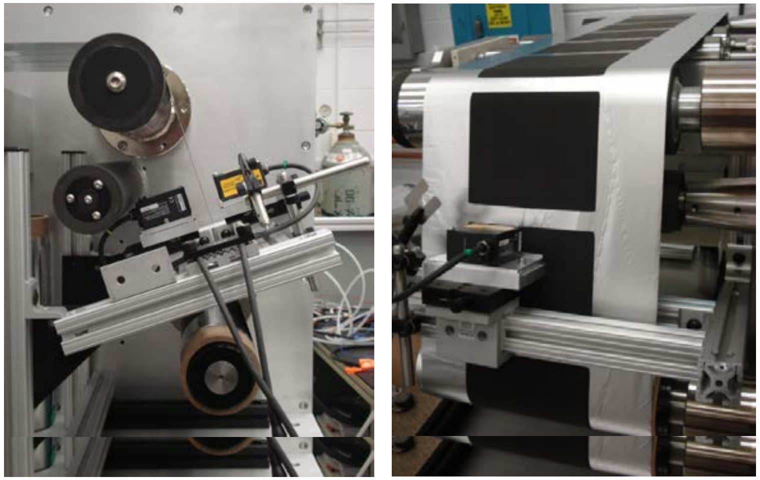
Areal loading (thickness) uniformity was Ñl.3%.

Thickness Measurement on Patch Coated Electrode (Continuous Scanning)



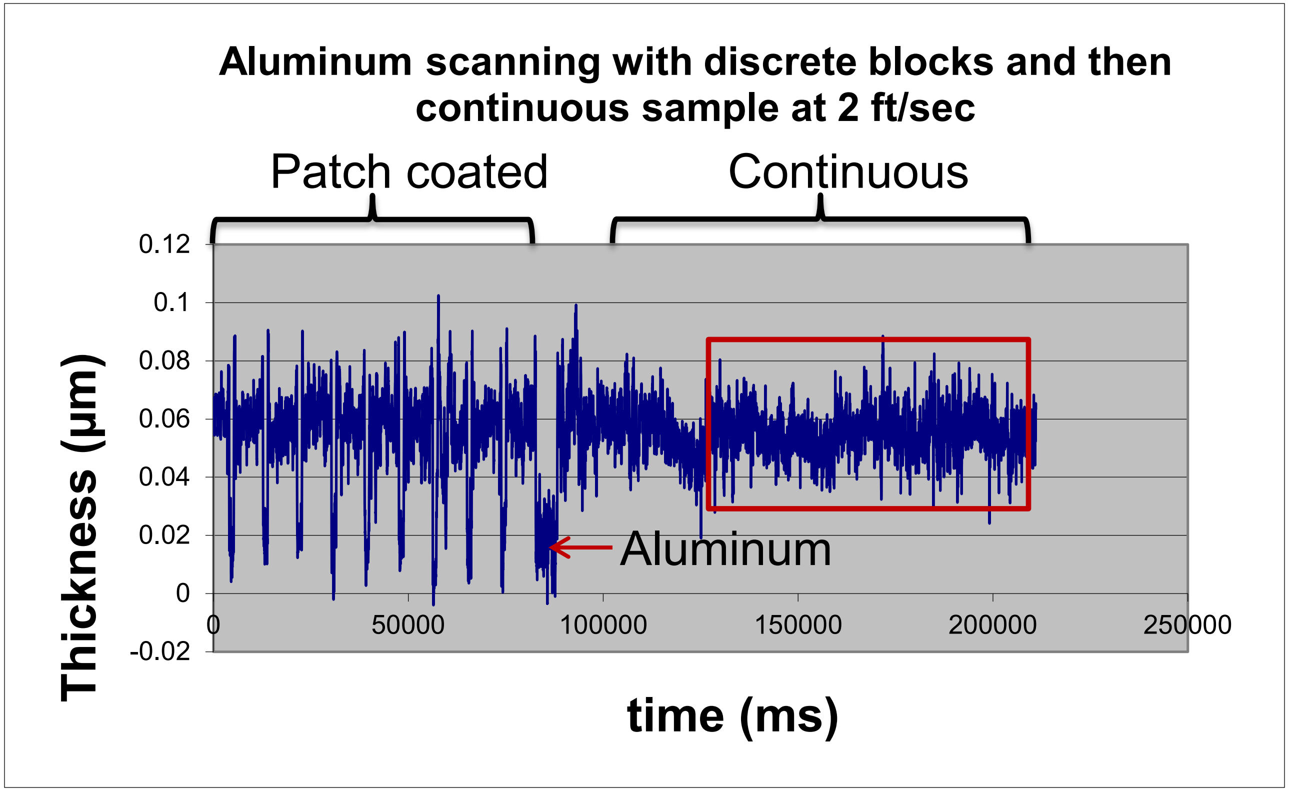






Images of alignment of two lasers for thickness measurement experiment

Measurement on Patch Coated and Continuous Electrode Areas



Average thickness of entire sample: 54.219 ± 13.638 µm
Average thickness of highlighted region : 55.378 ± 7.4 µm

Collaborations

- Partners
  - Keyence
  - Solar Metrology
- Collaboration is based on implementing partners' equipment into ORNL coating lines.
- Collaborative activities
  - Working with Keyence to determine the best laser sensor to use for lithium ion electrode thickness based on line speed, thickness range, etc.
  - Solar Metrology is involved with two main activities:
    - Validation of XRF technique for different cathode chemistries and compositions.
    - Engineering associated with transferring the off-line technique to an in-line one.

Future Work

- Remainder of FY12
  - Transfer in-line laser thickness sensor to slot-die coater (April 2012).
  - Obtain IR imaging data on slot-die coater (April 2012) and with mounted in-line IR camera (Sept. 2012).
  - Obtain in-line XRF thickness and composition data at Solar Metrology (June 2012) and on ORNL tape caster (Sept. 2012).
  - Obtain in-situ XRD results through 200 cycles with Toda HE5050 and NCM 523 (June 2012).
  - Correlate SQUID and TEM measurements with in-situ XRD data through 200 cycles to determine microstructural changes associated with capacity fade (Sept. 2012).
- Into FY13
  - Identify industrial partner to scale in-line QC methods.
  - Identify feedback control mechanisms for in-line measurements.

❖ Correlate electrode QC measurement with materials diagnostics.

Summary

- This project facilitates lowering unit energy cost of EVs and PHEVs by addressing the electrode scrap rate and the calendar life by addressing microstructure related capacity fade.
- Our approach implements QC measures utilized effectively in other industries.
  - Processing costs tied to QC are addressed.
  - Ease of implementation of measurement technology.
  - Long-term objective is to correlate in-line QC and materials diagnostics.
- All FY12 milestones are on schedule.
- High likelihood of technology transfer because of significant electrode production cost reduction benefits.
- Addition of industrial partner by the beginning of FY13 positions the project well for continuation and expansion.