IR Thermography as a Non-Destructive Evaluation (NDE) Tool for Lithium-Ion Battery Manufacturing

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Project ID ES207
Overview

Timeline
• Project Start: 10/1/14
• Project End: 9/30/19
• Percent Complete: 10%

Barriers
• Barriers Addressed
  – By 2020, further reduce EV battery cost to $125/kWh.
  – USDRIVE PHEV40 ultimate target of 5000 cycles and EV ultimate target of 1000 cycles to 80% DOD.
  – USDRIVE PHEV40 and EV ultimate calendar life target of 15 years.
  – USDRIVE ultimate performance targets of 750 Wh/L and 350 Wh/kg for EV cells (C/3 discharge rate).

Budget
• Total project funding
  – $9050k
• $1475k in FY15

Interactions/Collaborations
- National Laboratories: NREL
- Battery Manufacturers: XALT Energy, Navitas Systems
- Equipment Manufacturer: Frontier Industrial Technology

Partners
• Project Lead: ORNL
Relevance & Objectives

- **Main Objective**: To utilize the *non-destructive* technique of active IR thermography to: 1) identify electrode coating defects critical to long-term cell performance; and 2) measure important electrode processing parameters *in line* such as porosity and thickness.

  - Identify electrode coating defects such as pinholes, blisters, divots, large agglomerates, metal particle contaminants, etc., so these areas can be marked as scrap (ORNL).
  
  - Scrap electrode can be discarded before it is assembled helping to reduce the number of rejected finished cells and lower pack production cost.
  
  - Use electrode thermal excitation and associated IR emissivity to determine thermal diffusivity and ultimately porosity in line (NREL).
  
  - Use active IR thermography to determine electrode thickness or areal weight uniformity across and down the web (ORNL and NREL).

  - **Leverage** FCTO funds on fuel cell component in-line NDE with VTO funds on battery electrode in-line NDE.

- **Relevance to Barriers and Targets**

  - Implementation of critical NDE/QC methods to reduce scrap rate by *creating feedback loops* based on IR thermography data input (to meet $125/kWh 2020 VTO storage goal for EVs).
  
  - Pre-assembly identification of various electrode coating defects to increase cell life (to achieve 5000 cycles for PHEVs and 1000 deep-discharge cycles for EVs by 2020).
## Project Milestones

<table>
<thead>
<tr>
<th>Status</th>
<th>Milestone or Go/No-Go</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>On Schedule</td>
<td>FY15 Milestone</td>
<td>Produce defect-free ABR baseline electrode coatings, made via aqueous processing, as confirmed by laser thickness measurement and IR thermography techniques; demonstrate comparable (to NMP/PVDF baseline) rate performance and cycle life for 50 0.2C/-0.2C cycles and 150 1C/-2C cycles with electrode coating lengths of at least 200 ft (SMART Milestone – 6/30/15).</td>
</tr>
<tr>
<td>On Schedule</td>
<td>FY16 Milestone</td>
<td>Quantify long-term capacity fade (1000 1C/-2C cycles) for at least three different types of anode and cathode coating defects in full 1-Ah pouch cells and publish findings (i.e. transfer technology to domestic LIB manufacturers) (SMART Milestone – 6/30/16).</td>
</tr>
<tr>
<td>On Schedule</td>
<td>FY16 Milestone</td>
<td>Verify performance of an optimally configured active IR thermography system using ABR baseline anodes and cathodes with known thickness, porosity, and bulk density differences on the ORNL slot-die coating line (Stretch Milestone – 9/30/16).</td>
</tr>
</tbody>
</table>
Project Approach

- Problems:
  - Electrode coating defects are currently identified by optical CCD cameras, which miss many of the subtle inhomogeneities.
  - A low-cost method for in-line thickness and porosity is needed for electrode coating QC.
  - Useful feedback loops must be developed based on IR thermography input information to prevent coating defects and inhomogeneities.

- Overall technical approach and strategy:
  1. Use white light or thermal excitation of electrode coatings to generate a IR emissivity signature from electrode coatings.
  2. Take measured IR emissivity and correlate it to a coating T profile for input into a mathematical model based on electrode physical properties (IR absorbance, heat capacity, thermal conductivity, bulk density, etc.). Or experimentally obtained calibration curves could be used.
  3. Use model and measured heat loss down the web to generate porosity and thickness profiles.
Approach – In-Line Electrode Porosity Measurement Using Active IR Thermography

**Micro-scale** representation of battery cathode:

- particles
- air voids
- binder (PVDF)
- metal foil

**Macro-scale** modeling:

- Modeling bulk (cm-length scale) material properties and heating-source/IR-thermography experimental setup.
- Effective properties of the electrode are transferred to macro-scale model from the micro-scale representation.
- Numerical solution to a heat equation is computed to predict temperature distribution in the moving electrode.

A laminate of particle composite and metal backing is assumed for the material structure. To predict anisotropic thermal properties:

1. Mori-Tanaka based estimates for the particle composite are employed.
2. Series and parallel resistance equations for the laminate are used.
Technical Accomplishments – Executive Summary (FY15 Q1-2)

- Six different electrode coating defect types have been made, measured, and tested in full coin cells using the ORNL IR thermography setup.

- **Porosity** proof-of-concept experiments were completed at progressively more realistic conditions:
  - Stationary, steady state
  - Stationary, transient temperature decay
  - Line speed = 0.5 ft/min, pseudo-steady-state
  - Samples investigated → 1) thinner, high-porosity NMC 532; 2) thicker, low-porosity NMC 532; 3) thinner low-porosity CP A12; 4) thicker high-porosity CP A12

- Mathematical modeling results:
  - Comparison of modeling results with experimental measurements
  - Hypothetical samples (why anode responses were the same)
  - Effect of porosity on the temperature profile
  - Effect of thickness on the temperature profile
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 have been studied to determine relative importance.

- Exaggerated Non-Uniform Coating
- Metal Particle Contaminants
- Electrode Agglomerates
- Electrode Pinholes
- Electrode Divots
- Electrode Blisters

Diversity of Coating Defects
Technical Accomplishments – Pseudo-Steady-State Experimental Results (0.5 ft/min)

- Cathodes responded differently due to dissimilar electrode architectures, and temperature profiles of the anodes were identical despite the different porosities.
- Modeling clearly showed that differences in cathode porosity and thickness added up constructively to give strong measurable differences in temperature profiles.
- Anode behavior was likely due to cancelling out of thickness and porosity effects (and higher active-material thermal conductivity). The system sensitivity must be improved to measure these differences.
Technical Accomplishments – Material Properties and Modeling Electrode Structure

- The properties listed are for nonporous, solid forms of the materials.
- Properties of NMC532 (LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$) were not explicitly available. Assumed values correspond to averages for metal oxides (NiO, MnO, CoO).

<table>
<thead>
<tr>
<th>name</th>
<th>$K$ [W/(m K)]</th>
<th>$c_p$ [J/(kg K)]</th>
<th>$\rho$ [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMC532</td>
<td>40.</td>
<td>48.33</td>
<td>4770.</td>
</tr>
<tr>
<td>Graphite</td>
<td>140.</td>
<td>710.</td>
<td>2260.</td>
</tr>
<tr>
<td>Denka Black</td>
<td>140.</td>
<td>710.</td>
<td>2250.</td>
</tr>
<tr>
<td>SuperPLi Carbon Black</td>
<td>140.</td>
<td>710.</td>
<td>2250.</td>
</tr>
<tr>
<td>Air</td>
<td>0.02587</td>
<td>1007.</td>
<td>1.275</td>
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<tr>
<td>PVDF5130</td>
<td>0.2</td>
<td>1530.</td>
<td>1750.</td>
</tr>
<tr>
<td>PVDF9300</td>
<td>0.2</td>
<td>1530.</td>
<td>1750.</td>
</tr>
<tr>
<td>Copper</td>
<td>400.</td>
<td>384.4</td>
<td>8960.</td>
</tr>
<tr>
<td>Aluminum</td>
<td>235.</td>
<td>904.</td>
<td>2700.</td>
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</tbody>
</table>

**Type:**

**Cathode**

**Top layer:**

<table>
<thead>
<tr>
<th>name</th>
<th>weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMC532</td>
<td>0.9</td>
</tr>
<tr>
<td>Denka Black</td>
<td>0.05</td>
</tr>
<tr>
<td>PVDF5130</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Bottom layer:** 15μm thick aluminum

**Anode**

<table>
<thead>
<tr>
<th>name</th>
<th>weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.92</td>
</tr>
<tr>
<td>SuperPLi Carbon Black</td>
<td>0.02</td>
</tr>
<tr>
<td>PVDF9300</td>
<td>0.06</td>
</tr>
</tbody>
</table>

9μm thick copper
Technical Accomplishments – Micro-Scale Modeling of the Electrode (Mori-Tanaka)

Micro-scale modeling objective:

- Specific heat capacity:
  \[ C_p = \sum_{i} w_f_i \cdot C_{p_i} \]

- Density:
  \[ \rho = \left( \sum_{i} \frac{w_f_i}{\rho_i} \right)^{-1} \]

- Thermal conductivity: more complex…

Homogenous layer with the same effective properties calculated as a function of porosity and layer thickness
Technical Accomplishments – Extensions of Eshelby Model for Composite Thermal Conductivity

• Eshelby\(^1\) calculated analytically stresses around an ellipsoidal inclusion embedded in a matrix

• Mori-Tanaka and others\(^2\) extended the model to predict thermal heat flow and to take into account multiple inclusions of different types and derived the following formula for spherical inclusions:

$$T_i^{\text{sph}} = \frac{3 \ K_{\text{matrix}}}{2 \ K_{\text{matrix}} + K_i}$$

$$K_{\text{composite}} = \frac{\nu f_{\text{matrix}} K_{\text{matrix}} + \sum_i \nu f_{i}^{\text{inclusion}} K_i^{\text{inclusion}} T_i^{\text{sph}}}{\nu f_{\text{matrix}} + \sum_i \nu f_{i}^{\text{inclusion}} T_i^{\text{sph}}}$$

where \(K\) is thermal conductivity and \(\nu f\) is volume fraction; index \(i\) denotes \(i\)-th inclusion.

Technical Accomplishments – Macro-Scale FEM Simulations

Macro-scale (centimeter length scale) modeling is needed to predict temperature in a battery electrode moving underneath a linear heat source as a function of the electrode thickness and porosity.

Two versions of the heat equation were implemented:
• transient (speed=0, light is tuned on and then turned off after 40 sec)

\[
\begin{align*}
&c_p[y] \cdot \rho[y] \cdot \partial_t T[t, x, y] - K[y] \nabla^2_{x,y} T[t, x, y] = \\
&\text{NeumannValue}[Q_cv[t, x, y] + Q_{light}[x] \cdot \text{lightOff}[t], y = 0] + \text{NeumannValue}[Q_cv[t, x, y], y = -\text{thRod}] \\
&T[0, x, y] = T_f \\
&\text{DirichletCondition}[T[t, x, y] = T_f, x = 0 \mid x = L]
\end{align*}
\]

• standing wave case (speed \(ux=0.5\) ft/min, light is on all the time)

\[
\begin{align*}
&-ux \cdot c_p[y] \cdot \rho[y] \cdot \partial_x T[x, y] - K[y] \nabla^2_{x,y} T[x, y] = \\
&\text{NeumannValue}[Q_cv[x, y] + Q_{light}[x], y = 0] + \text{NeumannValue}[Q_cv[x, y], y = -\text{thRod}] \\
&\text{DirichletCondition}[T[x, y] = T_f, x = 0 \mid x = L]
\end{align*}
\]
Technical Accomplishments – Standing Wave Comparison with Experiment (Cathodes)

- Speed 0.5 ft/min
- Steady-state distribution of temperature was analyzed

Exactly the same effect was found with the model as in the experimental IR thermography measurements.

The difference between the maximum temperature is about two times larger in the experiment than in the model.
Technical Accomplishments – Standing Wave Comparison with Experiment (Anodes)

- Speed 0.5 ft/min
- Steady-state distribution of temperature was analyzed

For the two anodes, the same T profiles were obtained with the model despite the fact that the samples had different thickness and porosity.

The same behavior was observed in the experiment.
Technical Accomplishments – Modeling of Hypothetical Anodes (Offsetting Properties)

- The anode samples behaved differently than the cathodes. A12_SBR had both higher thickness and porosity compared to A12_TRD.
- Larger porosity causes increase in $T_{\text{max}}$; however, increase in thickness reduces $T_{\text{max}}$.
- These two effects are of opposite sign and similar magnitude and, therefore, they cancel each other, resulting in the same $T$ distribution for the two anode samples.
Technical Accomplishments – Correlating $T_{\text{max}}$ to Electrode Porosity Range

- The model shows that for the two considered cases $T_{\text{max}}$ changes almost linearly over entire range of porosities.
- Calibration of the QC (in-line porosity) measurement system will be simplified due to the nearly linear relationship of $T_{\text{max}}$ vs. porosity.
- Our model also allows for plotting heat capacity, thermal conductivity, and density of the electrode as a function of porosity.
Collaborations

• Partners
  – **Equipment Suppliers:** Frontier Industrial Technology
  – **Battery Manufacturers:** XALT Energy, Navitas Systems
  – **National Labs:** NREL

• Collaborative Activities
  – Vetting of NDE methods in this work with coating line supplier Frontier Industrial Technology and battery makers XALT Energy and Navitas Systems.
  – Leveraging of NREL FCTO funds to develop NDE and QC methods for PEM fuel cell components with ORNL VTO funds to develop NDE and QC methods for lithium-ion electrodes.
  – Long-term plans to publish in-line IR thermography techniques for measuring electrode porosity and thickness for implementation by U.S. battery manufacturing industry.
## Future Work

<table>
<thead>
<tr>
<th>FY</th>
<th>Type</th>
<th>Activity</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>Experimental</td>
<td>Double incident heating power for higher line speeds</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Use semiconductor cameras (InGaAs and InSb) and compare measurement noise</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Use new sample holder to avoid contact on the back side</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Look at effect of line speed</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Modeling</td>
<td>Tune heating power, convection coefficient, and other parameters of model, so simulation and experimental T curves overlap</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Simplify finite element representation if possible</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Check micro-scale model using finite element method (FEM)</td>
<td>7</td>
</tr>
<tr>
<td>2016</td>
<td>Experimental</td>
<td>Measure independently thermal conductivity of electrodes</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Modeling</td>
<td>Evaluate line speed and light power effects on required T measuring accuracy and precision</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Develop a better figure of merit representing the entire T profile (better than $T_{\text{max}}$)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evaluate response in 2D parametric space</td>
<td>11</td>
</tr>
</tbody>
</table>

- To hit FY16 stretch milestone (Slide 4), a prototype system will be installed on the NREL R2R equipment, which will lead to development of a system that can be constructed for the ORNL slot-die coating line.
Summary

- **Objective:** Utilization of non-destructive technique of active IR thermography to: 1) identify electrode coating defects critical to long-term cell performance; and 2) measure important electrode processing parameters in line such as porosity and thickness.

- **Approach:** Move state-of-the-art electrode QC beyond beta gauge and CCD cameras
  - Develop low-cost method for in-line thickness and porosity for optimal electrode coating QC
  - Develop feedback loops based on IR thermography input to prevent coating defects and inhomogeneities

- **Technical:** Two IR thermography approaches from ORNL and NREL are being unified and combined with modeling to yield a comprehensive technique that will give in-line porosity and/or thickness plus identify coating defects.

- All FY15-16 milestones are on schedule.

- **Collaborators:** NREL, XALT Energy, Navitas Systems, and Frontier Industrial Technology

- **Commercialization:** Publication of methods and results for implementation by U.S. battery manufacturers.
Acknowledgements

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

• Other ORNL/NREL Contributors:
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  • Seong Jin An
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• Technical Collaborators
  • Mike Wixom
  • Fabio Albano
  • David Telep
  • Jerry Forbes
Information Dissemination and Commercialization

• Refereed Journal Paper

• Presentations
Thank you for your attention!
Technical Back-Up Slides
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).


• Without feedback loops to electrode dispersion mixing and deposition steps, coating 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”).
Electrode Coating Equipment

- Tape Caster
- Slot-Die Coating Line
- Pre-Dried Electrode

- 9 Heating Zones
- 2 IR Lamps
- 7 Convective Air Zones
### Thermal Conductivity of Electrode

- Based on the literature the expected value for cathode’s top layer is 5 W/(m K)
- A few Eshelby based approaches were considered:

<table>
<thead>
<tr>
<th>Model considered</th>
<th>Matrix</th>
<th>Inclusions introduced using Eshelby model</th>
<th>Effective K of the composite with 50% porosity [W/(m K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>NMC532, Denka Black, PVDF</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>NMC532</td>
<td>Air, Denka Black, PVDF</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Parallel configuration of NMC532, Denka Black, PVDF</td>
<td>Air</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>Parallel configuration of NMC532, Denka Black and fraction PVDF in serial connection with the rest of PVDF (binding PVDF)</td>
<td>Air</td>
<td>Depends on the binder fraction; 5.0 for 10% of binding PVDF</td>
</tr>
</tbody>
</table>

- Model #4 gives the best estimate and was chosen for all subsequent calculations
Thermal Conductivity of Electrode

Graphical representation of the micro-scale modeling procedure #4:

• The model captures the fact that the matrix is solid and that there is a poorly conducting binder between particles.

• Assumed spherical shape of the air inclusions should not have a great impact on the effective thermal conductivity of composite.
Macro-Scale FEM Simulations

- The model consists of homogeneous top layer and metal foil at the bottom.
- The effective properties of the top layer of electrode are transferred from the micro-scale representation to the macro model.

As an example, a distribution of $K$ is shown below:

- 2D finite element representation: