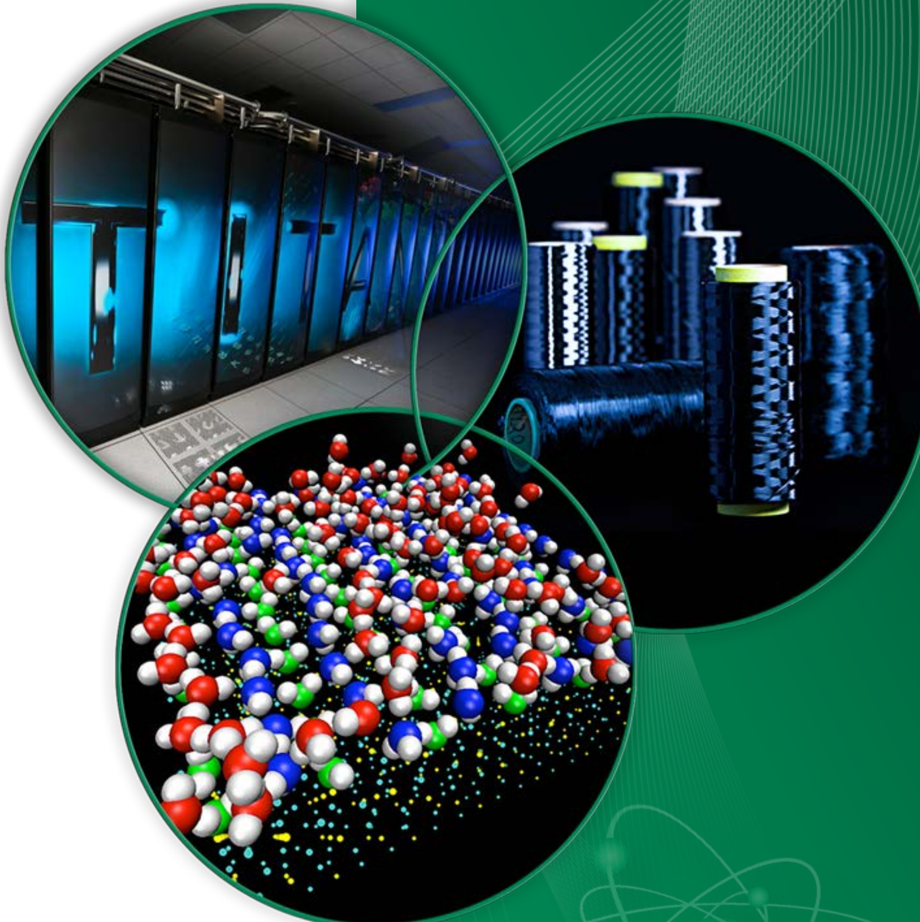
Roll-to-Roll Electrode Processing NDE for Advanced Lithium Secondary Batteries



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Oak Ridge National Laboratory

June 18, 2014

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID ES165

Overview

Timeline

- Project Start: 10/1/11
- Project End: 9/30/14
- Percent Complete: 75%

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 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
- $300k in FY14

Partners

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

Relevance & Objectives

- <u>Main Objective</u>: To reduce the amount of scrap electrode by at least 75% and the associated amount ***assembled into finished cells***.
  - Reduce lithium ion battery system cost by implementing in-line NDE and electrode QC.
  - Quantification of effects of different defect types on rate performance and cell lifetime.
  - Collaborate with NREL to establish thermal diffusivity and optical reflectance methods.
  - Routine in-line, cross-web laser sensing for electrode thickness monitoring.
  - Routine IR thermography for electrode coating defects (agglomerates, pinholes, blisters, divots, metal particles, etc.).
  - In-line XRF for areal-weight uniformity.
  - Cover Feature: *Anal. Methods*, **6** (3), 674 (2014).
- Relevance to Barriers and Targets
  - Implementation of critical QC methods to reduce scrap rate by ***creating feedback loops*** (to meet \$300/kWh 2015 VTO storage goal for PHEVs).
  - Quantification of various defect effects on cycle life (to achieve 3000-5000 cycles for PHEVs by 2015 and 750 cycles for EVs by 2020).

Showcasing research into the non-destructive evaluation of lithium secondary battery electrodes by Dr David L. Wood, III and colleagues from Oak Ridge National Laboratory, Tennessee, USA.

Non-destructive evaluation of slot-die-coated lithium secondary battery electrodes by in-line laser caliper and IR thermography methods

At the ORNL Battery Manufacturing Facility, we have systematically applied laser caliper and infrared thermography methods as non-destructive, in-line quality control methods for evaluating the thickness, homogeneity, and quality of lithium secondary battery electrodes during the slot-die coating process. These techniques are helpful for detection of electrode flaws and contamination during large-scale manufacturing and identification of flawed product prior to lithium-ion cell assembly.

This research at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Office Applied Battery Research Program (Program Managers: Peter Faguy and David Howell) of the Office of Energy Efficiency and Renewable Energy.

As featured in:

Analytical Methods

See Mohanty *et al.*, *Anal. Methods*, 2014, **6**, 674.

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Project Milestones

Status	Milestone or Go/No-Go	Description
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 ✔	No-Go	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.
12/2013 ✔	FY14 Milestone	Develop methods to generate different electrode coating defects such as pinholes, blisters, large agglomerates, divots, and metal particle contaminants for evaluation in full coin cell test matrix.
3/2014 ✔	FY14 Milestone	Obtain comprehensive, statistically representative full coin cell data on different types of electrode coating defects to determine which type of defects cause cell failures or substandard performance.
6/2014	FY14 Milestone	Correlate IR thermography electrode QC data with full coin cell statistical data quantifying capacity fade.
9/2014	FY14 Milestone	Develop pass/fail criteria for lithium-ion electrode coating defects such as metal particles, pinholes, blisters, divots, large agglomerates, etc.

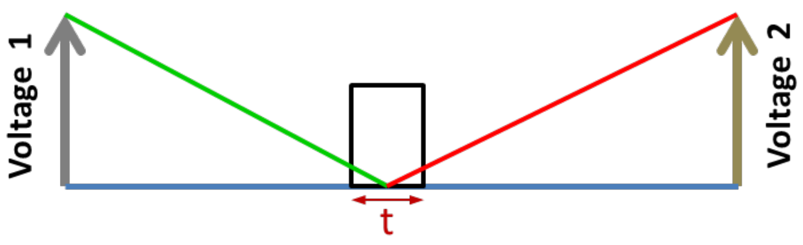
Project Approach

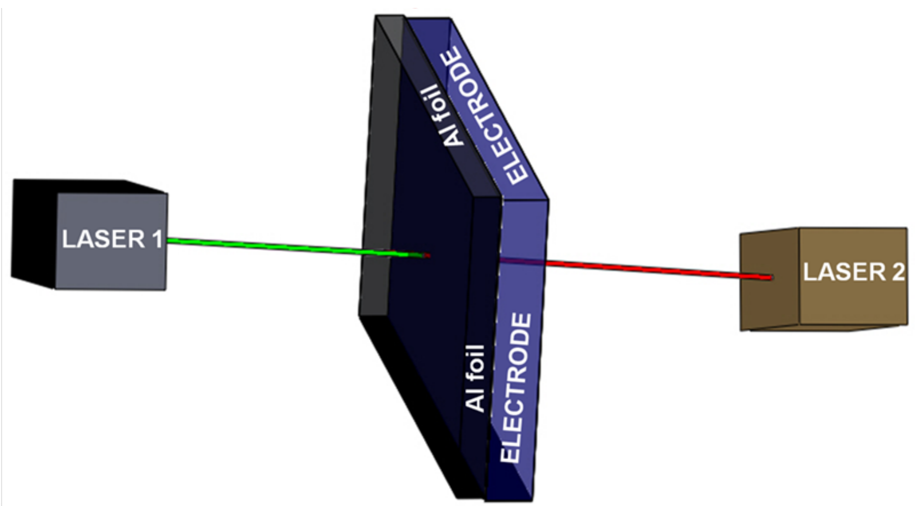
- **Problems to be addressed:**
  - Quantify effects of different types of defects on cell rate performance and cycle life.
  - Excessive scrap rates of electrodes and lack of ability to detect coating defects prior to formation cycling; novel, low-cost methods of NDE and QC are required.
  - Conventional electrode QC involves thickness/areal-weight measurement by beta gauge, which uses ionizing radiation (safety concern) and expensive equipment.
- **Overall technical approach and strategy:**
  1. Identify and demonstrate efficacy of in-line QC techniques utilized in other industries (plastics, textiles, ceramic coatings, photovoltaics, etc.) on ORNL pilot coating equipment.
  2. 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 and detection equipment has been installed).
  3. No-go decision made for in-line XRF due to incompatibilities with coating line speeds, frequency of metal particle contaminants, and areal weight inaccuracies.
  4. Collaborate with NREL to develop new methods of thermal diffusivity for measuring in-line porosity and optical reflectance for measuring coating defects CCD cameras cannot detect.
  5. Correlate in-line NDE and QC methods with systematic cell performance data of various defect types (i.e. identify defects and test electrodes with them in coin and pouch cells).
  6. Quantify effects on cell performance (power, energy and lifetime) and establish acceptance criteria.
- **Verify cost savings metrics for electrode scrap reduction with industry partner.**
  - How is electrode scrap related to cell acceptance rate and pack production costs?

Technical Accomplishments – Executive Summary

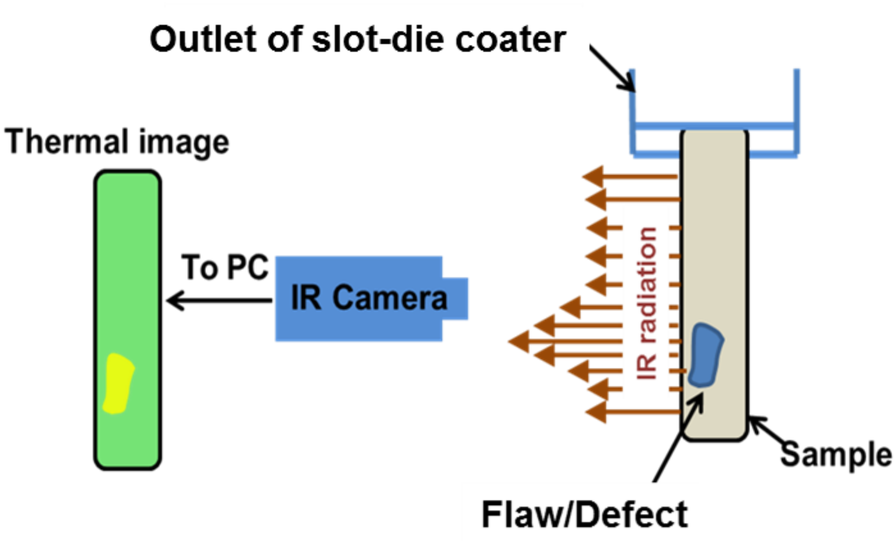
- FY12 Q1-2: Exploratory in-line measurement work and establishment of materials characterization methods (Presented at 2012 DOE AMR).
- FY12 Q3-4: Slot-die coater integration of in-line laser thickness and IR thermography measurements and in-situ XRD correlation with magnetic susceptibility and TEM (Presented at 2013 DOE AMR).
- 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 (Presented at 2013 DOE AMR).
- **FY13 Q3-4: Receipt of in-line XRF equipment and completion of initial experiments on tape caster (Technical Back-Up Slides); installation of laser thickness sensors and new IR camera onto ORNL slot-die coating line (Following Slides).**
- **FY14 Q1-2: Establish methods for intentionally introducing different defects and quantify effects in coin cells; preliminary data on optical reflectance method with NREL equipment (Following Slides).**
- FY14 Q3-4: Quantify effects of different defects in 1-Ah pouch cells; preliminary data on thermal diffusivity measurement of anode and cathode coatings with NREL equipment.
- Specific Accomplishments
  - Laser thickness and IR thermography methods are installed on ORNL slot-die coating line and routinely used for coating QC.
  - Collaboration with NREL leveraging FCTO funds and equipment for PEMFC electrode QC.

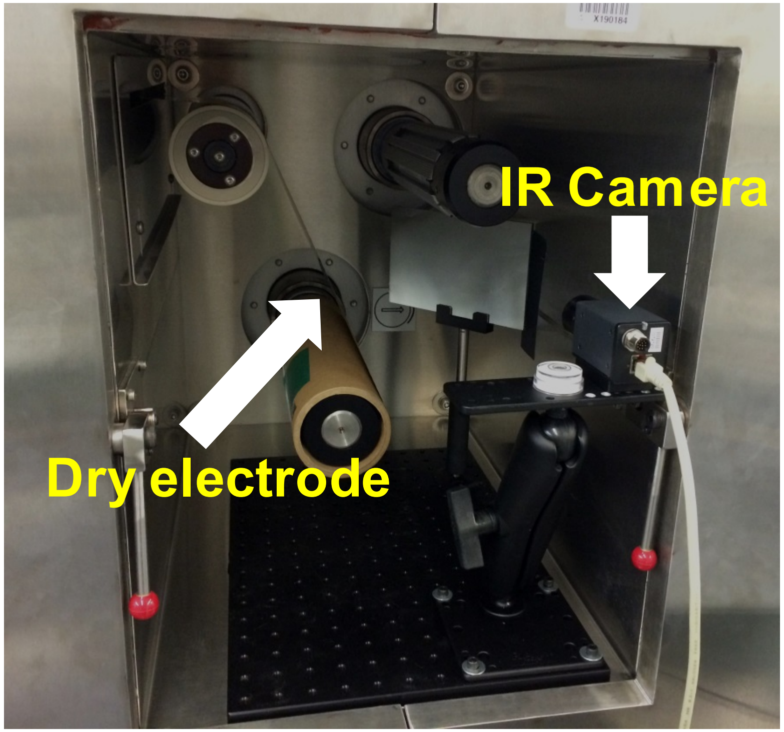
Technical Accomplishments – Installation of Low-Cost Laser Thickness Sensors





Technical Accomplishments – Installation of IR Thermography for Electrode Coating QC





Monitor temperature profile in IR thermograms on dry electrodes detecting any potential defects such as divots, pinholes, agglomerates, etc.

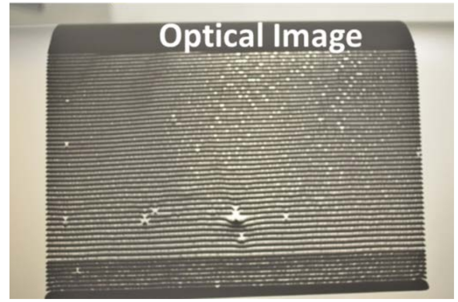
- Current IR Camera: FLIR A65
- Lens: 13 mm
- Resolution: 640 x 512 pixels

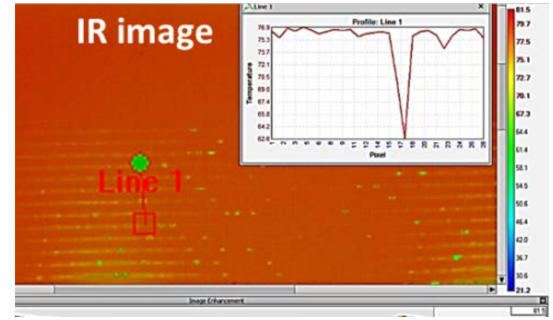
Technical Accomplishments – Systematic Study of Electrode Coating Defects

6 types of defects are being studied to determine relative importance.

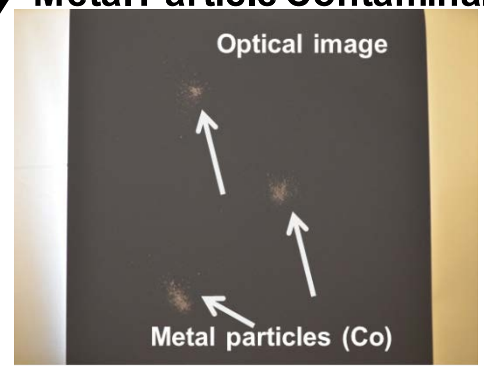
Diversity of Coating Defects

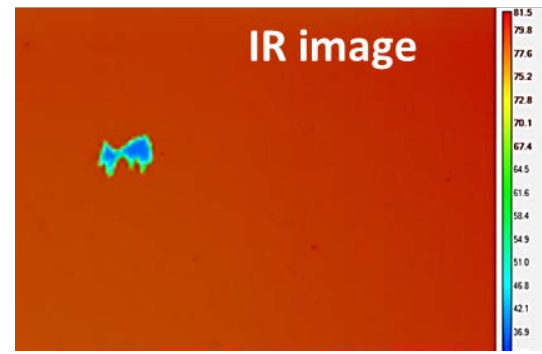
Exaggerated Non-Uniform Coating



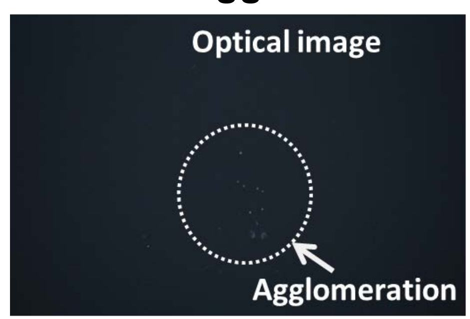


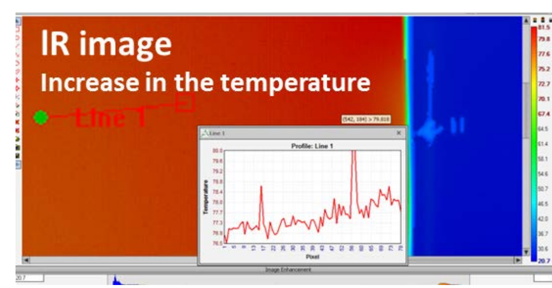
Metal Particle Contaminants





Electrode Agglomerates



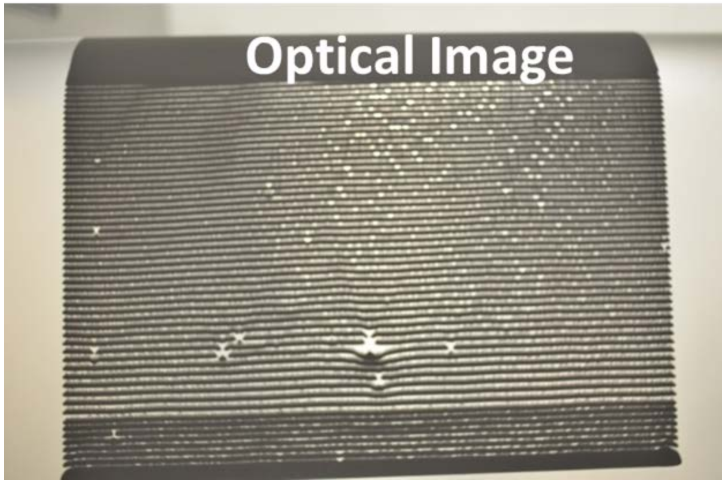


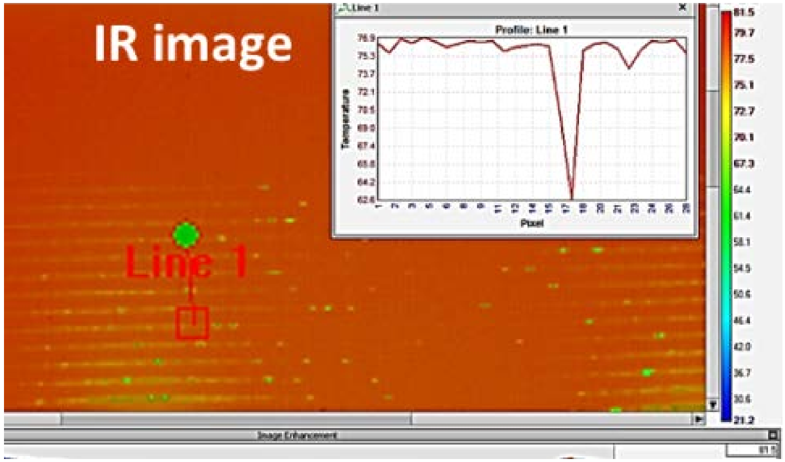
Electrode Divots

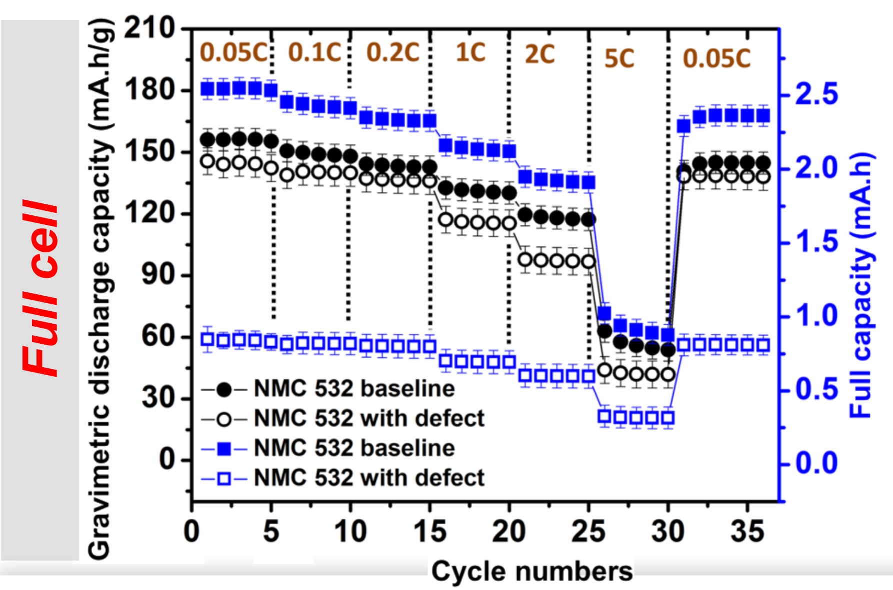
Electrode Pinholes

Electrode Blisters

Technical Accomplishments – Exaggerated Cathode Coating Non-Uniformity Causes Capacity Loss and Efficiency Decrease



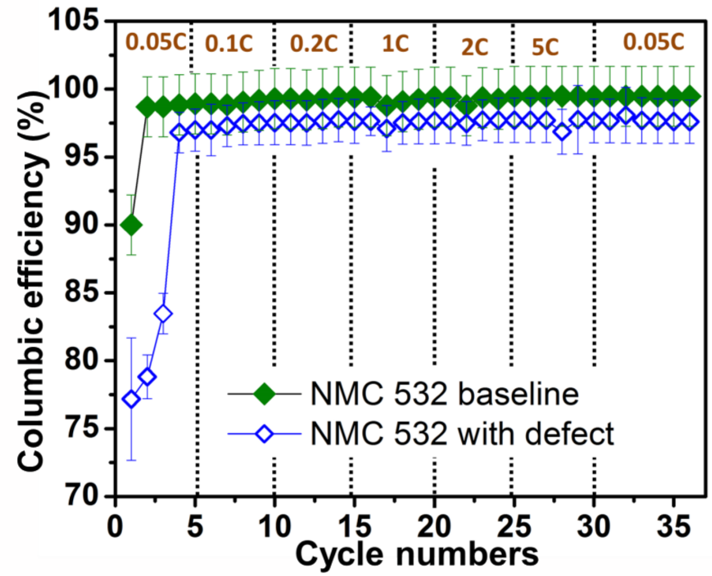




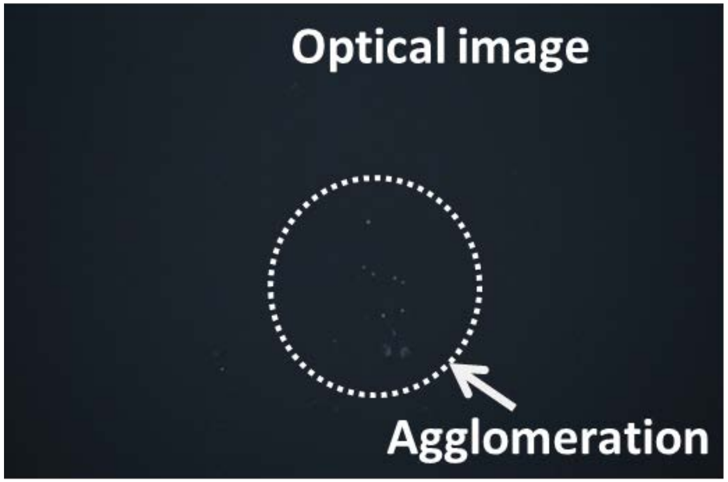
Active material amount is ~50% lower.

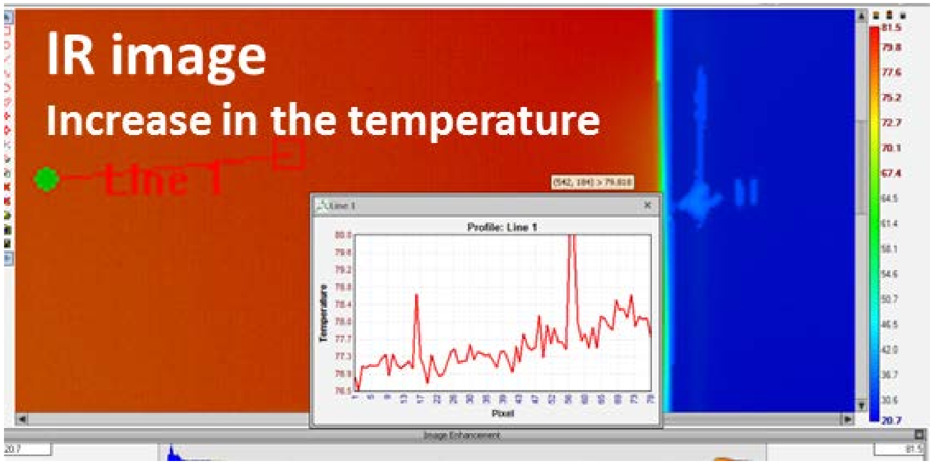
10-20% lower specific capacity.

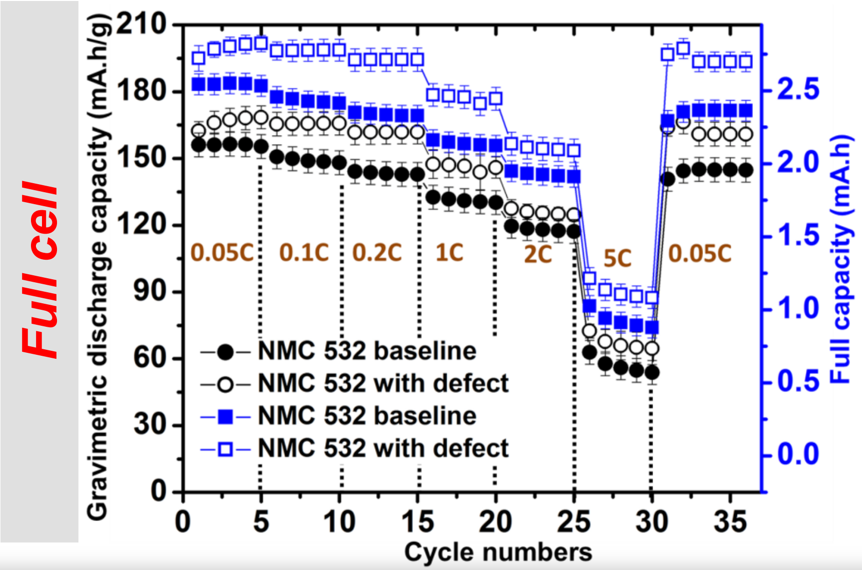
60-70% lower full cell capacity.

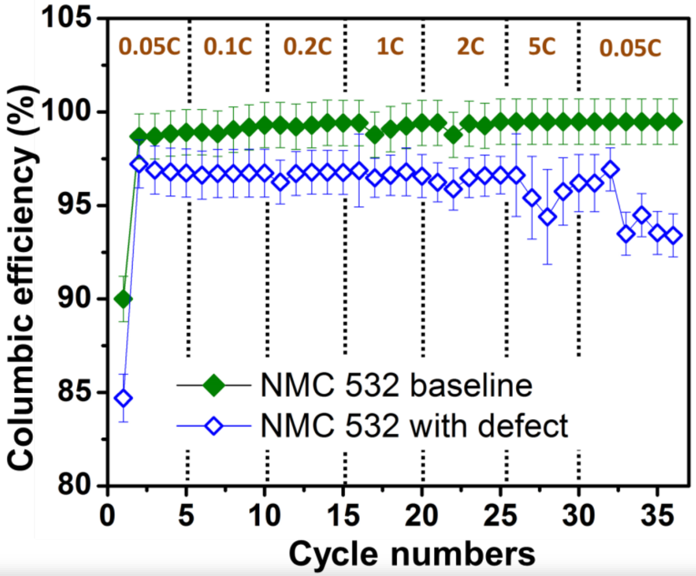


Technical Accomplishments – Effect of Cathode Coating Agglomerates on Rate Performance Is Less

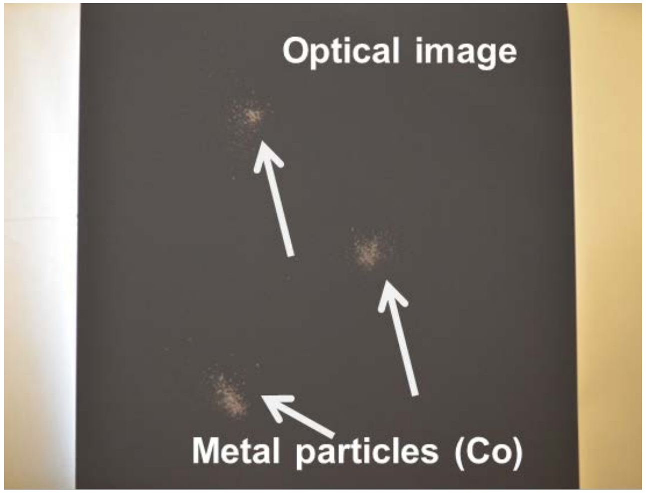


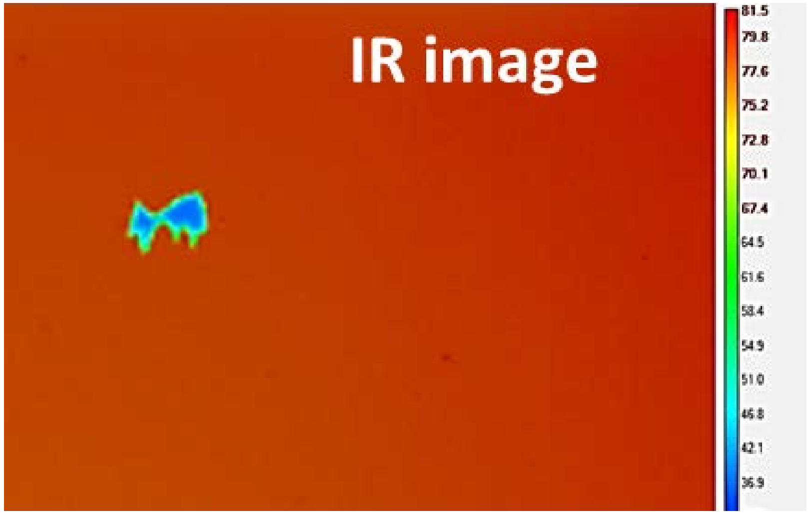


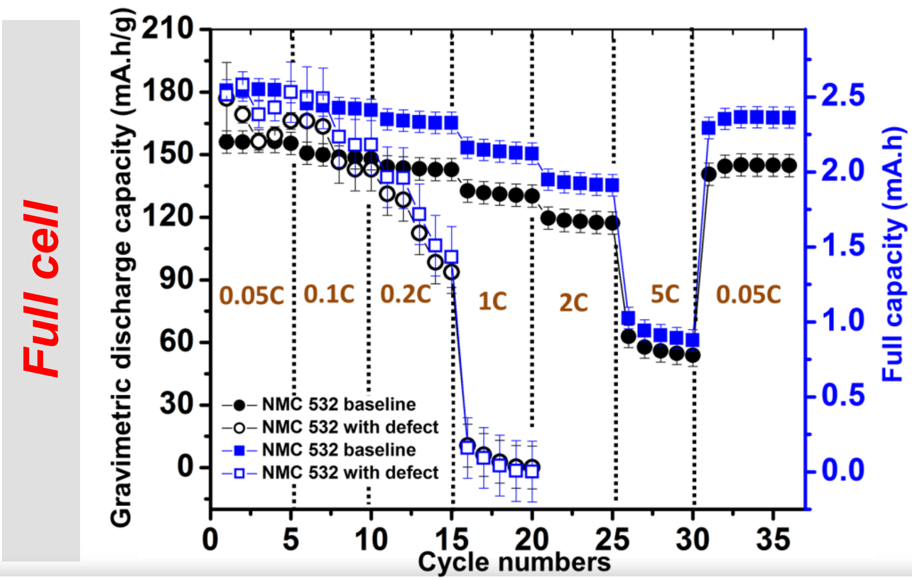


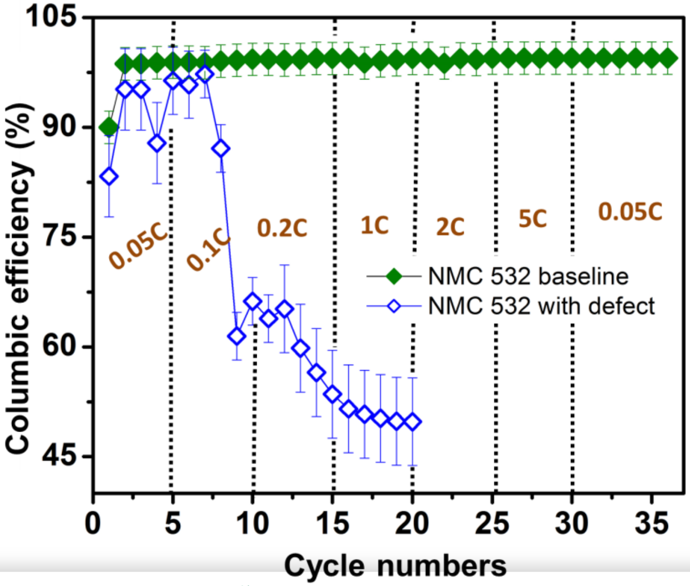


Technical Accomplishments – Effect of Metal Particle (Co Powder) Contaminants Is Detrimental





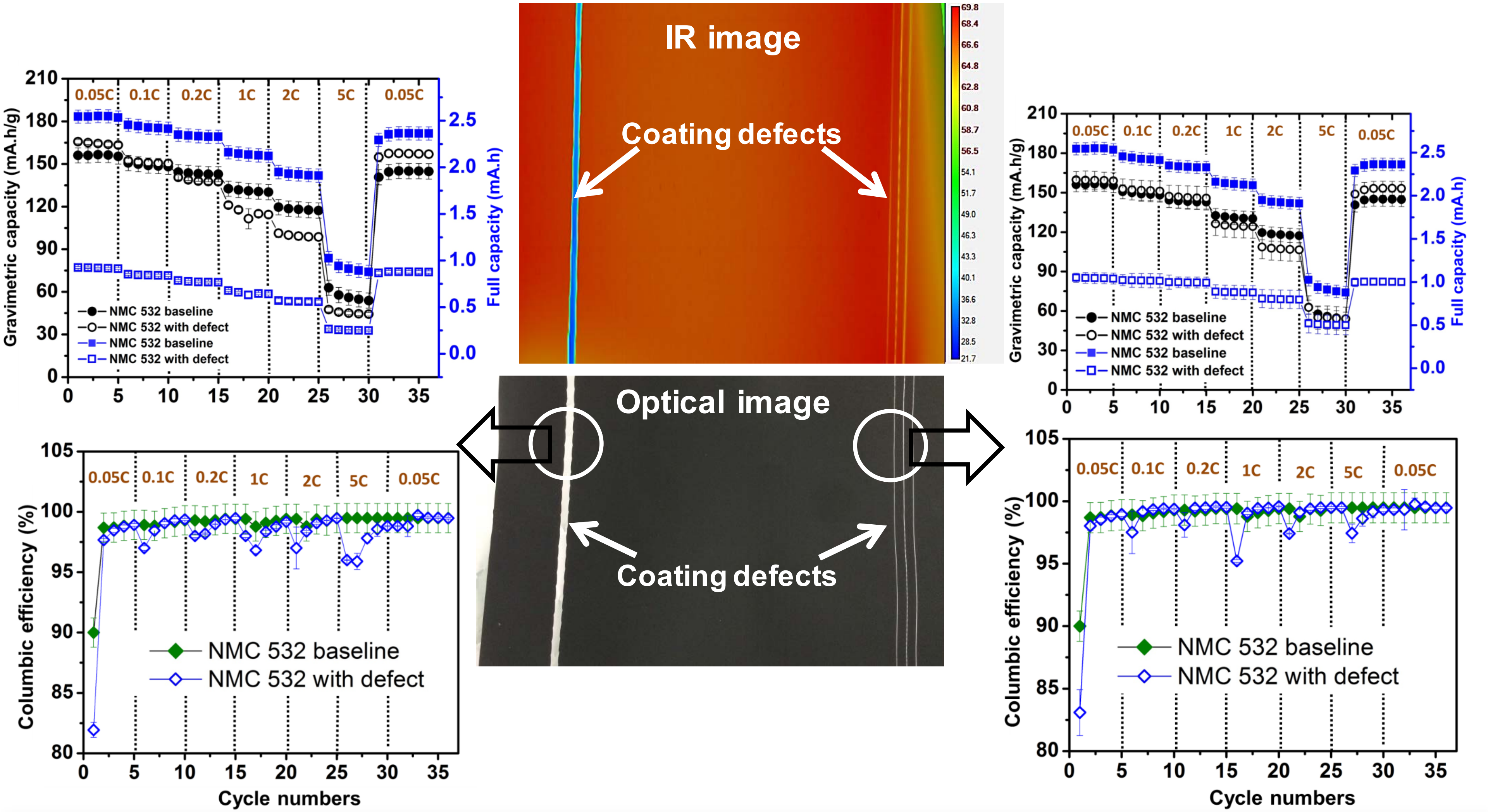




Technical Accomplishments – Relative Effect of Defects on Cell Performance

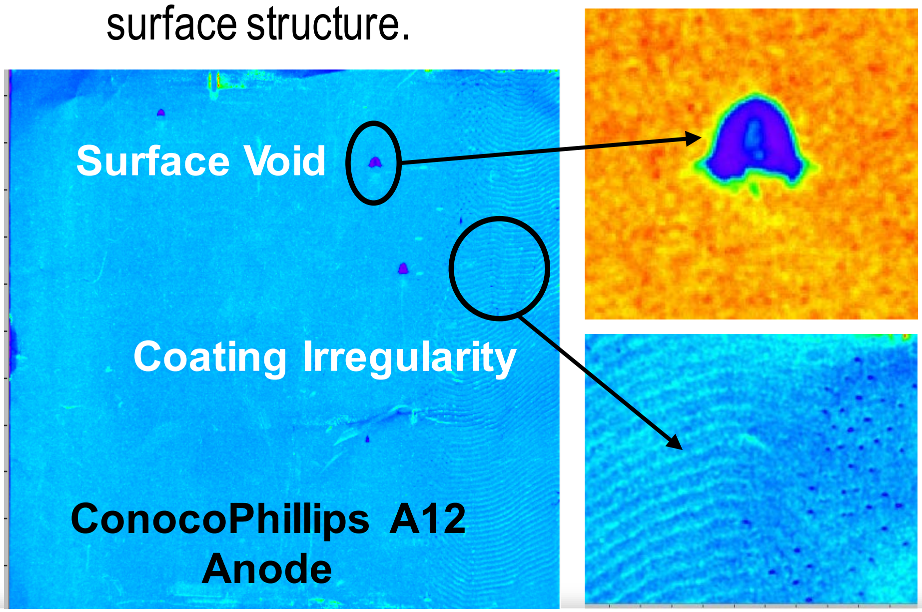
- Cathode agglomerates did not have a great effect on full cell discharge capacity, but aggravated cycle efficiency.
- Excessive metal particle contaminants (in this case, Co powder) have an extremely negative effect on performance, especially at higher C rates.
- Exaggerated cathode coating inhomogeneities (strips with missing coating) result in disproportionate drops in cell total capacity.
- Examination of effects of pinholes, divots, and Al foil pieces is in progress.
- Inhomogeneous cathode coating (especially missing areas and agglomerates) leads to unbalanced N/P ratio, which affects gravimetric capacity and reduces Coulombic efficiency.

Technical Accomplishments – Specific Design of Experiments to Explain Observations Related to Missing Coating



Technical Accomplishments – ORNL/NREL Collaboration on Electrode NDE

- **Optical Reflectance:**
  - Evaluate and develop technique for LIB electrode surface structure and morphology.
- **Accomplishments to Date:**
  - Completed feasibility testing with Baseline ABR anode and cathode samples.
  - Demonstrated imaging of electrode surface structure.



- **Active IR Thermography:**
  - Evaluate and develop technique to determine the uniformity of LIB electrode bulk properties.
  - Integrate material modeling with real-time measurement to quasi-quantitatively evaluate material properties, e.g. porosity or thermal conductivity.
- **Accomplishments to date:**
  - Initiated review of materials models from previous NREL work.
  - Initial experiments with prototype optical excitation source showed sufficient thermal response from electrode layer.

Selected Responses to Specific FY13 DOE AMR Reviewer Comments – 1

- At the goal level, Reviewer 2 thought it could be important to have more specific data on the justification for the program. The reviewer asked how much scrap was generated due to the issues addressed in this program, just how big an issue this was, and wondered what the size of the opportunity was.
  - The opportunity for electrode scrap reduction is quite large – 10-20% scrap is routine now in battery plants, although it is difficult to get exact number from LIB manufacturers.
  - The most important aspect is to **identify and eliminate** scrap to reduce the number of defective cells and wasted value-added during cell assembly.
- Reviewer 2 also wondered whether effects of defects on cell performance should be addressed in the project, and whether the scope should be limited to NDE and improved QC.
  - We see these two issues as interlinked. Determining which defects are most important to rate performance and cell lifetime determines what NDE techniques should be used to identify coating defects.
- Reviewer 5 would like the researchers to restate success goal as percent reduction in scrap at electrode coating operation because the present 99% cell-level goal was unrealistic. The root causes for failure include factors that would not be caught by the methods being developed.
  - This is a good suggestion, and the stated main goal has been modified in Slide 3 accordingly.

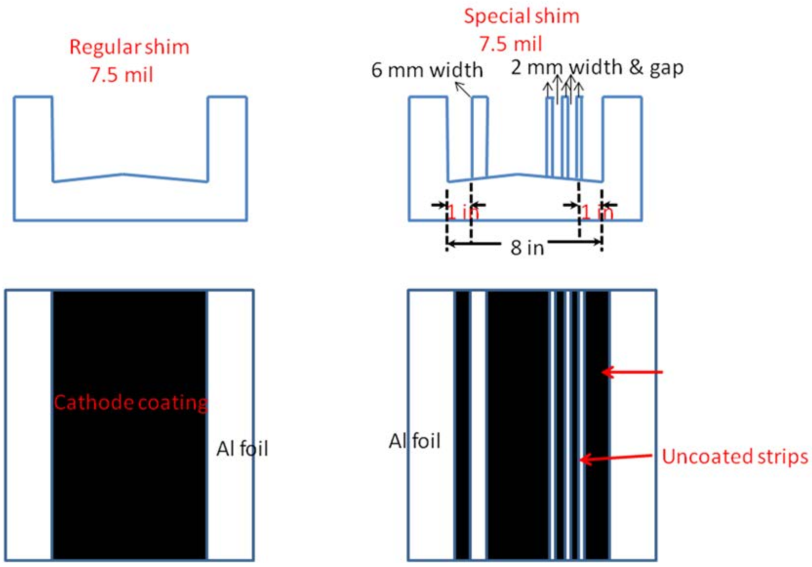
Collaborations

- Partners
  - Equipment Suppliers: Ceres Technologies, Keyence, FLIR Systems
  - Battery Manufacturers: A123 Systems, XALT Energy, Navitas Systems
  - Raw Materials Suppliers: TODA America, ConocoPhillips
  - National Labs: ANL, NREL

- Collaborative Activities
  - Working with NREL to develop new methods of in-line porosity measurement based on thermal diffusivity and defect detection based on optical reflectance.
  - Ongoing discussion with industry partners XALT Energy, Navitas Systems, and A123 Systems on implementation of IR thermography, laser thickness measurement, optical reflectance, and thermal diffusivity techniques on industrial electrode production lines.

Future Work

- Remainder of FY14
  - Implement optical reflectance and thermal diffusivity measurement methods for identifying coating defects and in-line porosity, respectively (in collaboration with NREL).
  - Scale cell testing of different coating defects to 1-Ah pouch cells for identifying which types of defects are critical to cycle life.
  - Develop feedback loop for dispersion pumping rate with in-line thickness measurement as input.
  - Identify industrial partner to scale selected in-line QC methods.



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 with low equipment cost.
  - Quantify effect of electrode coating defects such as divots, blisters, pinholes, agglomerates, and metal-particle contaminants on cell rate performance and cycle life.
- **Technical:** Successful implementation of laser thickness measurement and IR thermography equipment on ORNL slot-die coater; identified defects critical to rate performance.
- All FY14 Milestones Are on Schedule.
- **Collaborators:** Active discussions with industry partners XALT Energy and Navitas Systems on scaling measurement techniques; developing new in-line NDE and QC techniques based on thermal diffusivity and optical reflectance with NREL.
- **Commercialization:** High likelihood of technology transfer because of strong industrial collaboration, significant electrode production cost reduction, and lower-cost QC measurement equipment.

Acknowledgements

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- ORNL Contributors:
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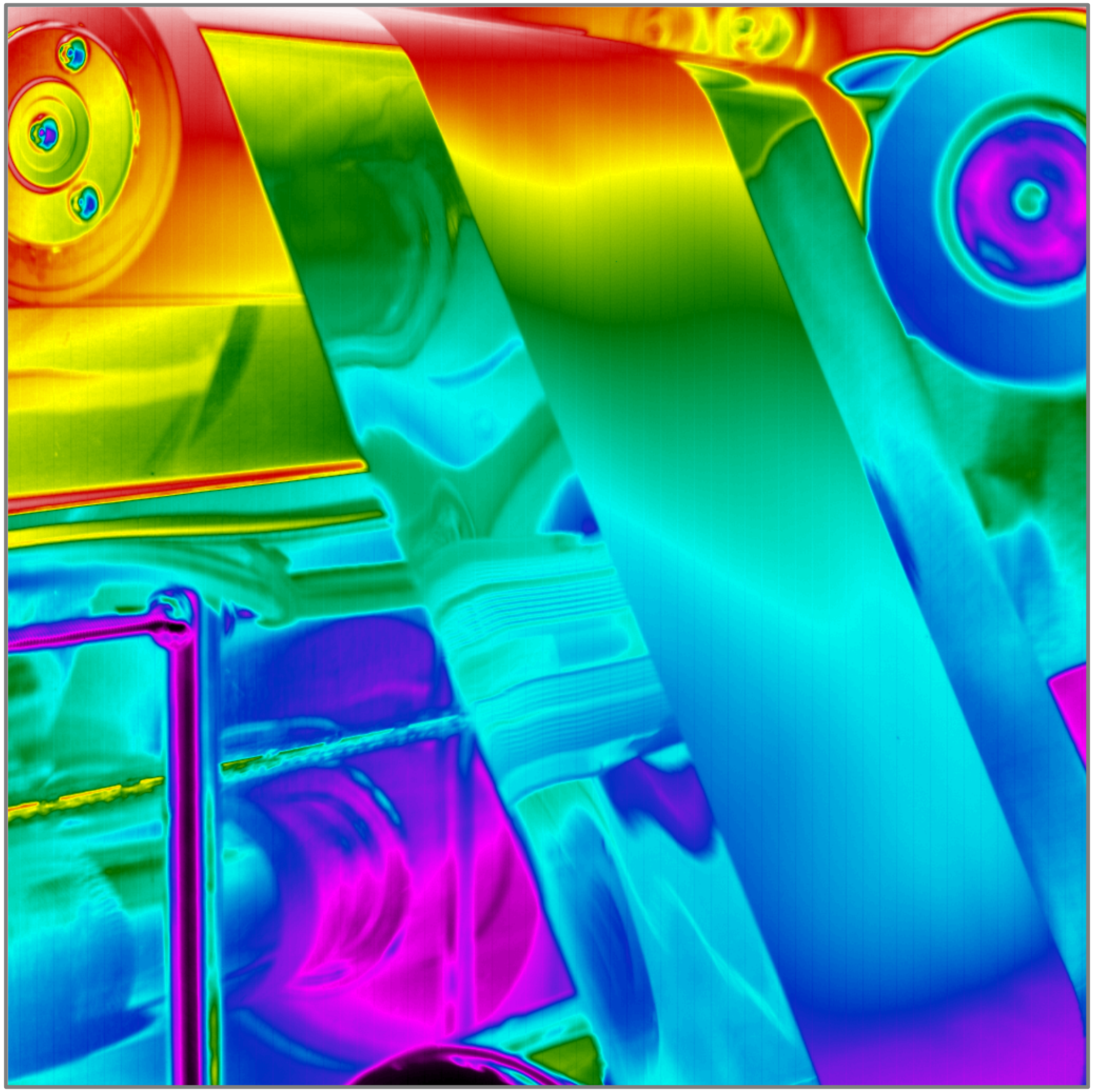
  - Shrikant Nagpure
  - Ralph Dinwiddie
  - Curt Maxey
  - Brad Brown

Technical Collaborators

- Guido Bender
- Michael Ulsh
- Bhushan Sopori
- Frank Reilly
- Mike Wixom
- Maneesh Bahadur
- David Telep
- Erin O'Driscoll

Information Dissemination and Commercialization

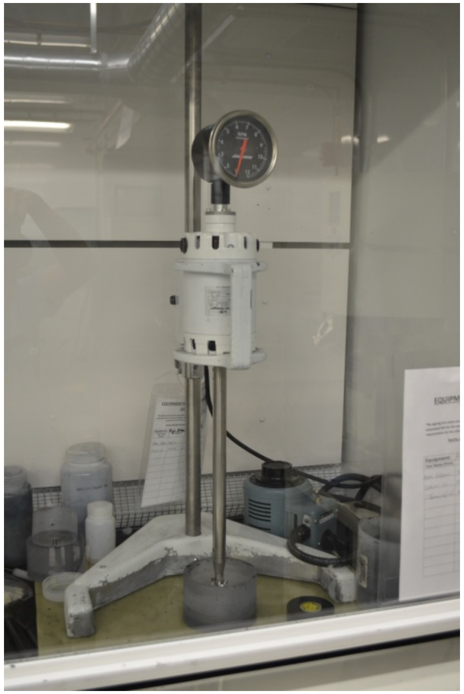
- Refereed Journal Papers
  1. D. Mohanty, S. Kalnaus, R.A. Meisner, K.J. Rhodes, E.A. Payzant, D.L. Wood, and C. Daniel, "Structural Transformation of a Lithium-Rich $Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$ Cathode During High Voltage Cycling Resolved by In-Situ X-Ray Diffraction," *Journal of Power Sources*, **229**, 239–248 (2013).
  2. 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*, **3**, 7479–7485 (2013).
  3. 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*, **1**, 6249–6261 (2013).
  4. D. Mohanty, A. Huq, E.A. Payzant, A. Safa-Sefat, J. Li, D.P. Abraham, D.L. Wood, and C. Daniel, "Neutron Diffraction and Magnetic Susceptibility Studies on a High-Voltage $Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}0O_2$ Lithium-Ion Battery Cathode; an Insight to the Crystal Structure," *Chemistry of Materials*, **25**, 4064–4070 (2013).
  5. D. Mohanty, A. Safa-Sefat, J. Li, R.A. Meisner, A.J. Rondinone, E.A. Payzant, D.P. Abraham, D.L. Wood, and C. Daniel, "Correlating Cation Ordering and Voltage Fade in a Lithium-Manganese-Rich Layered-Layered Lithium-Ion Battery Cathode Oxide; a Joint Magnetic Susceptibility and TEM Study," *Physical Chemistry Chemical Physics*, **15**, 19496–19509 (2013).
  6. D. Mohanty, J. Li, R. Born, L.C. Maxey, R.B. Dinwiddie, C. Daniel, and D.L. Wood, "Non-Destructive Evaluation of Slot-Die-Coated Lithium Secondary Battery Electrodes by In-Line Laser Caliper and IR Thermography Methods," *Analytical Methods*, **6**, 674–683 (2014).
  7. D. Mohanty, J. Li, A. Safa-Sefat, A. Huq, D.P. Abraham, E.A. Payzant, D.L. Wood, and C. Daniel, "Layer to Spinel Transformation Mechanisms in a Lithium-Rich High-Voltage Lithium-Ion Battery Cathode," *Advacned Energy Materials*, Submitted, 2014.
- Presentations (3 of 5)
  1. D. Mohanty, J. Li, C.L. Maxey, R.B. Dinwiddie, C. Daniel, and D. Wood, "In-Line Non-Destructive Testing of a Lithium-Ion Battery Electrode by Laser Caliper and Thermography," 2013 MRS Fall Meeting & Exhibit, Boston, Massachusetts, December 1-6, 2013.
  2. D. Mohanty, J. Li, A. Huq, E.A. Payzant, D.L. Wood, III, and C. Daniel, "Understanding Voltage Fade Mechanism in a Lithium and Manganese Rich Layered-Layered High-Voltage Lithium-Ion Battery Cathode by Neutron Diffraction Studies," 2013 MRS Fall Meeting & Exhibit, Boston, Massachusetts, December 1-6, 2013.
  3. D. Mohanty, J. Li, D.L. Wood, III, and C. Daniel, "Understanding the Structural Transformation in High-Voltage $Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$ Lithium-Ion Battery Cathode *via* Neutron Diffraction and Magnetic Susceptibility Studies," 2014 MRS Spring Meeting & Exhibit, San Francisco, California, April 21-25, 2014.



Thank you for your attention!

Technical Back-Up Slides

Electrode Dispersion Mixing and Current Collector Surface Treatment

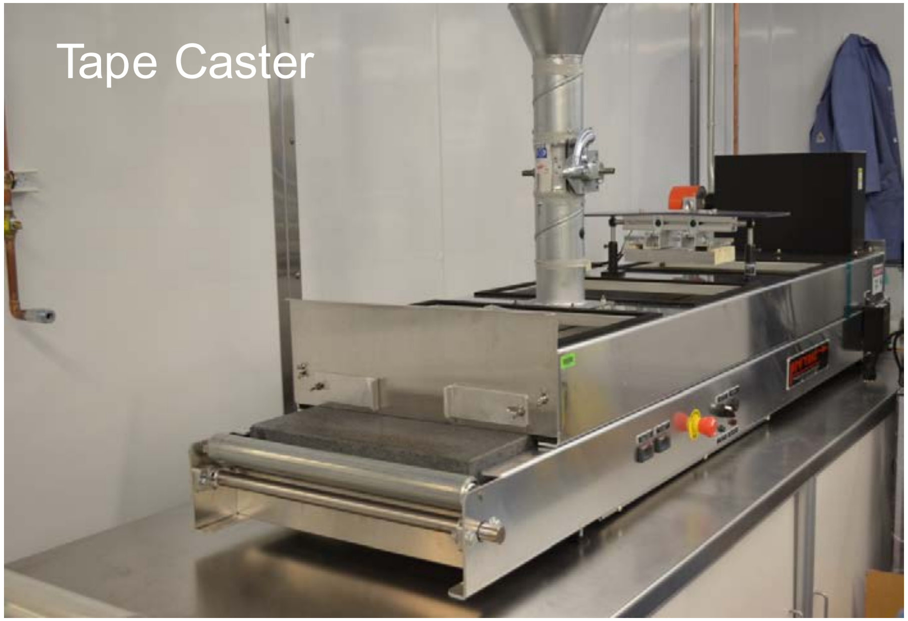


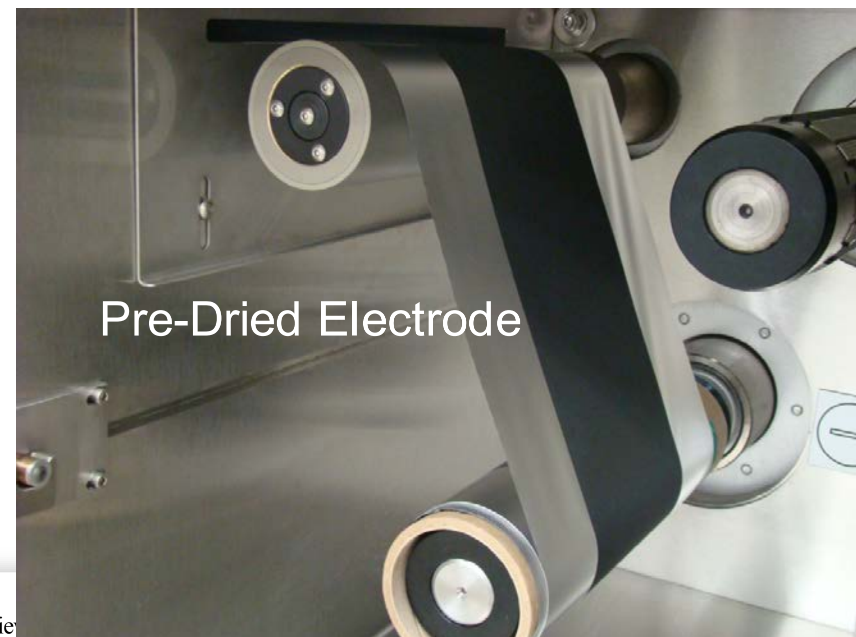
High-Shear Mixer (≤300 mL)

Planetary Mixer (≤2 L)

Corona Plasma Treater (Surface Energy Modification

Electrode Coating Equipment

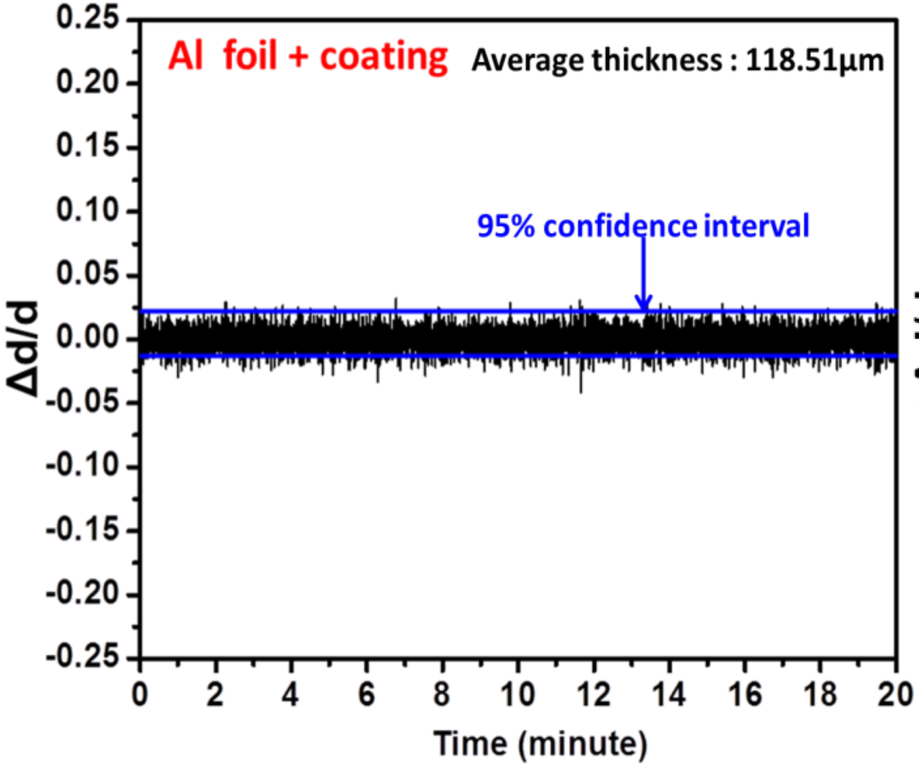


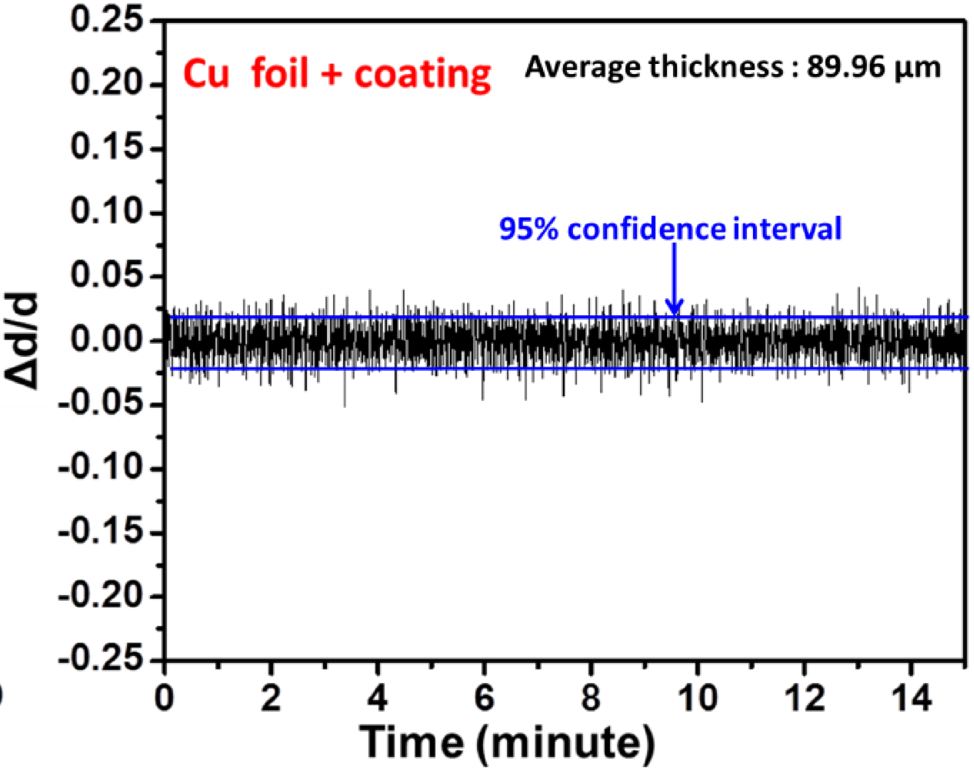


Overview of Lithium Ion Electrode QC State-of-the-Art

- 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.

Examples of Routine High Degree of Electrode Coating Uniformity



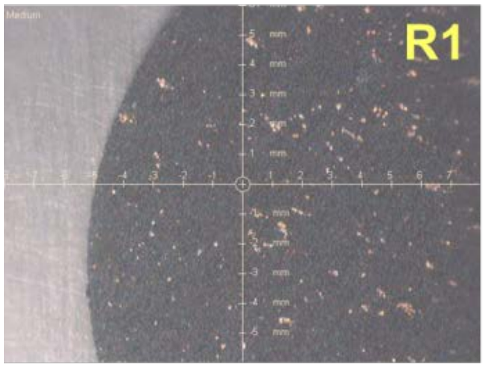


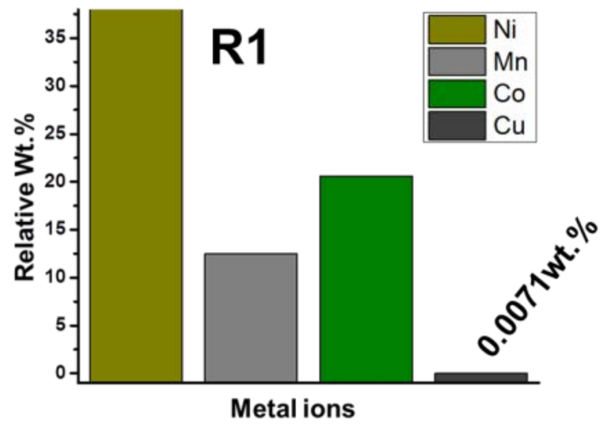
LMR-NMC TODA HE5050
Thickness = 118.5 ± 2.6 µm

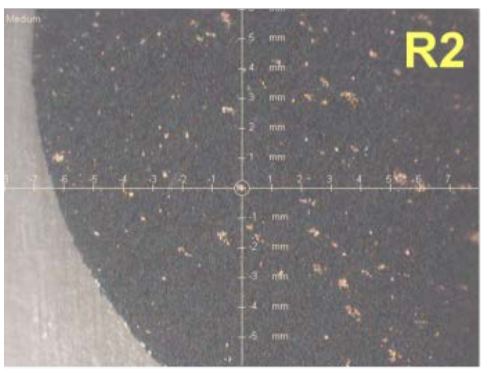
ConocoPhillips A12 Graphite
Thickness = 90.0 ± 1.3 µm

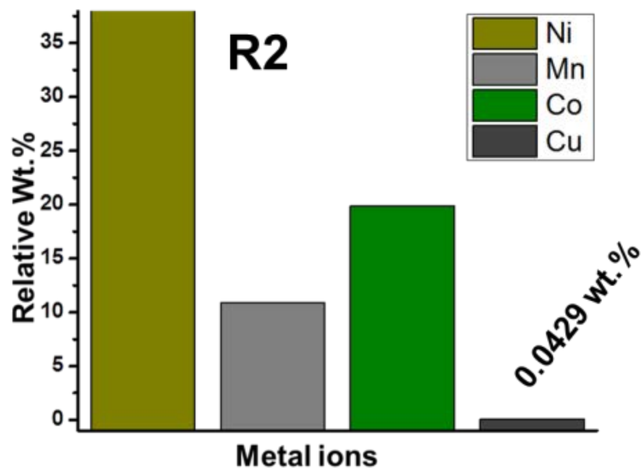
Where d is coating thickness and Δd is the difference between two continuous thickness values.

Technical Accomplishments – XRF Identification of Cu Powder Contaminants



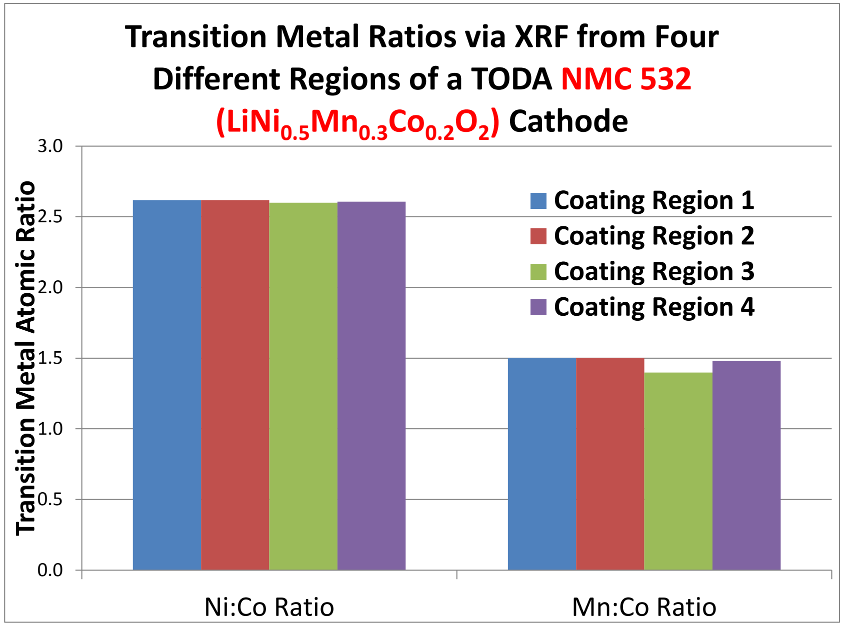


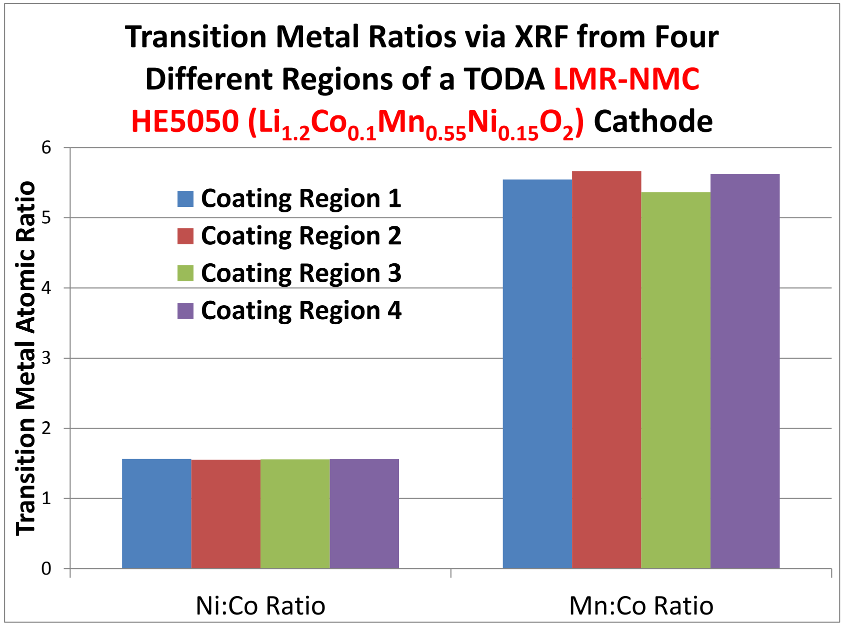




- A small amount of Cu powder was sprinkled over a NMC 532 cathode and identified by off-line XRF.
- Proof-of-concept established, but identification of isolated metal particles at high line speed by in-line XRF would be extremely difficult.

No-Go Decision Reached on Feasibility of In-Line XRF





Precision of measurement was excellent, but accuracy was a problem. Three separate areal weight measurements of NMC 532 areal weight:

Point 1 (Edge of the electrode)
Areal Loading: 10.92 mg/cm^2 (by weight) and 10.13 mg/cm^2 (by XRF); Error = 7%

Point 2 (Middle of the electrode)
Areal Loading: 11.94 mg/cm^2 (by weight) and 11.23 mg/cm^2 (by XRF); Error = 6%

Point 3 (Between Point 1 and 2)
Areal Loading: 11.70 mg/cm^2 (by weight) and 10.65 mg/cm^2 (by XRF); Error = 9%