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


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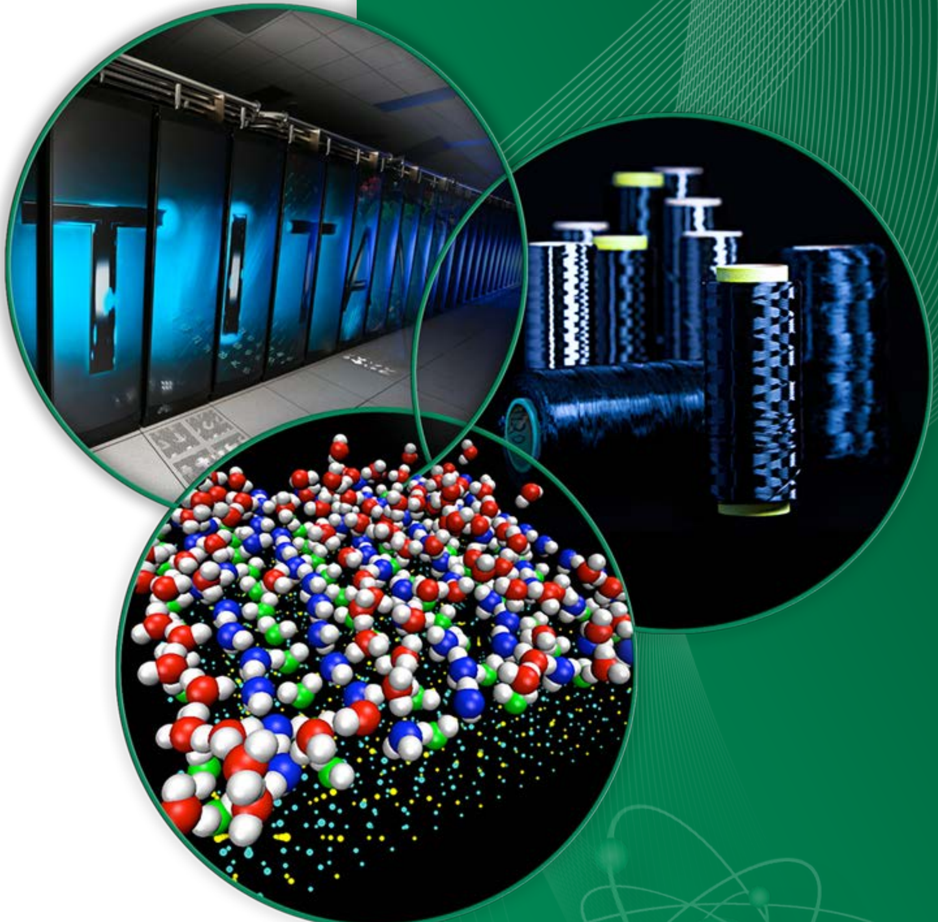
Oak Ridge National Laboratory


May 14, 2013



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Project ID ES165

# Overview

## Timeline

- Project Start: 10/1/11
- Project End: 9/30/14
- Percent Complete: 45%

## Barriers

- Barriers addressed
  - **By 2015, reduce PHEV-40 battery cost to $300/kWh**
  - **By 2020, further reduce EV battery cost to $125/kWh.**
    - **Materials processing cost reduction and electrode quality control (QC) enhancement.**
  - **Achieve 500 Wh/L energy density.**
  - **Achieve deep discharge cycling target of 3000-5000 cycles for PHEVs (2015) and 750 cycles for EVs (2020).**

## Budget

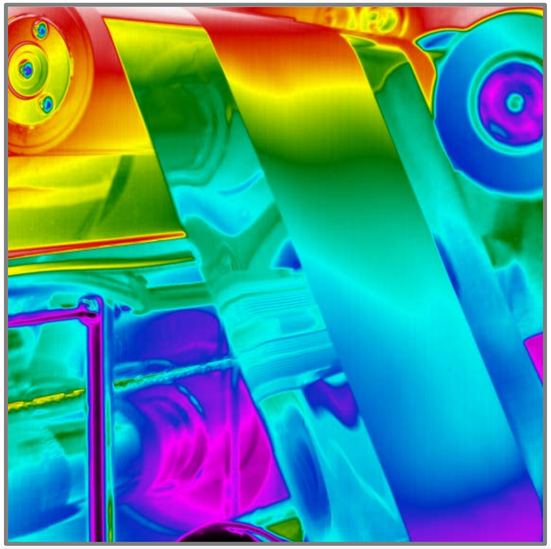
- Total project funding
  - $900k
- $300k in FY12
- $300k in FY13

## Partners

- Interactions/Collaborations
  - Equipment Suppliers: Ceres Technologies, Keyence, FLIR
  - Battery Manufacturers: Dow Kokam, A123 Systems
  - Materials Suppliers: TODA America
  - National Laboratories: ANL, NREL
- Project Lead: ORNL

# Project Objectives

- Main Objective: To raise the production yield of lithium secondary ***batteries*** to 99% by reducing electrode scrap and the amount of defective electrode assembled into cells.
  - Reduce lithium ion battery system cost by implementing in-line NDE and electrode QC.
  - In-line, cross-web laser sensing for electrode thickness monitoring.
  - IR thermography for electrode coating defects (agglomerates, pinholes, blisters, etc.).
  - In-line XRF for active material composition and areal-weight uniformity.
  - Secondary objective to enable high-energy cathodes: in-situ and ex-situ microstructural and magnetic analysis and explanation of advanced active-material capacity fading mechanisms.
- Relevance to Barriers and Targets
  - Implementation of critical QC methods to reduce scrap rate by ***creating electrode processing feedback loops*** (to meet $300/kWh 2015 VTP storage goal for PHEVs).
  - Correlation of cathode microstructural changes and electrode processing parameters to meet 500 Wh/L and long-term cell performance needs.



# Project Milestones

| Status | Milestone or Go/No-Go | Description |
|---|---|---|
| Complete ✓ | FY12 Go/No-Go | Correlate in-situ XRD with ex-situ magnetic susceptibility data. |
| Complete ✓ | FY12 Milestone | Correlate wet and dry thickness using in-line laser thickness measurement (wet) and ex-situ XRF (dry). |
| Complete ✓ | FY12 Milestone | In-situ XRD results through 100 cycles with TODA HE5050. |
| 3/2013 | FY12 Milestone | An in-line XRF prototype demonstration by Ceres Technologies. |
| Complete ✓ | FY12 Milestone | Identification of an appropriate Keyence laser thickness sensor(s). |
| 6/2013 | FY12 Go/No-Go | Determine feasibility of in-line XRF with respect to required electrode coating line speeds. |
| 6/2013 | FY13 Milestone | Determine feasibility of measurement of deliberately introduced metal contaminants into cathodes with in-line XRF. |
| 6/2013 | FY13 Milestone | Correlate wet and dry thickness using cross-web laser thickness measurement (wet) and in-line XRF (dry) to within ±10%. |
| 7/2013 | FY13 Milestone | Ceres Technologies to lock final design of in-line XRF system. |
| 9/2013 | FY13 Milestone | Transfer technology associated with these three techniques to industry partner. |

# Project Approach

- Problems to be addressed:
  - Excessive scrap rates of electrodes and lack of ability to detect coating defects prior to formation cycling.
  - Conventional electrode QC involves thickness/areal-weight measurement by beta gauge, which uses ionizing radiation (safety concern) and expensive equipment.
  - Need correlation of in-situ and ex-situ materials characterization with electrode production quality and long-term performance.
- 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 measurement and in-house IR imaging technology (for detection of coating defects) has been demonstrated on ORNL slot-die coating line.
  - In-line XRF is being demonstrated on the ORNL tape casting line for cathode areal weight and compositional uniformity.
  - Work is underway with NREL to develop in-line electrode porosity uniformity.
  - Establish the diagnostic tools in-situ XRD, TEM, electron diffraction, magnetic susceptibility, and neutron scattering to quantify effect of microstructural changes on capacity fade and relationship to electrode coating quality.
- Link electrode NDE and diagnostic tool information
  - Are electrode QC issues exacerbating capacity fade mechanisms?

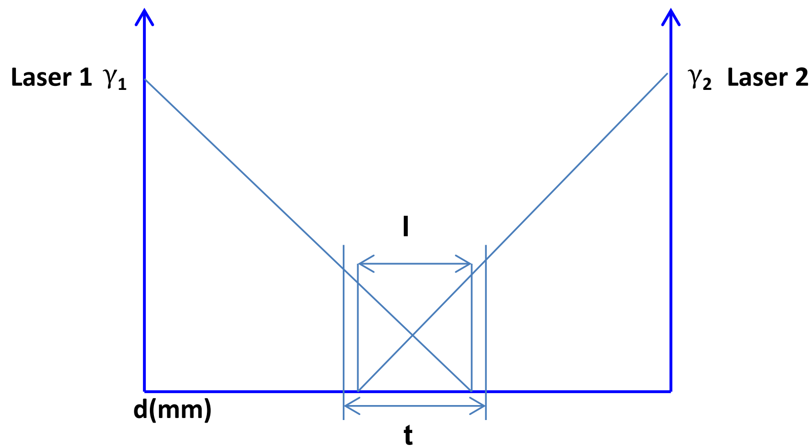
# Technical Accomplishments – Executive Summary

- FY12 Q1-2: Exploratory in-line measurement work and establishment of materials characterization methods (Presented at 2012 DOE AMR).
- **FY12 Q3-4: Slot-die coater integration of in-line laser thickness and IR thermography measurements and in-situ XRD correlation with magnetic susceptibility and TEM (Following Slides).**
- **FY13 Q1-2: Implementation of cross-web laser thickness measurement, installation of IR camera on slot-die coater, and identification of capacity fade mechanisms for TODA HE5050 (Following Slides).**
- FY13 Q3-4: Receipt of in-line XRF equipment and completion of initial experiments on tape caster; correlation of thickness measurements between laser, IR, and XRF techniques; and full suite of materials characterization on TODA HE5050 after 1000 half-cell cycles (2014 DOE AMR).
- Specific Accomplishments
  - **Precision of in-line laser thickness measurement improved to << ±2%** (calibrated with bare Al foil with ±3.7% thickness deviation).
  - Thickness deviation of cathodes typically ±2.3-2.0%, and for anodes typically ±2.2-2.6%.
  - IR imaging has been completed on (TODA HE5050 and NCM 523) cathodes and (CP A12 graphite) anodes and both heat-trapping and heat-releasing defects have been found.
  - Design of Ceres Technologies in-line XRF instrument is complete.
  - Both TEM and magnetic susceptibility data were correlated with in-situ XRD results for TODA HE5050 cathode (spinel phase formation and structural oxygen release identified).

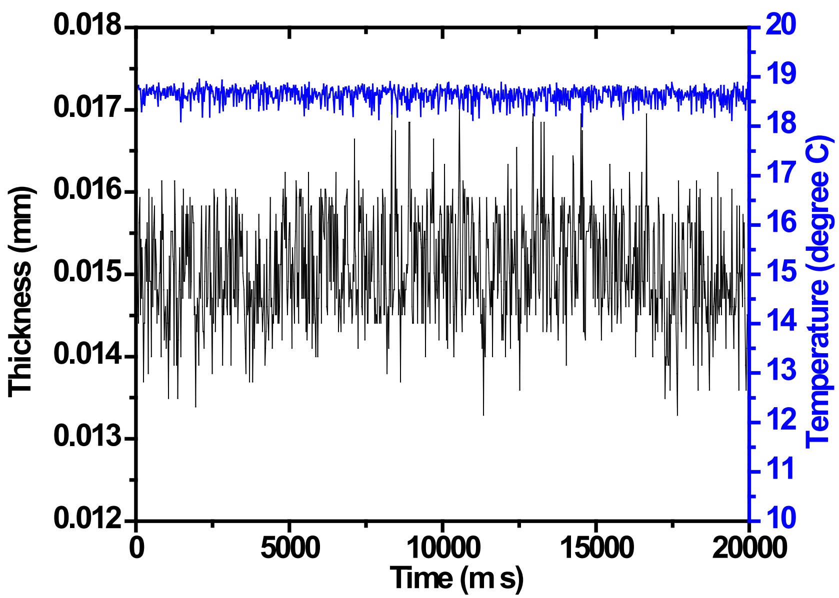
# Overview of Lithium Ion Electrode QC State-of-the-Art

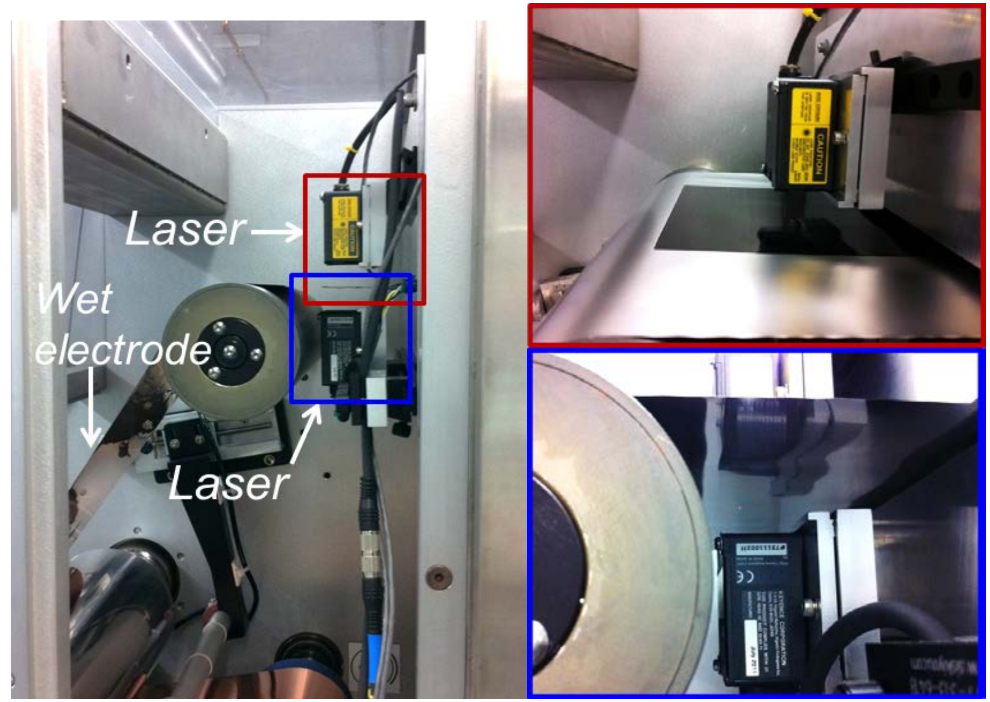
- Conventional in-line thickness and/or areal weight by beta transmission gauge:
  - Thickness measurement precision of ±0.2% over 2-1000 µm
  - But expensive equipment (several hundred thousand dollars or more)
  - And ionizing radiation hazard (typically 300-1000 mCi sources)
- Optical inspection with HR-CCD cameras (only uses visible light for detection).
- Optical and beta transmission techniques provide no compositional information.
- Raman microscopy – Panitz and Novák, *J. Power Sources*, **97-98**, 174 (2001).
- Without feedback loops to electrode dispersion mixing and deposition steps, laser and XRF NDE methods will not reduce scrap rate (i.e., “electrode QC”).
- However, QC will still be improved by simply removing scrap (i.e. IR NDE) to avoid assembling defective electrode area into cells (i.e. “cell QC improvement”).
- Pass/fail criteria must be established industry wide for NDE methods to be meaningful and provide “cell QC”; ***proposed criteria***:
  - Thickness (laser or XRF) → ±1% measurement precision and ±2% thickness deviation.
  - Areal weight (XRF) → ±2% measurement precision and ±3-4% areal-weight deviation.
  - Coating defects (IR) → mark small sections for removal from electrode rolls.

# High-Precision Thickness Measurement




$$\text{Thickness (t)} = \frac{\gamma_1+\gamma_2}{m} - l$$

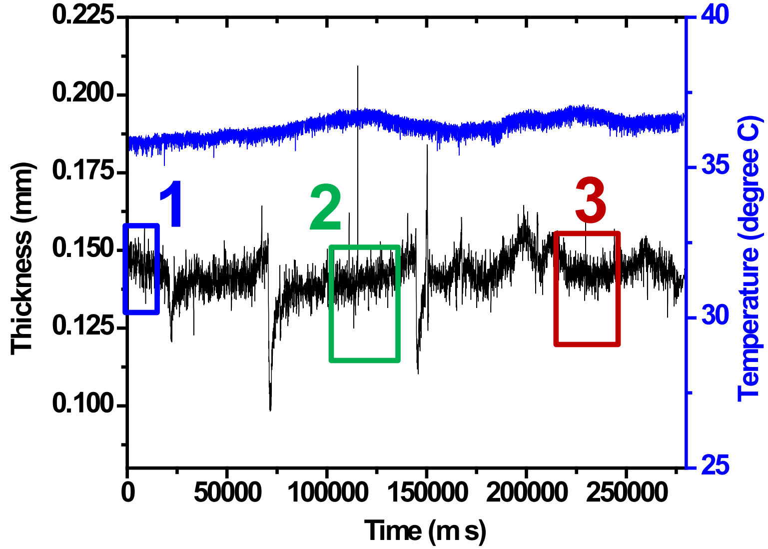


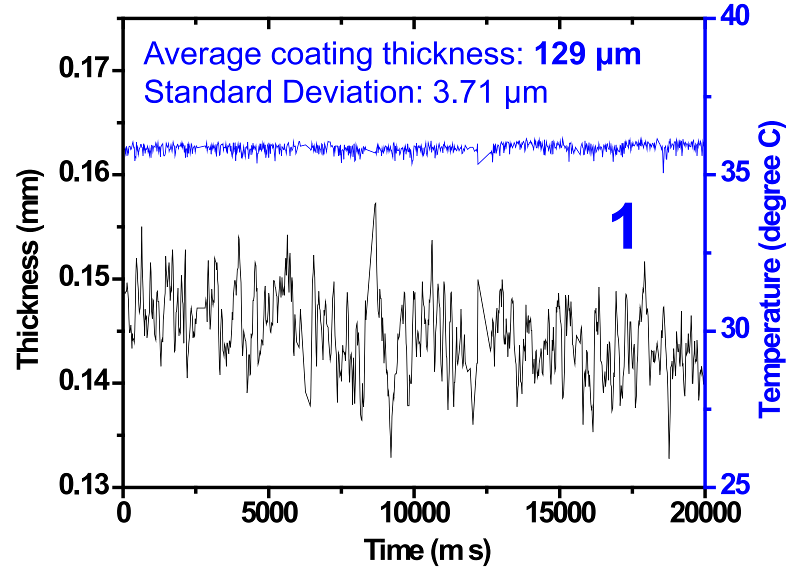



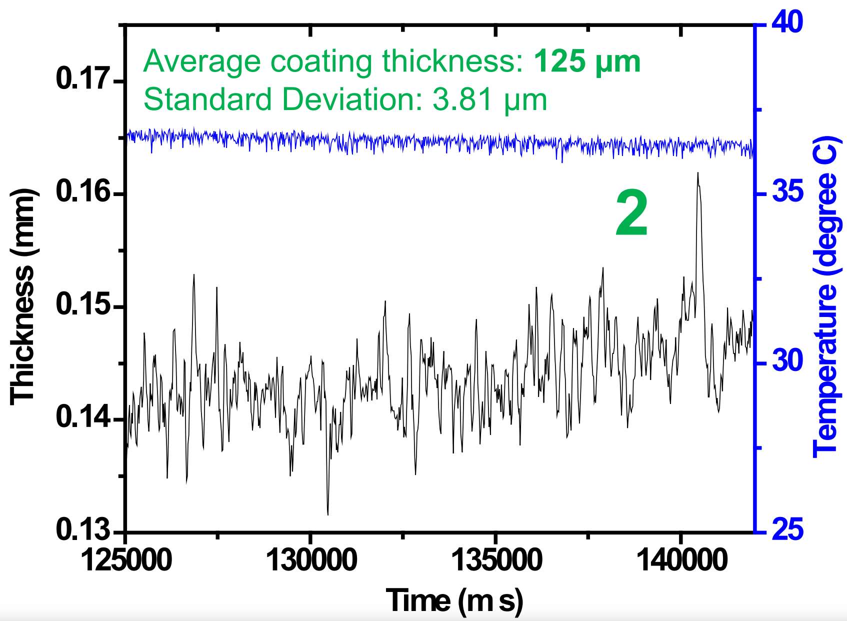

- Laser calibration with bare Al foil
  - Average Thickness: 15.07 μm
  - Standard Deviation: 0.56 μm
  - Nominal Al foil thickness = 15 μm
  - Room Temperature = 18.5°C

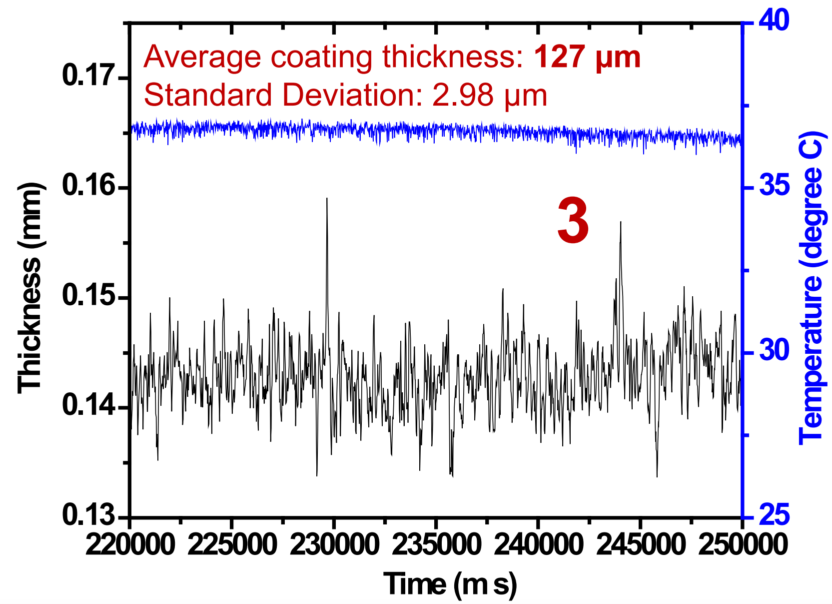
# TODA NCM 523 Cathode Thickness Measurement

ABR Baseline Cathode (Entire Run)

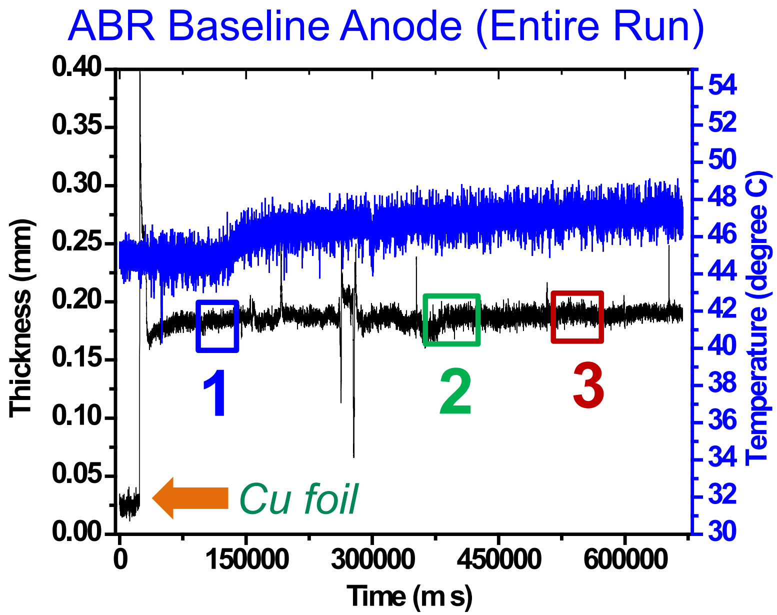


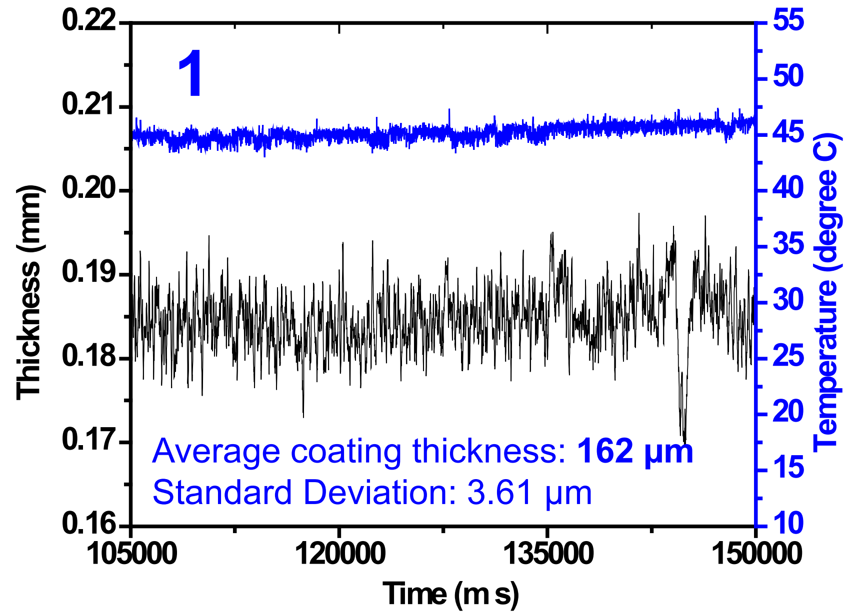



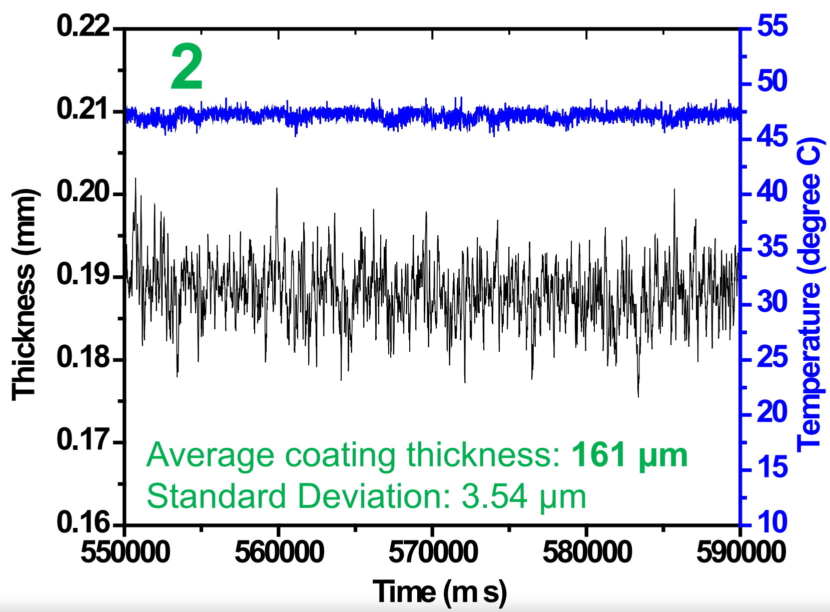



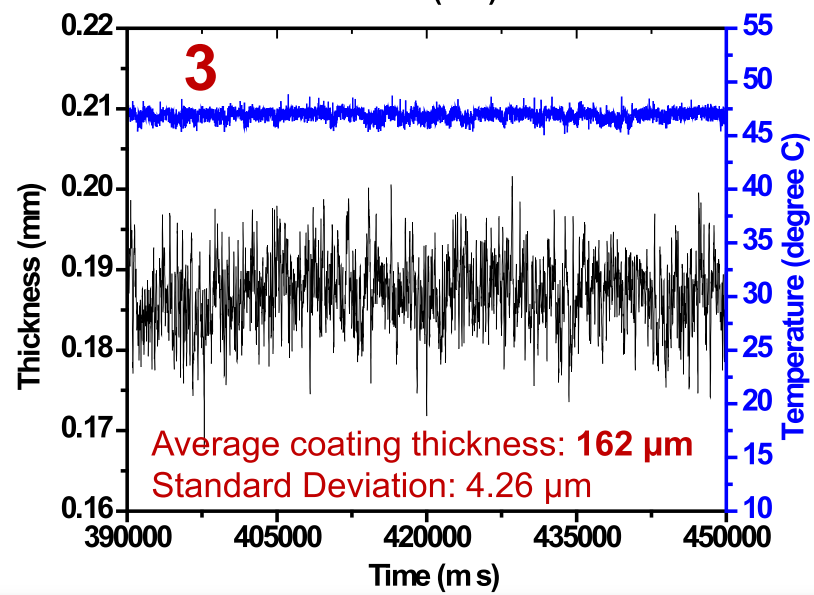



# CP A12 Graphite Anode Thickness Measurement

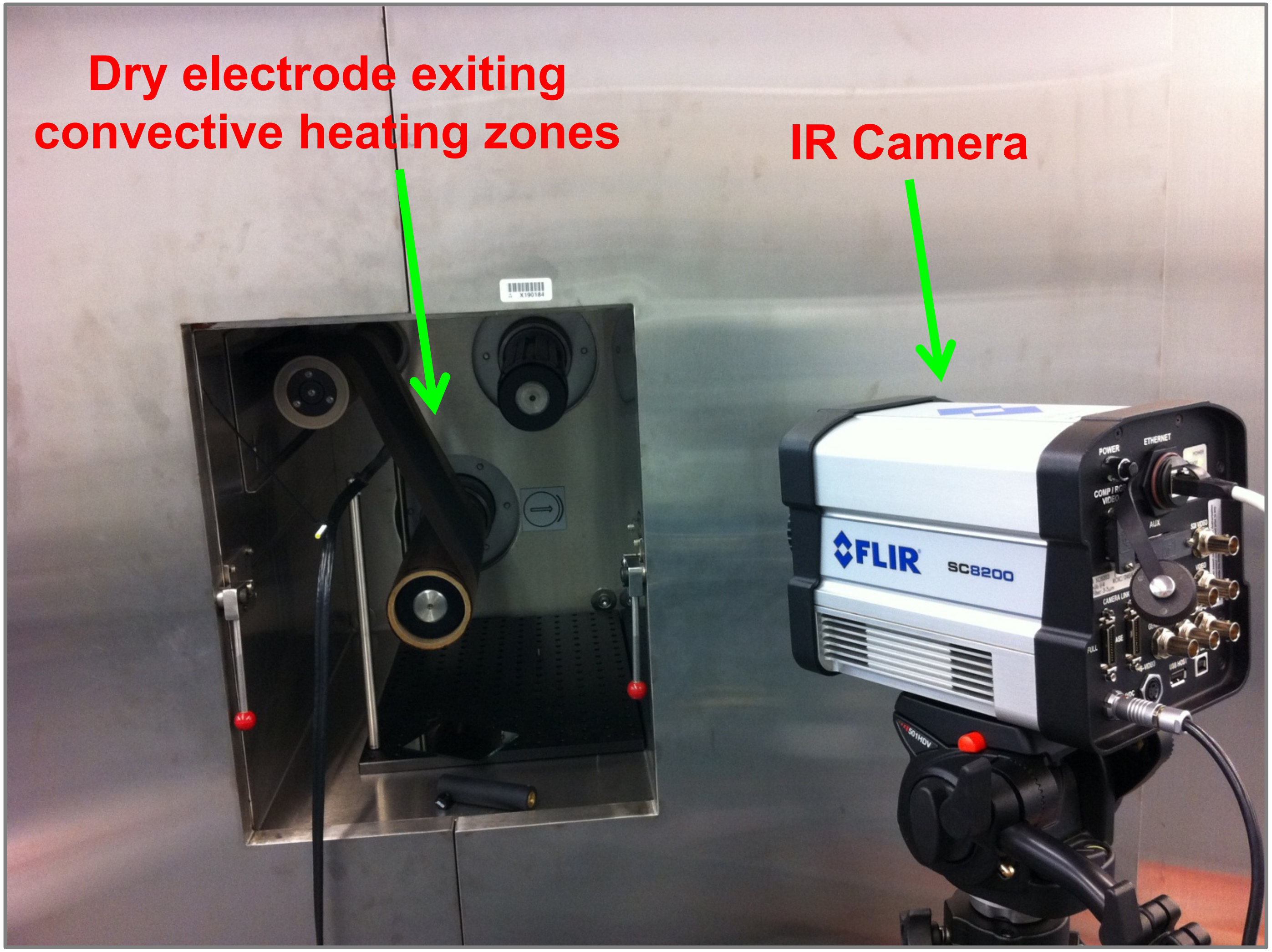


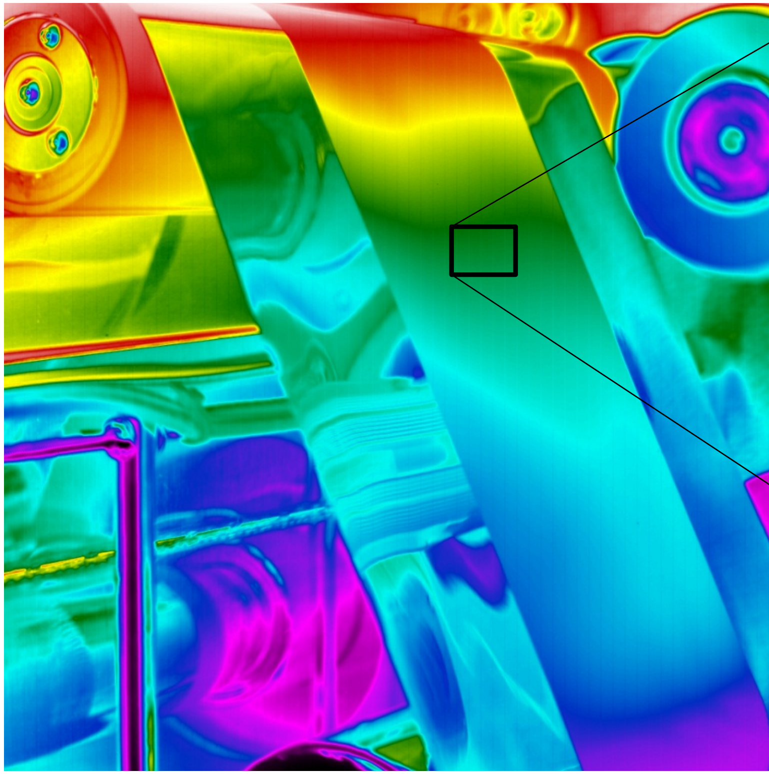



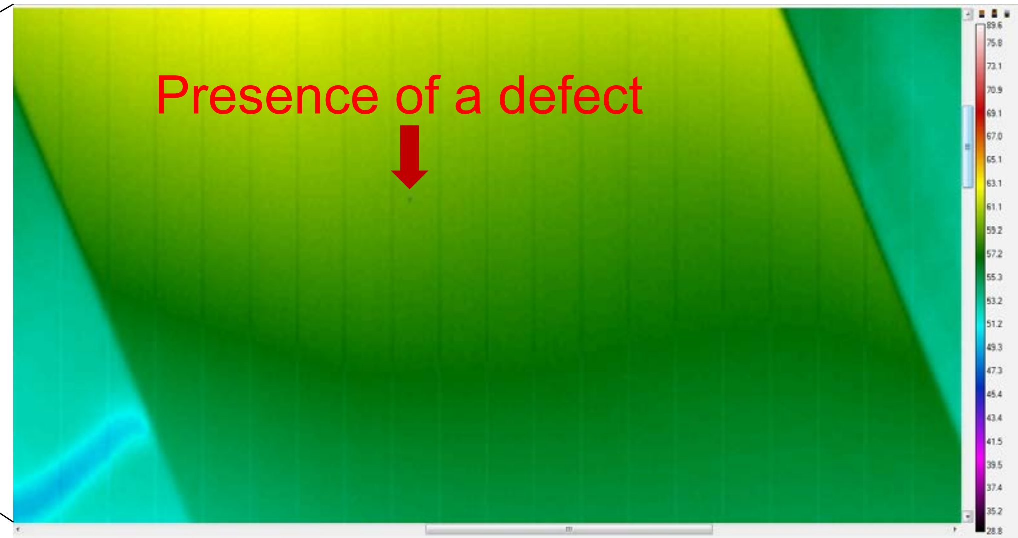
# IR Thermography Setup with ORNL Slot-Die Coater

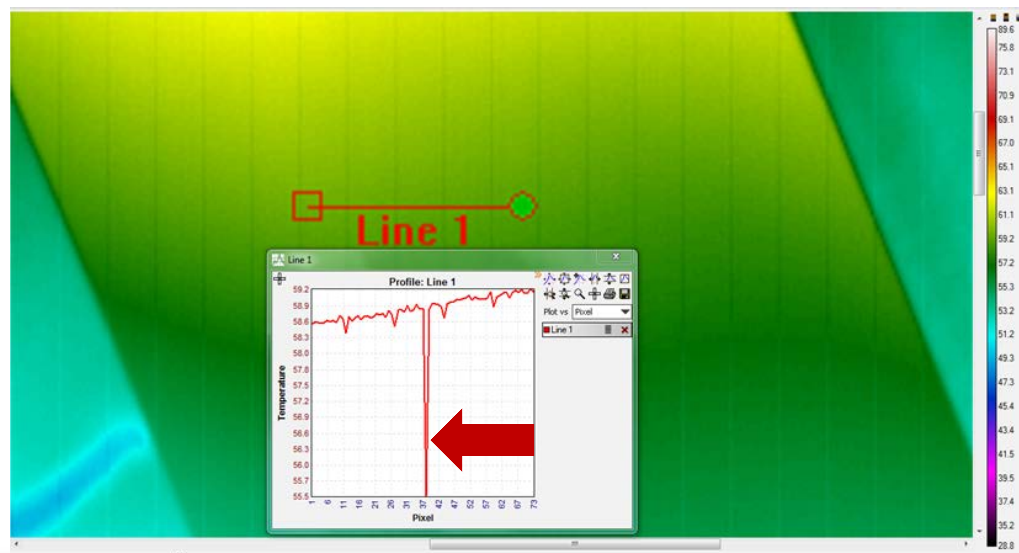



- Current IR Camera: FLIR SC-8200
- Lens: 25 mm, no filters or extender rings
- Flash System: Hensel 6000 Joules
- Flash Power: 60%
- Next generation IR camera will be mounted at the oven exit (rewind)

# IR Imaging Evaluation on ConocoPhillips A10/A12 Graphite Coating






Temperature line scan across defect region shows decrease – divot, pinhole, etc.



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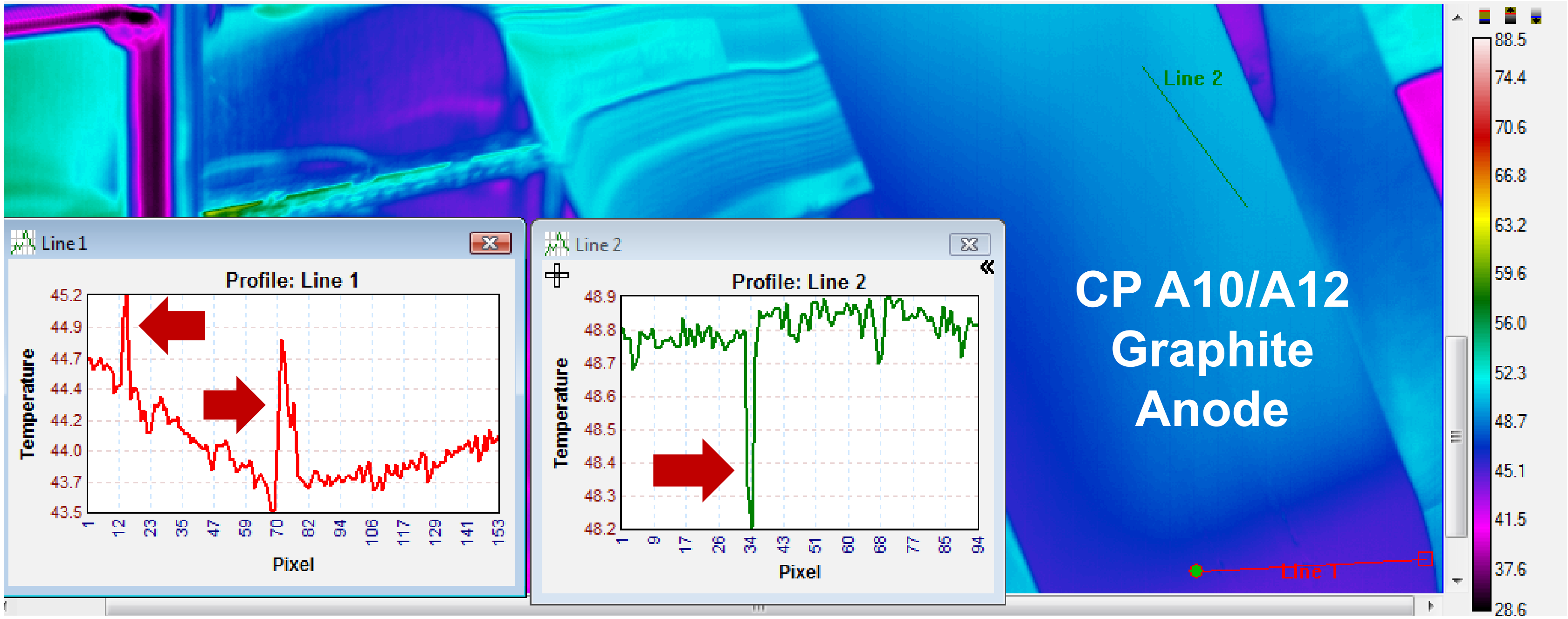
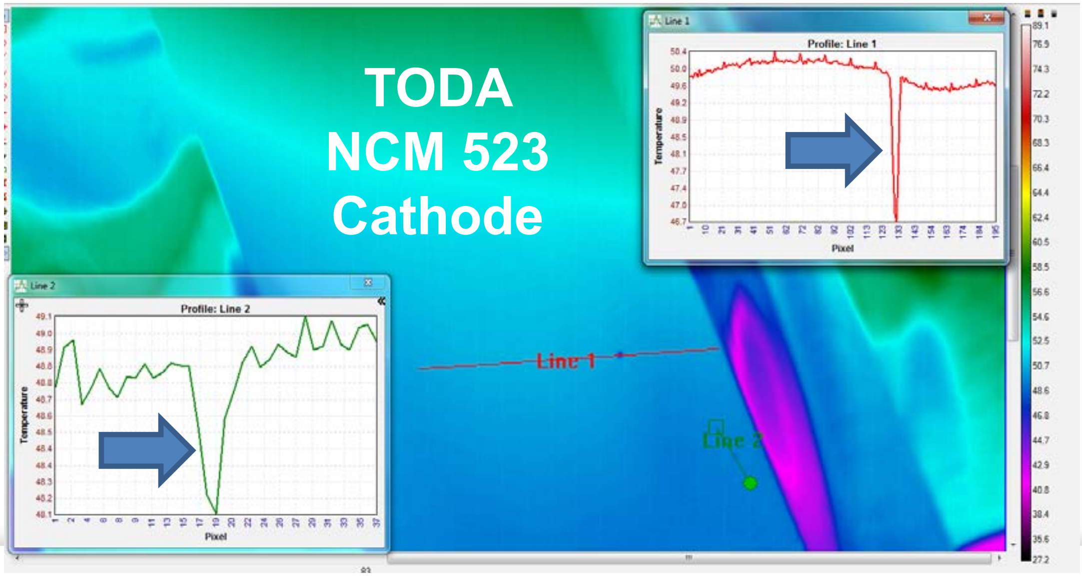
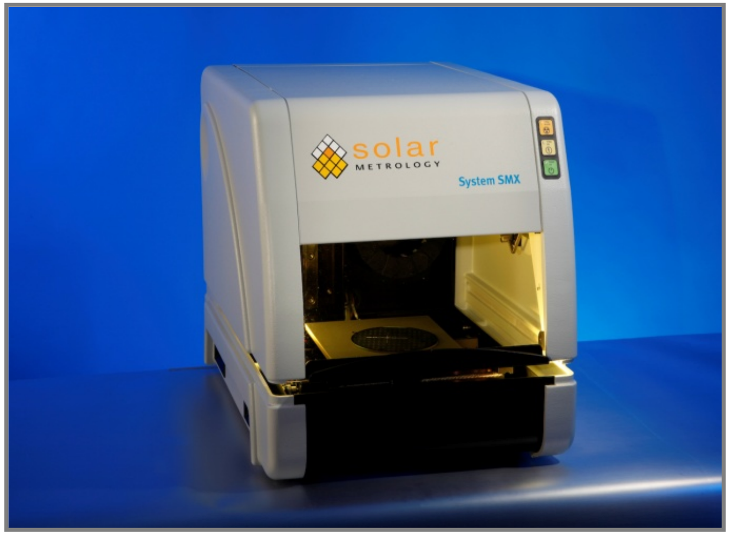
# IR Imaging Detects Different Defects




- A temperature increase across defect region corresponds to a blister or agglomerate where heat can't be released as fast.
- Temperature decreases correspond to pinholes and divots where heat is released faster.

# Areal Weight and Compositional Uniformity Using In-Line XRF




**Desktop Unit for Off-line Measurement**


**Industrial Unit for In-Situ Measurement**

- Unit designed for ORNL is a hybrid that is desktop sized, but it allows for in-situ measurement of cathode coatings (delivery date is scheduled for the end of March 2013).
- XRF unit will be placed at the end of ORNL tape casting line.
- Key process parameter is line speed that the detector can handle, which will be evaluated.

# LMR-NMC (TODA HE5050) High-Voltage Cathode Challenges

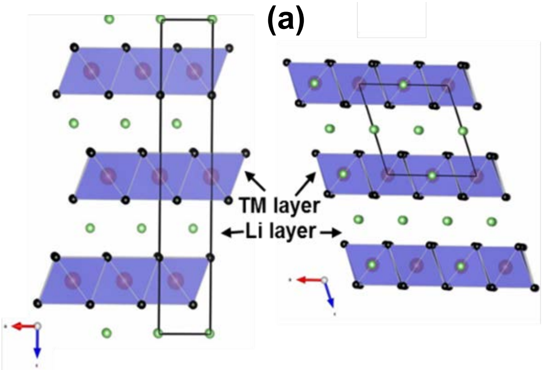
***Composition:*** $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$

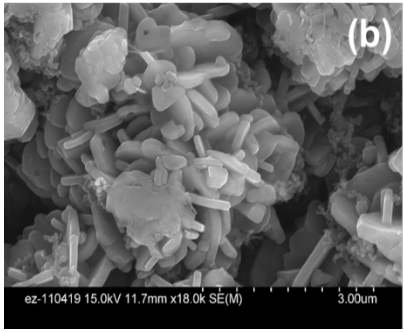
↓

$0.5\ LiNi_{0.27}Mn_{0.27}Co_{0.27}O_2 \cdot 0.5\ Li_2MnO_3$

*R-3m Trigonal ( Hexagonal or Rhombohedral or O3)*

*C2/m Monoclinic*



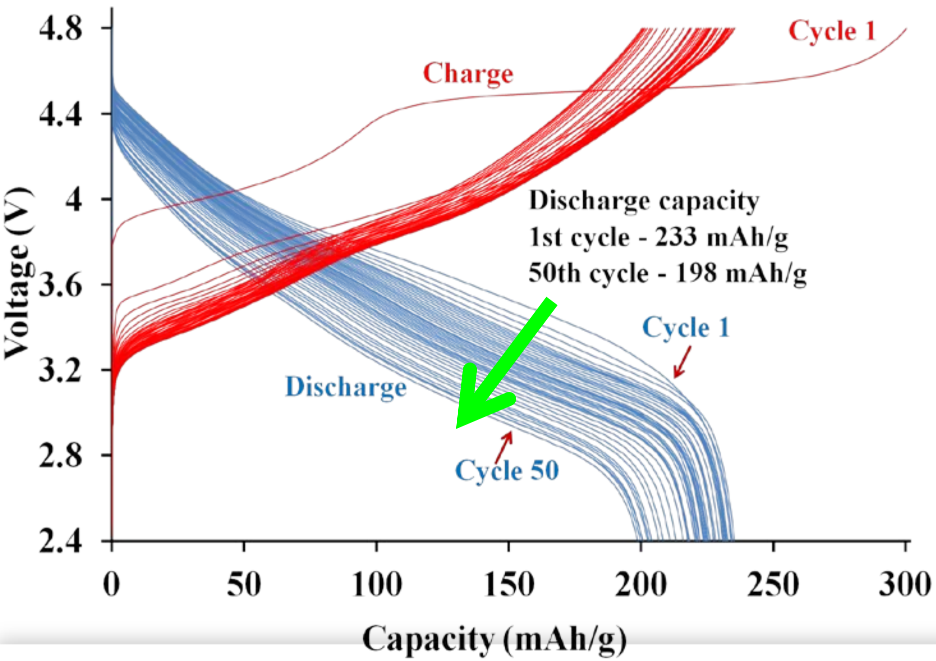




D. Mohanty et al., *Journal of Power Sources*, **229**, 239–248 (2013).

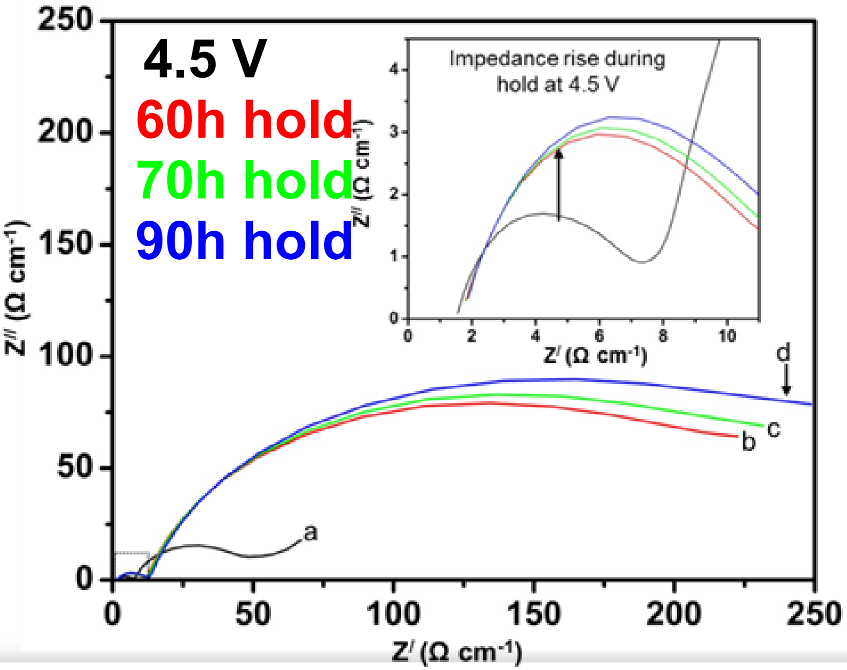
D. Mohanty et al., *Journal of Materials Chemistry A*, Under Review, 2013.

## *Major obstacles*

### 1. Voltage decay/fade (≥4.5 V)



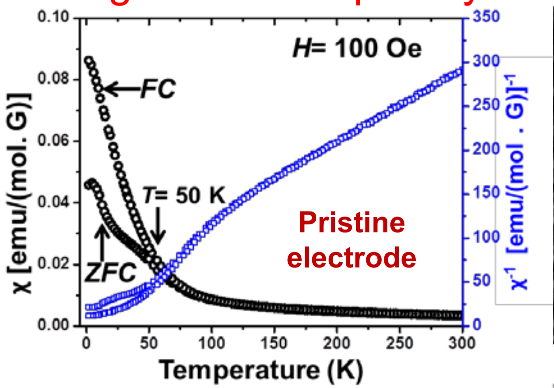

### 2. Impedance rise during holding at 4.5 V

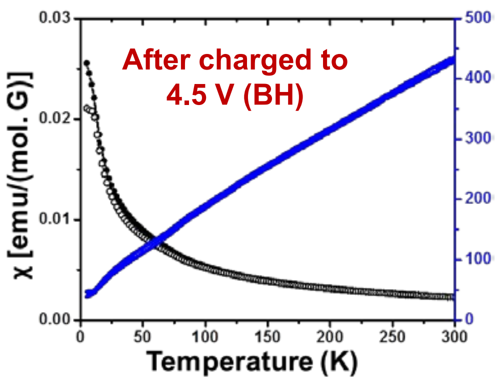


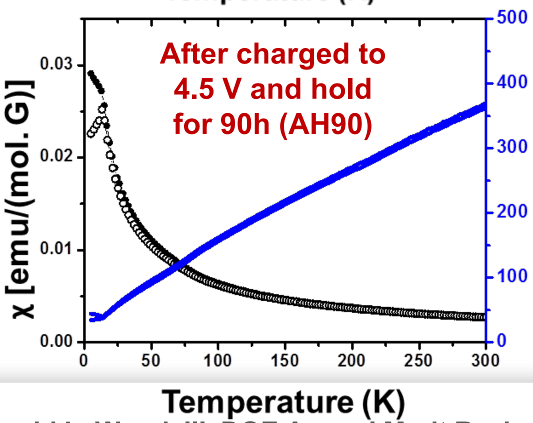
# Advanced Materials Characterization Applied to Understanding High-Voltage Cathode Phase Transformation

D. Mohanty et al., *Journal of Materials Chemistry A*, Under Review, 2013.

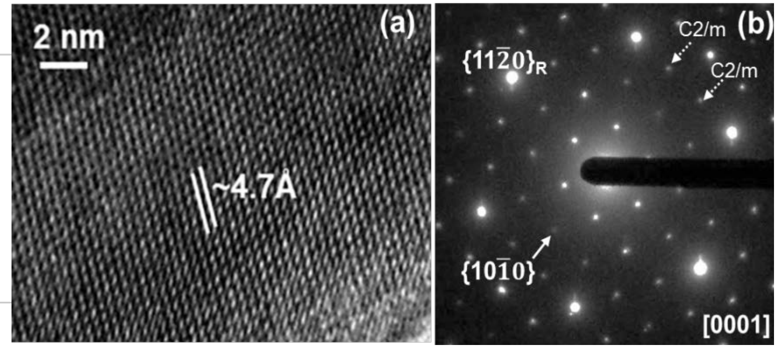
## Magnetic Susceptibility



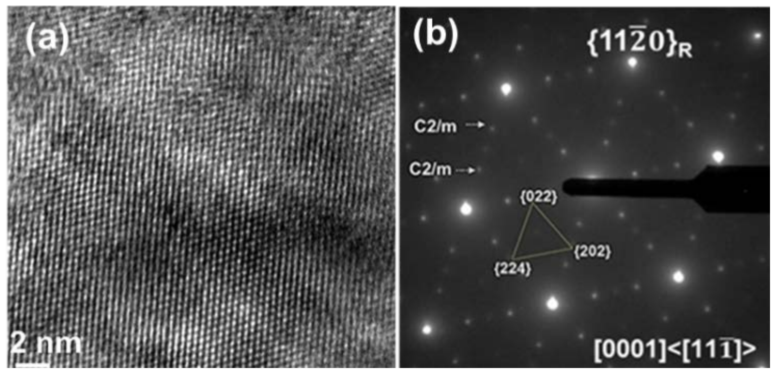




## TEM / SAED



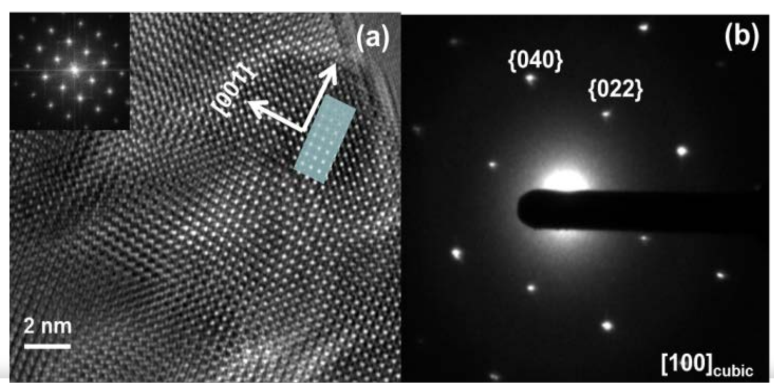

$\mu_{eff}$ =3.08 $\mu_B$

*Layered trigonal and monoclinic reflection*




$\mu_{eff}$ =2.70 $\mu_B$

*Layered+ Spinel (faint) reflections*




**$\mu_{eff}$ = 2.89 $\mu_B$**

**Oxidation state changes**

*Strong spinel phase*

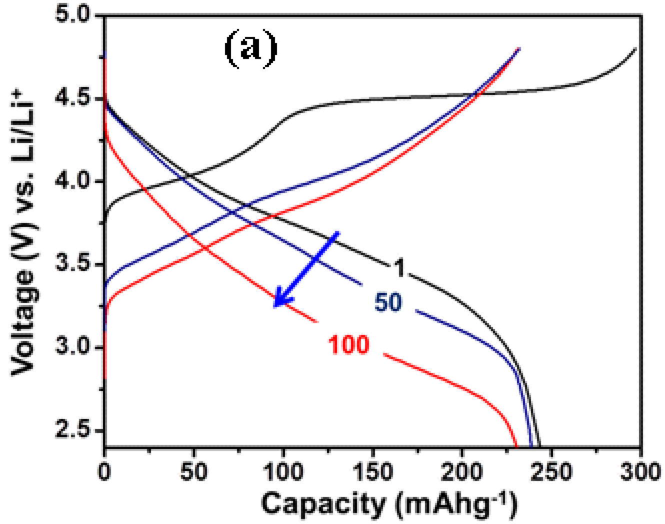
# Magnetic Susceptibility Measurement Applied to Elucidating LMR-NMC Voltage Fade

- Disappearance of magnetic ordering in TODA HE5050 structure after 100 cycles when cutoff voltage was 4.8 V.
- Magnetic ordering is retained after 100 cycles when cutoff voltage was 4.2 V.

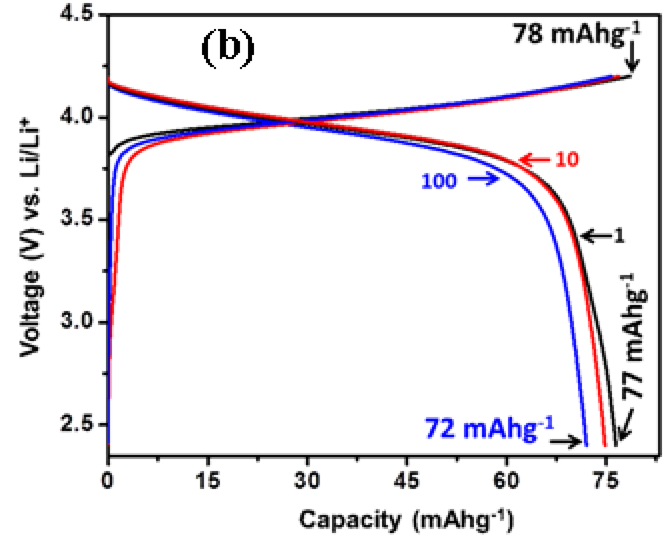
❖ **Illustrates the change in cation -ordering in LMR-NMC during high voltage cycling (4.8 V) causing voltage fade.**

D. Mohanty et al., *Journal of Materials Chemistry A*, In Preparation, 2013.

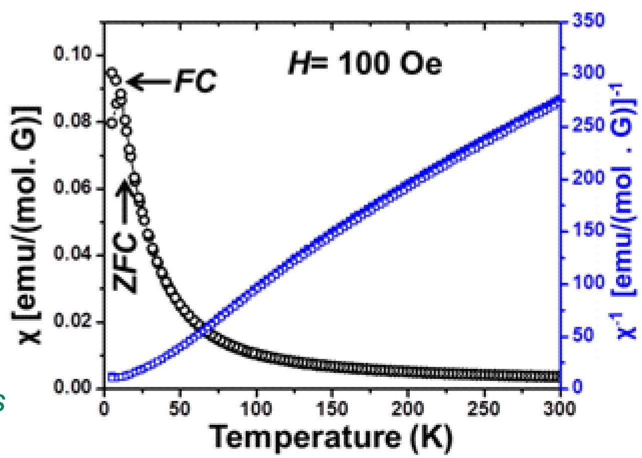
**Cutoff V = 4.8 V**



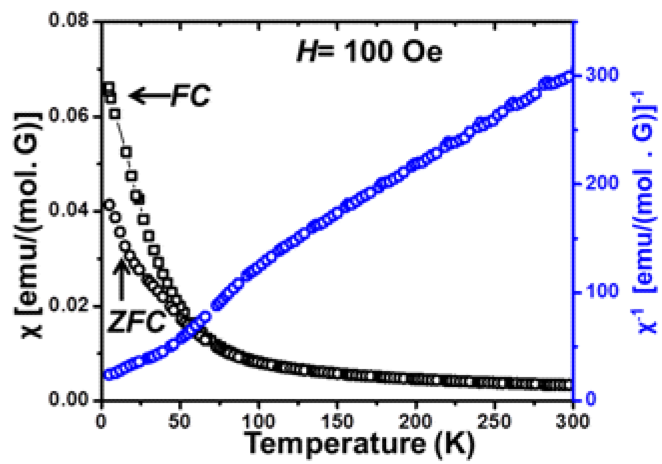

**Cutoff V = 4.2 V**



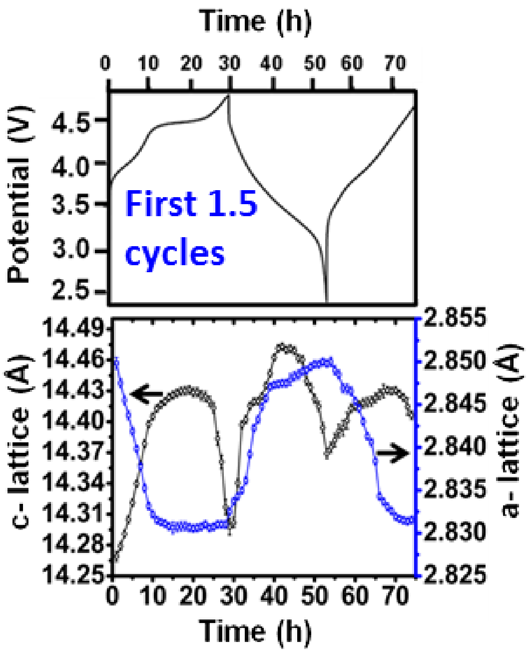

**Cutoff V = 4.8 V**

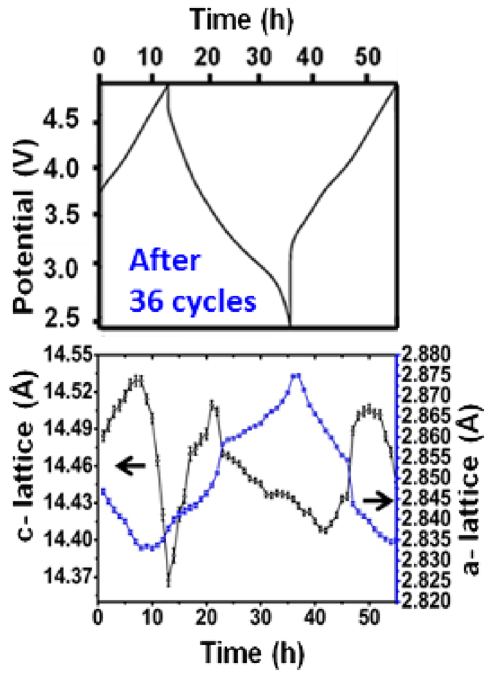


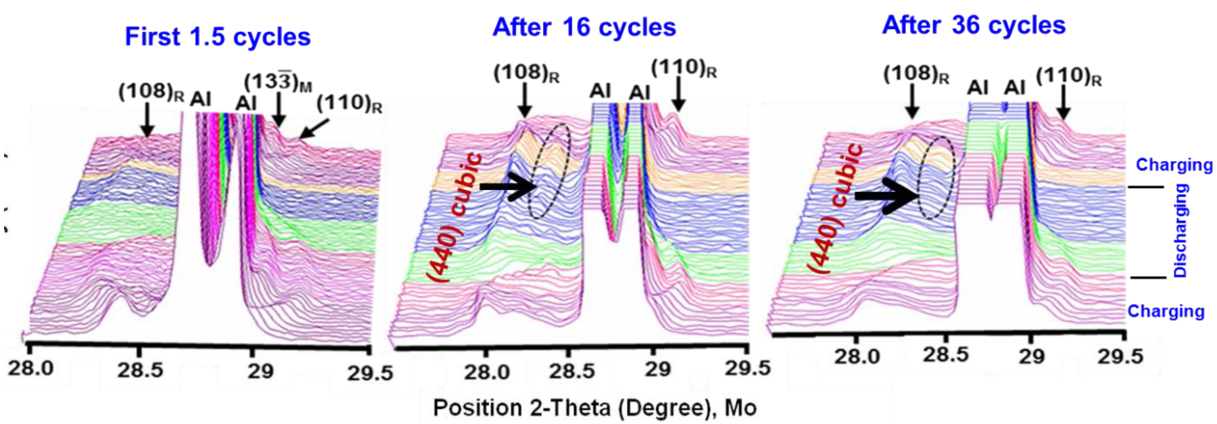

**Cutoff V = 4.2 V**



# Understanding LMR-NMC Voltage Fade via In-Situ XRD



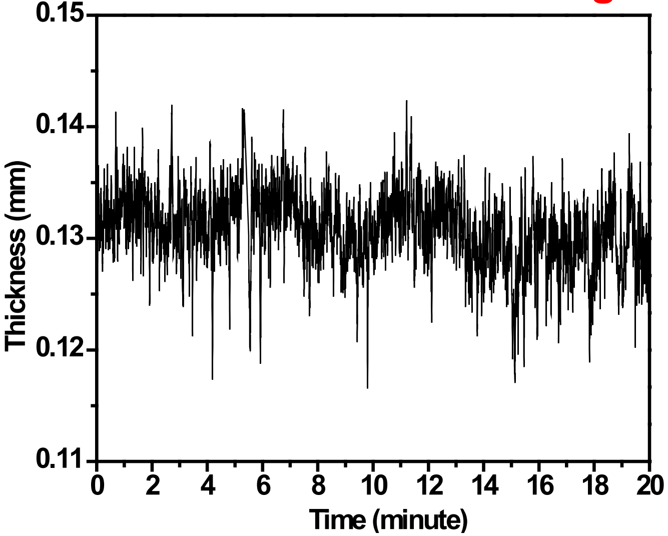

D. Mohanty et al., *Journal of Power Sources*, **229**, 239–248 (2013).

- **In-situ XRD patterns reveal a different trend in lattice parameter change for TODA HE5050 cathode after subsequent cycles compared to the first 1.5 cycles.**
- ***a-* lattice parameter remained constant during first cycle plateau region (4.4-4.6 V), which confirms oxygen release.**
- **(440) spinel reflection was successfully detected during *low-voltage discharge (3.5-2.4 V)* after 16(36) cycles, which confirms phase transformation in the TODA HE5050 cathode.**

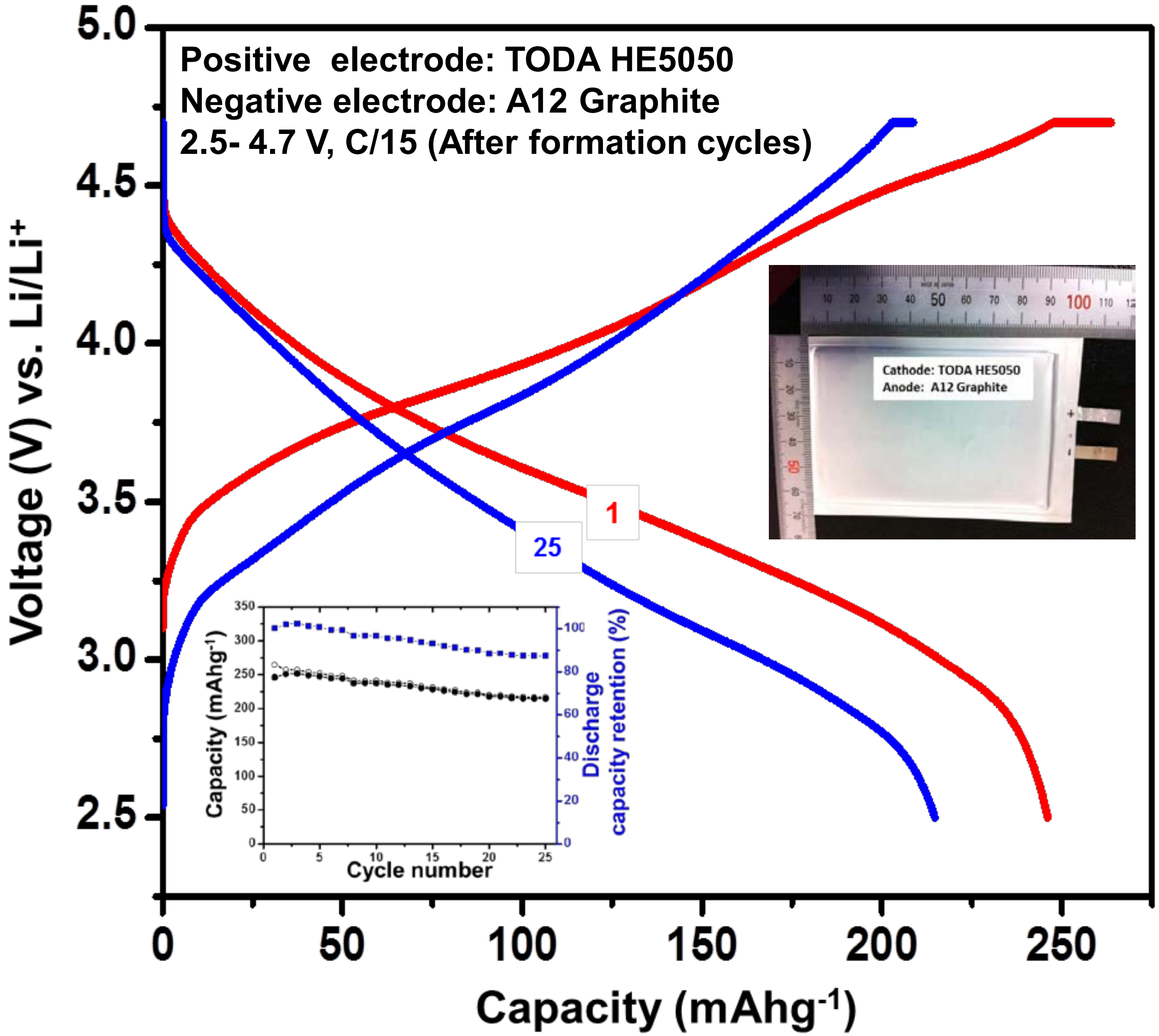
❖ **Layer to spinel phase transformation causes the voltage fade in LMR-NMC cathodes.**

# TODA HE5050 – Coatings to Pouch Cells

**In-line laser thickness measurement of coating**




- In-line QC is used to improve pouch cell reliability.
- We will correlate laser thickness, IR thermography, and XRF data with diagnostic tool (in-situ XRD, TEM, electron diffraction, and magnetic susceptibility) information.
- Neutron diffraction experiments with pouch cells are in progress.



# Collaborations

- Partners
  - <u>Equipment Suppliers:</u> Ceres Technologies, Keyence, FLIR Systems
  - <u>Battery Manufacturers:</u> A123 Systems, Dow Kokam
  - <u>Raw Materials Suppliers:</u> TODA America, ConocoPhillips
  - <u>National Labs:</u> ANL, NREL
- Collaborative activities
  - Determining best laser sensors to use with Keyence for electrode thickness based on line speed, thickness range, etc. for cross-web measurement.
  - Development of an in-line XRF measurement system with Ceres Technologies tailored for measuring lithium ion cathode areal weights and compositional uniformity.
  - Working with NREL to develop new method of in-line porosity measurement based on thermal diffusivity.
  - Ongoing discussion with industry partners Dow Kokam and A123 Systems about implementation of these techniques on industrial electrode production lines.
  - Continued collaboration with ANL on TODA HE5050 voltage fade and impedance rise issues.
  - Collaboration with ANL on neutron scattering of HE5050 cathode at ORNL SNS.

# Future Work

- Remainder of FY13
  - Mount in-line IR camera onto oven exit of ORNL slot-die coater (May 2013).
  - Obtain in-line XRF thickness and composition data on ORNL tape caster (May 2013).
  - Full analysis of first neutron scattering data set for TODA HE5050 cathode for identification of lithium, transition metal, and oxygen site occupancy (May 2013).
  - Transition from point scan to line or multipoint (cross-web) scan for in-line laser thickness measurement on ORNL slot-die coater (June 2013).
  - Obtain in-situ XRD results through 1000 cycles on TODA HE5050 cathode (August 2013).
  - Correlate TODA HE5050 magnetic susceptibility and TEM measurements with in-situ XRD data through 1000 cycles to determine microstructural changes associated with capacity fade (Sept. 2013).
  - Obtain 200 cycles with full pouch cells using TODA HE5050 cathode and CP A12 graphite (Sept. 2013).
  - Proof-of-concept measurements for in-line electrode porosity uniformity with NREL (Sept. 2013).
- Into FY14
  - Develop feedback loop for dispersion pumping rate with in-line thickness measurement as input.
  - Identify industrial partner to scale selected in-line QC methods.
  - ❖ Detailed correlation of electrode QC measurements with diagnostic tool information.

# Summary

- **Objective:** this project facilitates lowering unit energy cost of EVs and PHEVs by addressing the electrode scrap rate, QC enhancement, and calendar life.
- **Approach:** implements QC measures utilized effectively in other industries.
  - Processing costs tied to QC are addressed.
  - Ease of implementation of measurement technology at low equipment cost.
  - Long-term objective is to correlate in-line coating defect measurement data with diagnostic tool information and develop QC feedback loops.
- **Technical:** Successful implementation of laser thickness measurement and IR thermography equipment on ORNL slot-die coater; demonstrated successful measurements with in-line XRF on ORNL tape caster.
- **Collaborators:** Active discussions with industry partners Dow Kokam and A123 Systems on scaling measurement techniques; developing next in-line technique based on thermal diffusivity with NREL.
- **Commercialization:** High likelihood of technology transfer because of tight industrial collaboration, significant electrode production cost reduction, and lower-cost QC measurement equipment.

# Acknowledgements


- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)

- ORNL Contributors:
  - Claus Daniel
  - Jianlin Li
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# Information Dissemination and Commercialization

- Refereed Journal Papers
  - D. Mohanty, S. Kalnaus, R.A. Meisner, K.J. Rhodes, E.A. Payzant, D.L. Wood, and C. Daniel, "Structural Transformation of a Lithium-Rich $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ Cathode During High Voltage Cycling Resolved by In-Situ X-Ray Diffraction," *Journal of Power Sources*, **229**, 239–248 (2013).
  - D. Mohanty, S. Kalnaus, R.A. Meisner, A. Safa-Sefat, J. Li, K.J. Rhodes, E.A. Payzant, D.L. Wood, and C. Daniel "Structural Transformation in a $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ Lithium-Ion Battery Cathode During High-Voltage Hold," *RSC Advances*, **DOI:10.1039/C3RA40510A**, 2013.
  - D. Mohanty, A. Safa-Sefat, S. Kalnaus, J. Li, R.A. Meisner, E.A. Payzant, D.P. Abraham, D.L. Wood, and C. Daniel, "Investigating Phase Transformation in $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ Lithium-Ion Battery Cathode During High-Voltage Hold (4.5 V) via Magnetic, X-ray Diffraction and Electron Microscopy Studies," *Journal of Materials Chemistry A*, Under Review, 2013.
  - D. Mohanty, A. Safa-Sefat, J. Li, S. Kalnaus, R.A. Meisner, D.L. Wood, and C. Daniel, "Investigating the Voltage Fading Mechanism in a $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ High-Voltage Lithium Ion Battery Cathode via Magnetic and Diffraction Studies," *Journal of Materials Chemistry A*, In Preparation, 2013.
  - D. Mohanty, J. Li, E.A. Payzant, A. Safa-Sefat, R.A. Meisner, D.P. Abraham, D.L. Wood, and C. Daniel, "Investigating the Voltage Fading Mechanism in a Li-Rich Cathode During High Voltage Lithium Ion Battery Cycling: A Combined Neutron Diffraction and Magnetic Susceptibility Study," *Journal of The American Chemical Society*, In Preparation, 2013.
  - D. Mohanty, A. Safa-Sefat, J. Li, S. Kalnaus, R.A. Meisner, D.L. Wood, and C. Daniel, "Investigating Cation Ordering and Microstructure in $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ During First-Cycle Charge and Discharge by Magnetic Susceptibility and Transmission Electron Microscopy," *Chemistry of Materials*, In Preparation, 2013.
  - D. Mohanty, L.C. Maxey, R.B. Dinwiddie, J. Li, and D.L. Wood, "Improved QC of Slot-Die Coated Lithium Ion Battery Electrodes by IR Thermography and Laser Thickness Techniques," *Analytical Methods* , In Preparation, 2013.
- Presentations
  - D. Mohanty, S. Kalnaus, R. Meisner, A. Safa-Sefat, J. Li, D.L Wood, and C. Daniel, "Structural Evolution in Lithium-Rich $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ Cathode During High Voltage Cycling; an *In Situ* X-Ray Diffraction Investigation", MRS 2012, Boston, Massachusetts, November 25, 2012.
  - D. Mohanty, A. Safa-Sefat, J. Li, S. Kalnaus, R.A. Meisner, D.L. Wood, and C. Daniel, "Investigating the Cation-Ordering in $0.5Li_2MnO_3.0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ Cathode by Magnetic and Transmission Electron Microscopy Studies," ACS Spring Meeting, New Orleans, Louisiana, April 7, 2013 (Accepted as *ACS Presentation On Demand*).

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**Pictured Left to Right above:**
**David Wood (ORNL), Mike Wixom (A123 Systems), Erin O'Driscoll (Dow Kokam), Claus Daniel (ORNL), and Secretary of Energy Steven Chu at the ORNL Battery Manufacturing Facility (BMF)**

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Thank you for your attention!