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

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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

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

- 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)

Average coating thickness: 129 µm
Standard Deviation: 3.71 µm

Average coating thickness: 125 µm
Standard Deviation: 3.81 µm

Average coating thickness: 127 µm
Standard Deviation: 2.98 µm
CP A12 Graphite Anode Thickness Measurement

ABR Baseline Anode (Entire Run)

Average coating thickness: 162 µm
Standard Deviation: 3.61 µm

Average coating thickness: 161 µm
Standard Deviation: 3.54 µm

Average coating thickness: 162 µm
Standard Deviation: 4.26 µm

1

2

3

Cu foil

Average coating thickness: 162 µm
Standard Deviation: 3.61 µm
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)

Dry electrode exiting convective heating zones

IR Camera
IR Imaging Evaluation on ConocoPhillips A10/A12 Graphite Coating

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

• 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.

Desktop Unit for Off-line Measurement

Industrial Unit for In-Situ Measurement
**LMR-NMC (TODA HE5050) High-Voltage Cathode Challenges**

**Composition:**

\[
\text{Li}_{1.2}\text{Co}_{0.1}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{O}_2 + 0.5 \text{LiNi}_{0.27}\text{Mn}_{0.27}\text{Co}_{0.27}\text{O}_2 \cdot 0.5 \text{Li}_2\text{MnO}_3
\]

- \text{R-3m Trigonal}  
- (Hexagonal or Rhombohedral or O3)  
- \text{C2/m Monoclinic}

**Major obstacles**

1. Voltage decay/fade (≥4.5 V)
2. Impedance rise during holding at 4.5 V

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[Graphs and images showing voltage vs. capacity and impedance spectra with data points labeled.]
Advanced Materials Characterization Applied to Understanding High-Voltage Cathode Phase Transformation

Magnetic Susceptibility

TEM / SAED

\[ \mu_{\text{eff}} = 3.08 \, \mu_B \]

Layered trigonal and monoclinic reflection

\[ \mu_{\text{eff}} = 2.70 \, \mu_B \]

Layered+ Spinel (faint) reflections

\[ \mu_{\text{eff}} = 2.89 \, \mu_B \]

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.

Understanding LMR-NMC Voltage Fade via In-Situ XRD

- 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.

• 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
  – Equipment Suppliers: Ceres Technologies, Keyence, FLIR Systems
  – Battery Manufacturers: A123 Systems, Dow Kokam
  – Raw Materials Suppliers: TODA America, ConocoPhillips
  – National Labs: 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).

• 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.
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  • Frank Reilly
  • Mark Ewen
  • Maneesh Bahadur
  • David Telep
  • Erin O’Driscoll

Information Dissemination and Commercialization

• **Refereed Journal Papers**
  - 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.

• **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$_2$MnO$_3$·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$_2$MnO$_3$·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).
Thank you for your attention!

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)

Jianlin Li (Staff Researcher)  Bradley Brown (Lab Technician)