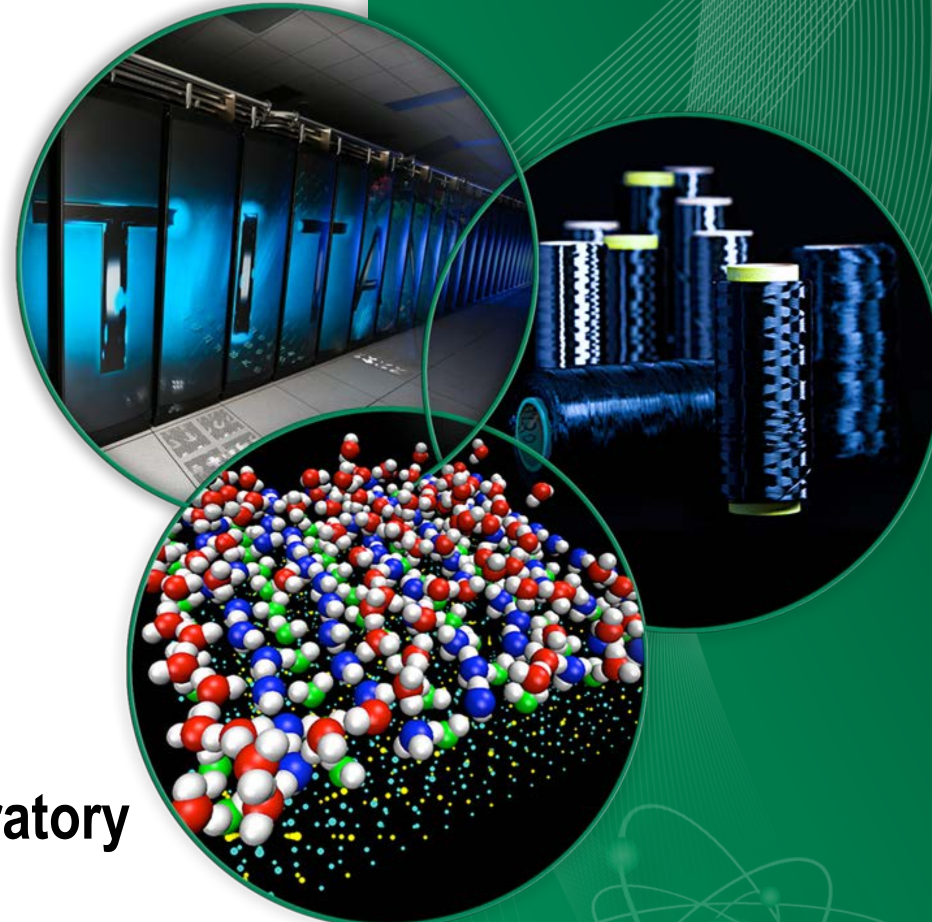
IR Thermography as a Non-Destructive Evaluation (NDE) Tool for Lithium-Ion Battery Manufacturing



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June 10, 2015

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

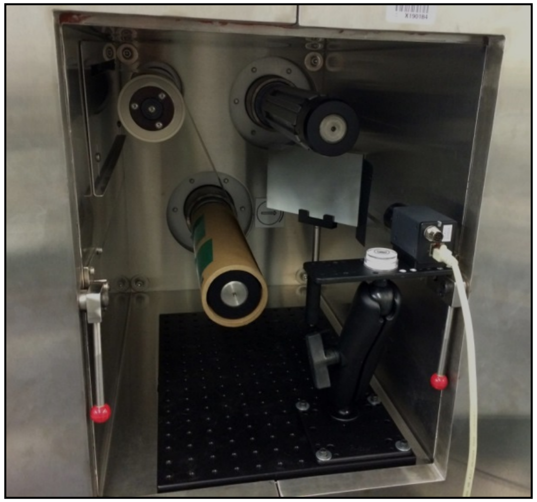
Partners

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

Relevance & Objectives

Vehicle Technologies Office
Fuel Cell Technologies Office

- 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.**



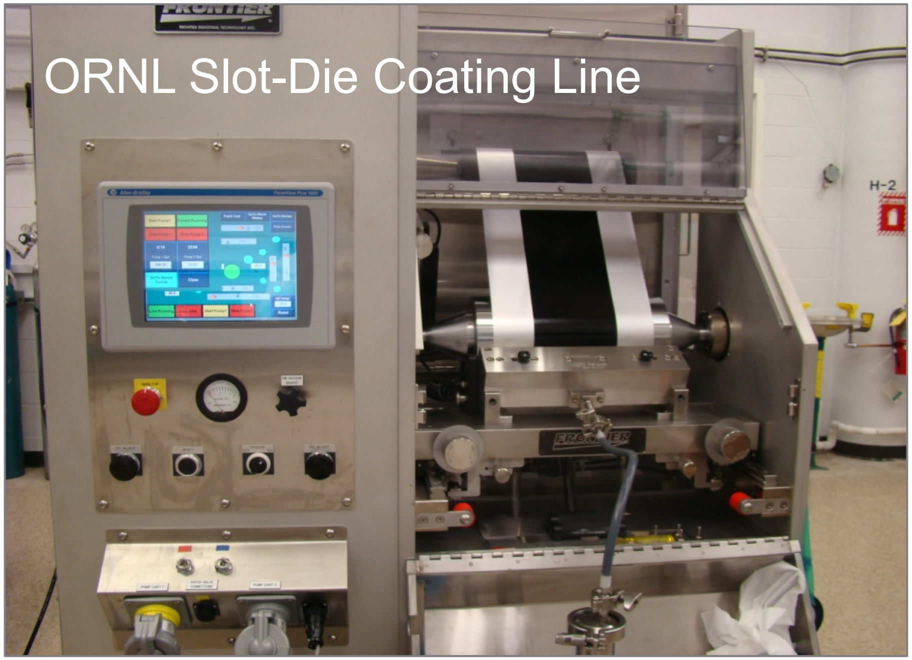
- Relevance to Barriers and Targets
  - Implementation of critical NDE/QC methods to reduce scrap rate by ***creating feedback loops*** based on IR thermography data input (to meet $125/kWh 2020 VTO storage goal for EVs).
  - Pre-assembly identification of various electrode coating defects to increase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

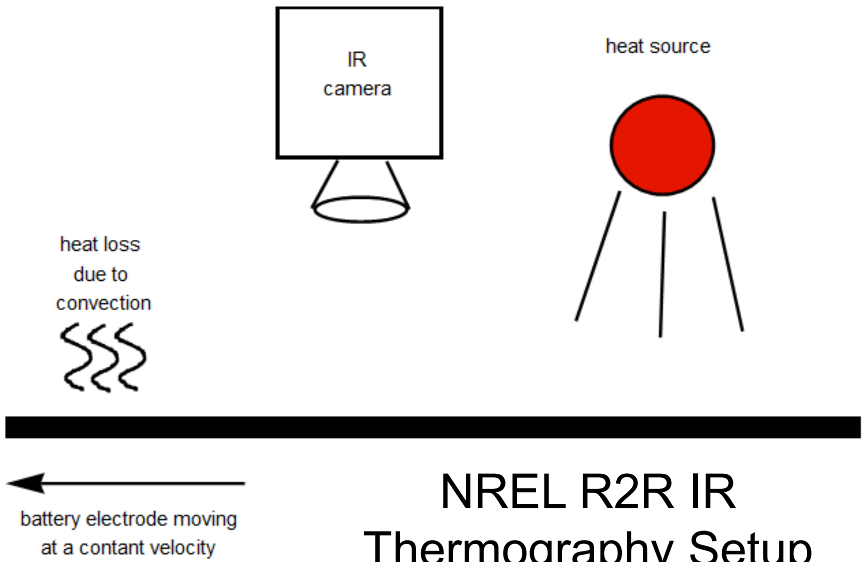
Project Milestones

Status	Milestone or Go/No-Go	Description
On Schedule	FY15 Milestone	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).
On Schedule	FY16 Milestone	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).
On Schedule	FY16 Milestone	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).

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.

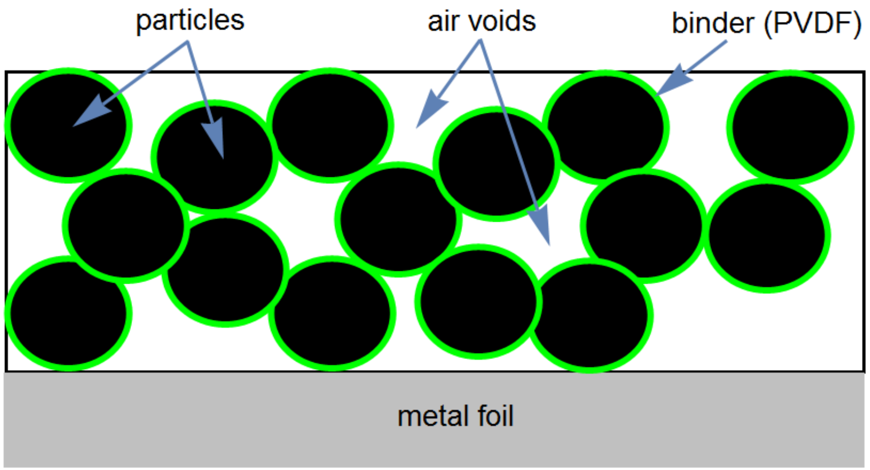




NREL R2R IR Thermography Setup

Approach – In-Line Electrode Porosity Measurement Using Active IR Thermography

Micro-scale representation of battery cathode:



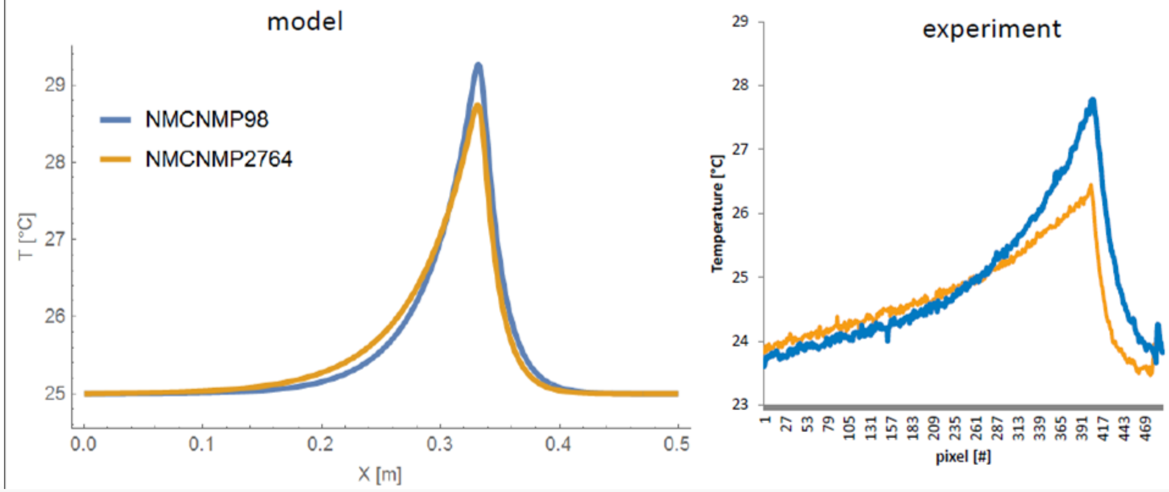
Macro-scale modeling:

- 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.

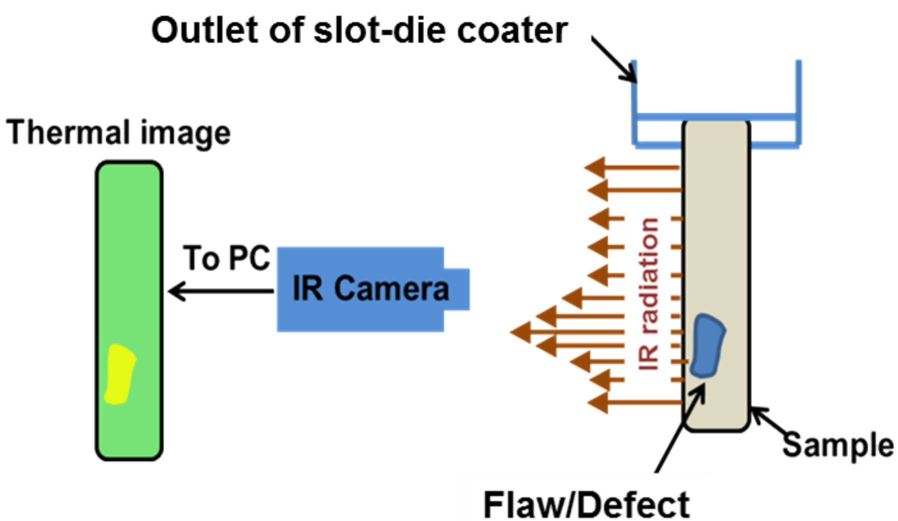
- Speed 0.5 ft/min
- Steady-state distribution of temperature is analyzed

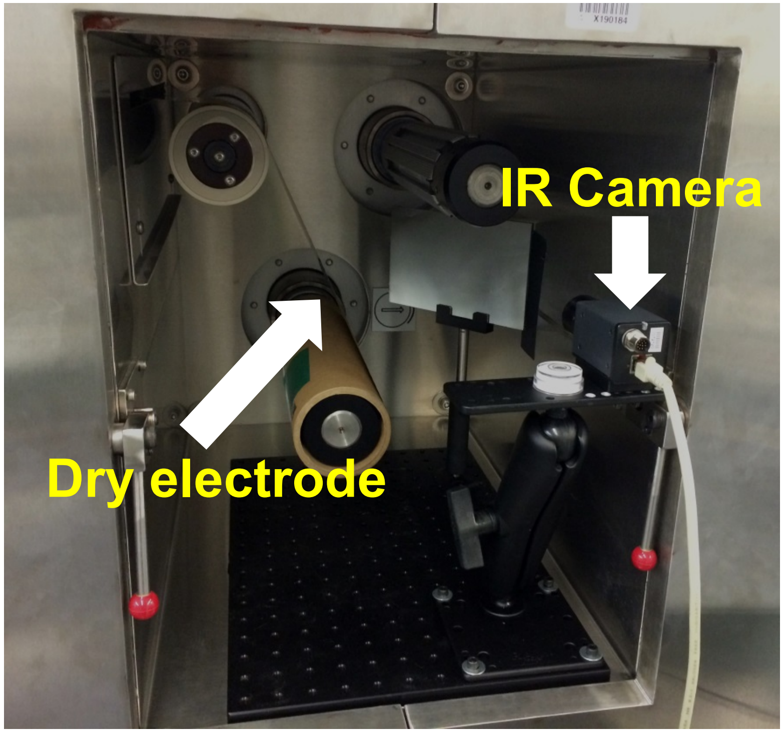


Technical Accomplishments – Executive Summary (FY15 Q1-2)

- 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

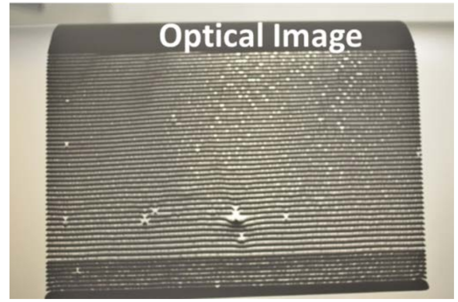
Technical Accomplishments – Systematic Study of Electrode Coating Defects

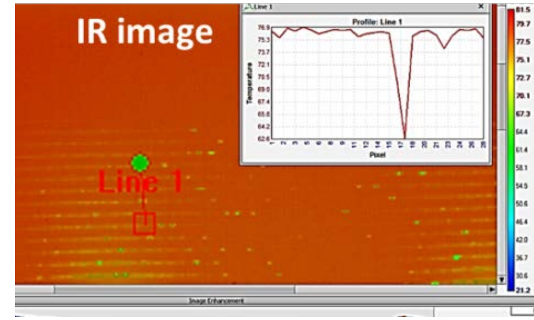
6 types of defects have been studied to determine relative importance.

Diversity of Coating Defects

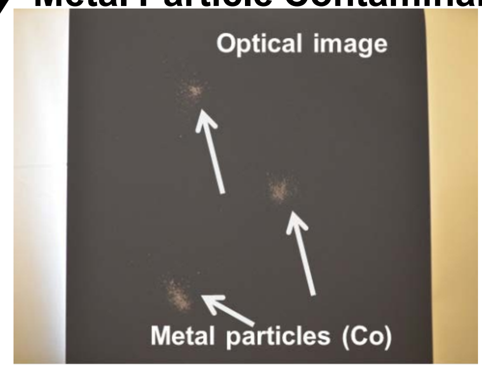
- Exaggerated Non-Uniform Coating
- Metal Particle Contaminants
- Electrode Agglomerates
- Electrode Divots
- Electrode Pinholes
- Electrode Blisters

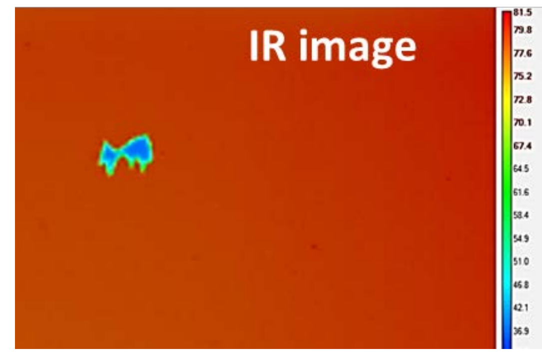
Exaggerated Non-Uniform Coating



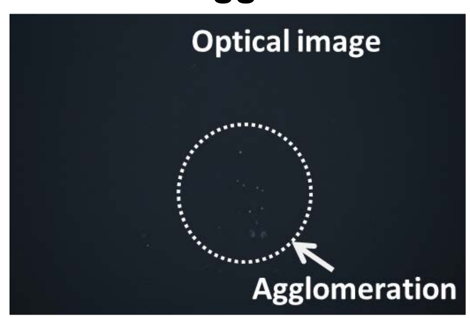


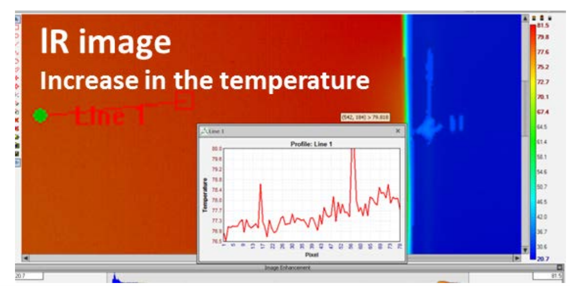
Metal Particle Contaminants





Electrode Agglomerates





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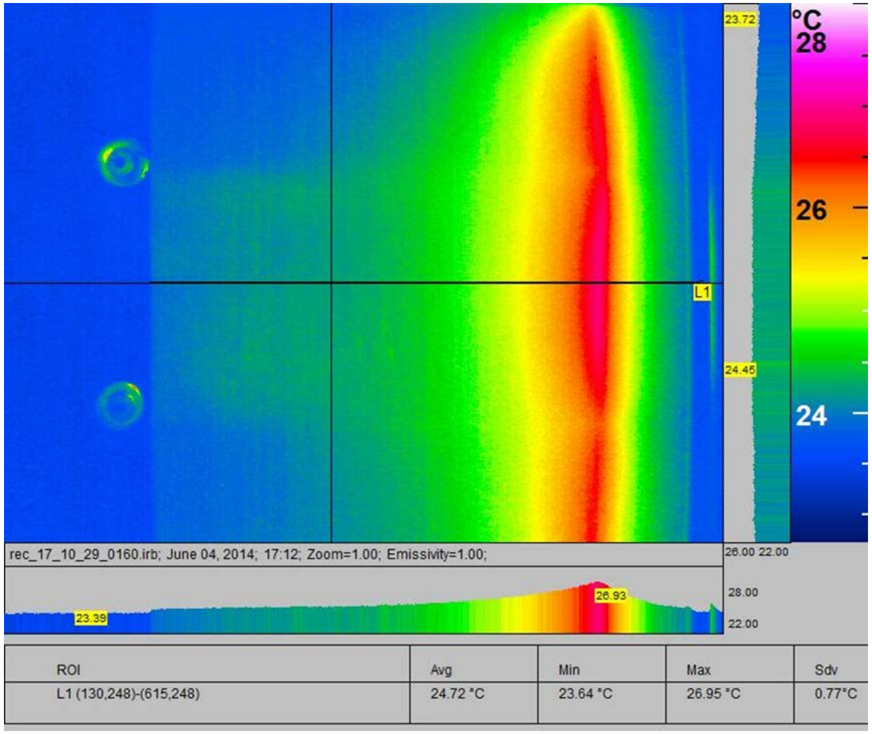
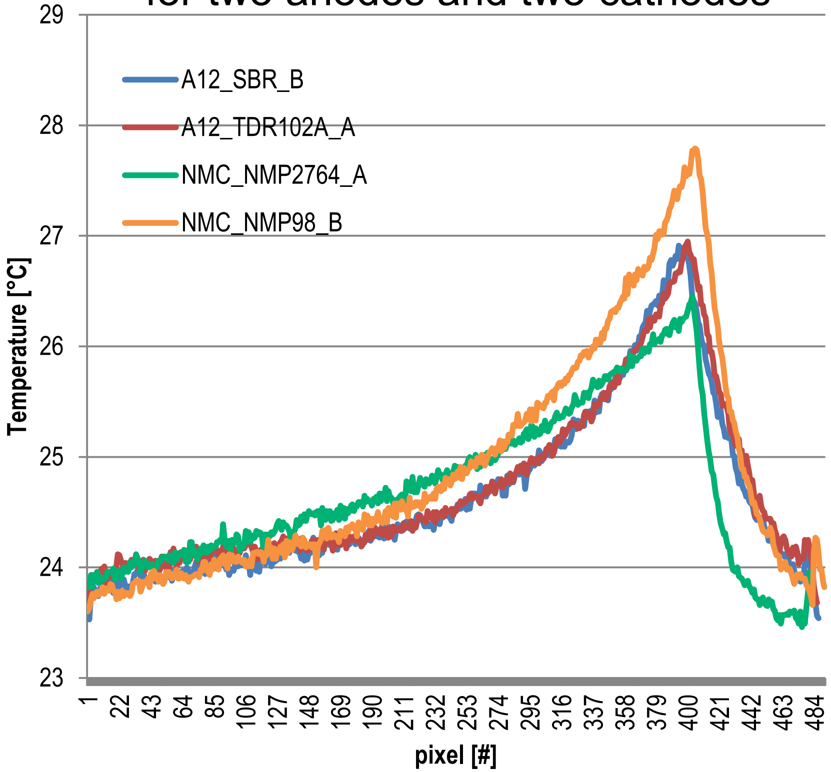
Technical Accomplishments – Pseudo-Steady-State Experimental Results (0.5 ft/min)

Temperature distribution of A12_SBR_B



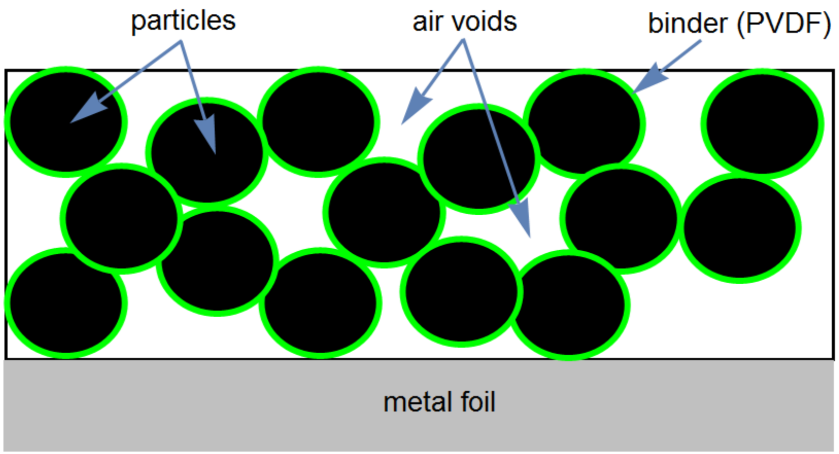
Sample moves to the left. On the right hand side the specimen is screened by the light source.

Temperature profiles along line L1 for two anodes and two cathodes



- 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



name	K [W/(m K)]	c_p[J/(kg K)]	ρ [kg/m³]
NMC532	40.	48.33	4770.
Graphite	140.	710.	2260.
Denka Black	140.	710.	2250.
SuperPLi Carbon Black	140.	710.	2250.
Air	0.02587	1007.	1.275
PVDF5130	0.2	1530.	1750.
PVDF9300	0.2	1530.	1750.
Copper	400.	384.4	8960.
Aluminum	235.	904.	2700.
2 levels | 36 elements			

- 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).

Type: **Cathode** | **Anode**

Top layer:

Cathode:

name	weight fraction
NMC532	0.9
Denka Black	0.05
PVDF5130	0.05
2 levels | 6 elements	

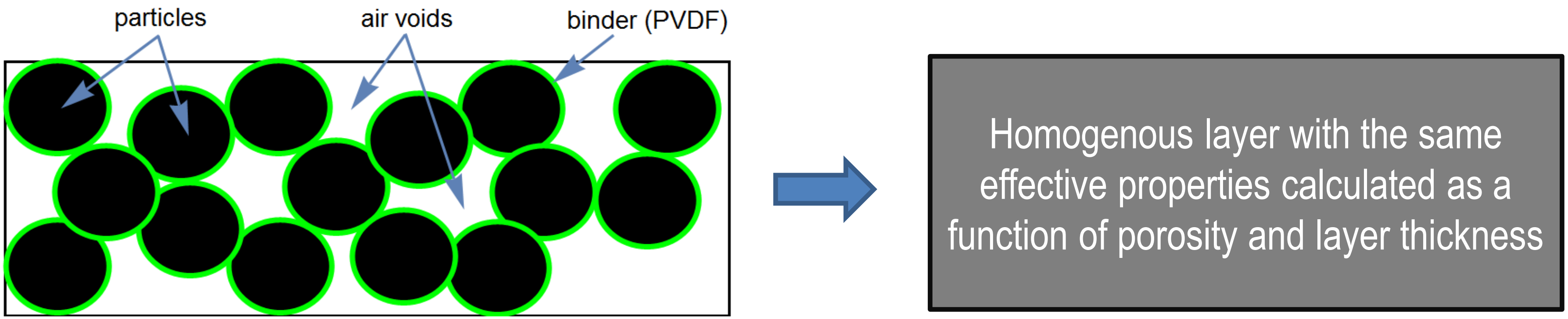
Anode:

name	weight fraction
Graphite	0.92
SuperPLi Carbon Black	0.02
PVDF9300	0.06
2 levels | 6 elements	

Bottom layer: 15μm thick aluminum (Cathode); 9μm thick copper (Anode)

Technical Accomplishments – Micro-Scale Modeling of the Electrode (Mori-Tanaka)

Micro-scale modeling objective:



- Specific heat capacity: $$C_p = \sum_i wf_i \cdot C_{pi}$$
- Density: $$\rho = \left(\sum_i \frac{wf_i}{\rho_i} \right)^{-1}$$
- Thermal conductivity: more complex…

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:

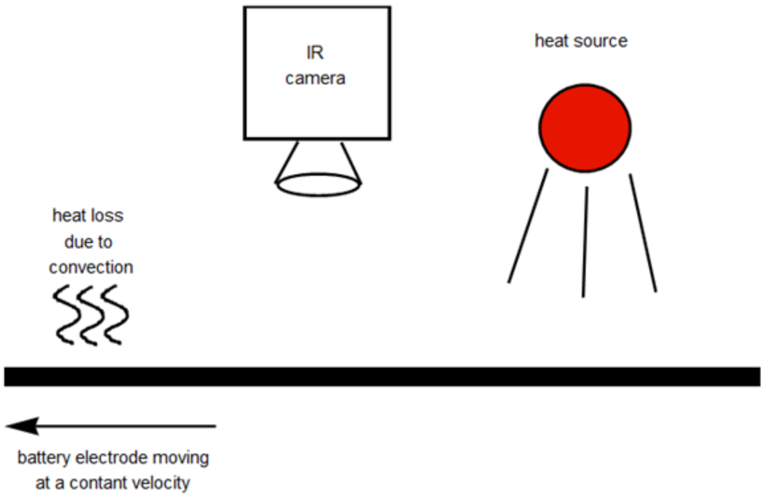
$$T_i^{sph} = \frac{3\,K^{matrix}}{2\,K^{matrix} + K_i^{inclusion}}$$

$$K^{composite} = \frac{vf^{matrix}\,K^{matrix} + \sum_i vf_i^{inclusion}\,K_i^{inclusion}\,T_i^{sph}}{vf^{matrix} + \sum_i vf_i^{inclusion}\,T_i^{sph}}$$

where K is thermal conductivity and vf is volume fraction; index i denotes i-th inclusion.

1) Eshelby, J. D. “The Determination of the Elastic Field of an Ellipsoidal Inclusion, and Related Problems.” doi:10.1098/rspa.1957.0133.
2) Stránský, Jan, Jan Vorel, Jan Zeman, and Michal Šejnoha. “Mori-Tanaka Based Estimates of Effective Thermal Conductivity of Various Engineering Materials.” doi:10.3390/mi2020129.

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)

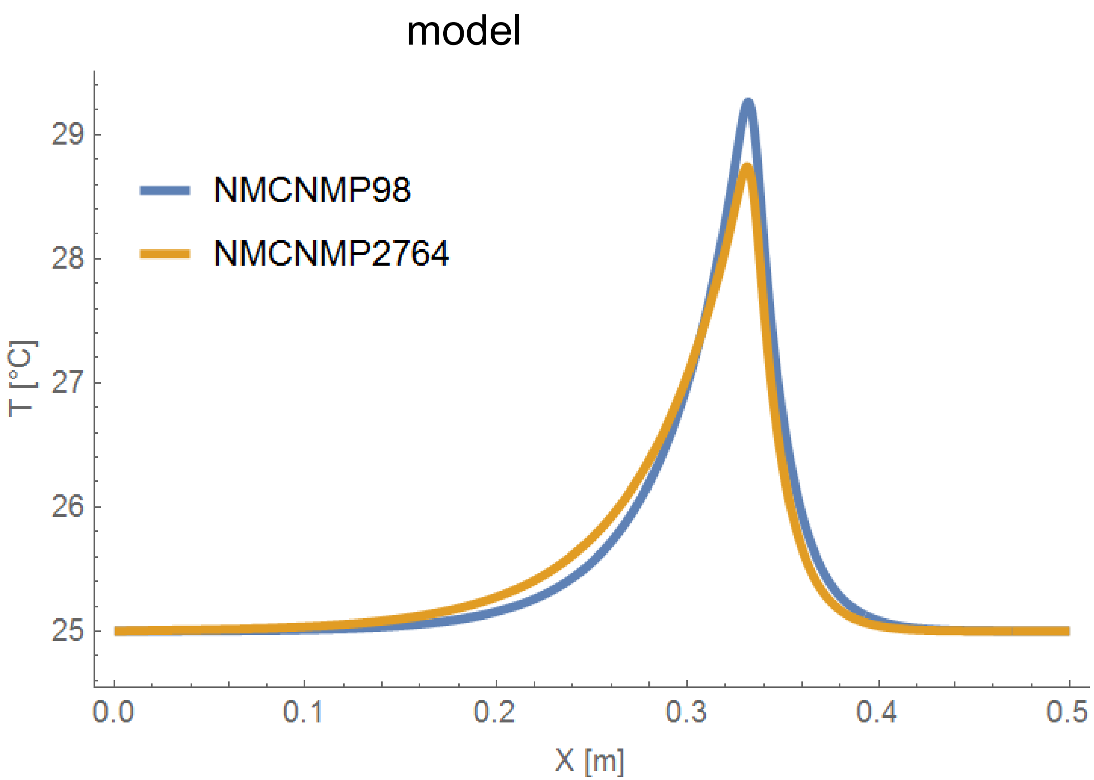
$$\mathrm{cp}[y]*\rho[y]*\partial_t \mathrm{T}[t,\ x,\ y] - \mathrm{K}[y]\ \nabla^2_{\{x,y\}}\mathrm{T}[t,\ x,\ y] ==$$
$$\mathrm{NeumannValue}[-\mathrm{Qcv}[t,\ x,\ y] + \mathrm{Qlight}[x]*\mathrm{lightOff}[t],\ y == 0] + \mathrm{NeumannValue}[-\mathrm{Qcv}[t,\ x,\ y],\ y == -\mathrm{thRod}]$$
$$\mathrm{T}[0,\ x,\ y] == \mathrm{Tf}$$
$$\mathrm{DirichletCondition}[\mathrm{T}[t,\ x,\ y] == \mathrm{Tf},\ x == 0\ ||\ x == \mathrm{L}]$$

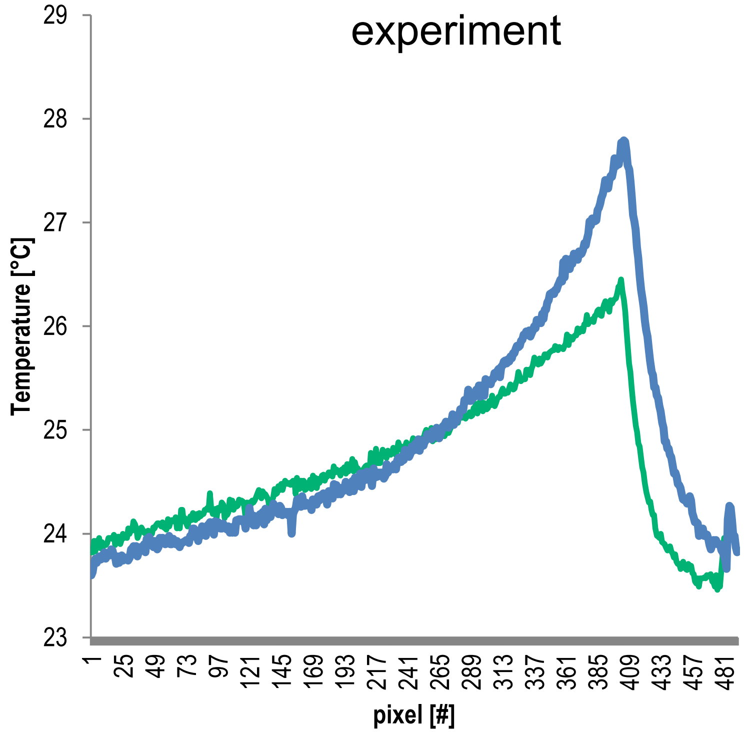
- standing wave case (speed ux=0.5 ft/min, light is on all the time)

$$-\mathrm{ux}*\mathrm{cp}[y]*\rho[y]*\partial_x \mathrm{T}[x,\ y] - \mathrm{K}[y]\ \nabla^2_{\{x,y\}}\mathrm{T}[x,\ y] ==$$
$$\mathrm{NeumannValue}[-\mathrm{Qcv}[x,\ y] + \mathrm{Qlight}[x],\ y == 0] + \mathrm{NeumannValue}[-\mathrm{Qcv}[x,\ y],\ y == -\mathrm{thRod}]$$
$$\mathrm{DirichletCondition}[\mathrm{T}[x,\ y] == \mathrm{Tf},\ x == 0\ ||\ x == \mathrm{L}]$$

Technical Accomplishments – Standing Wave Comparison with Experiment (Cathodes)

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

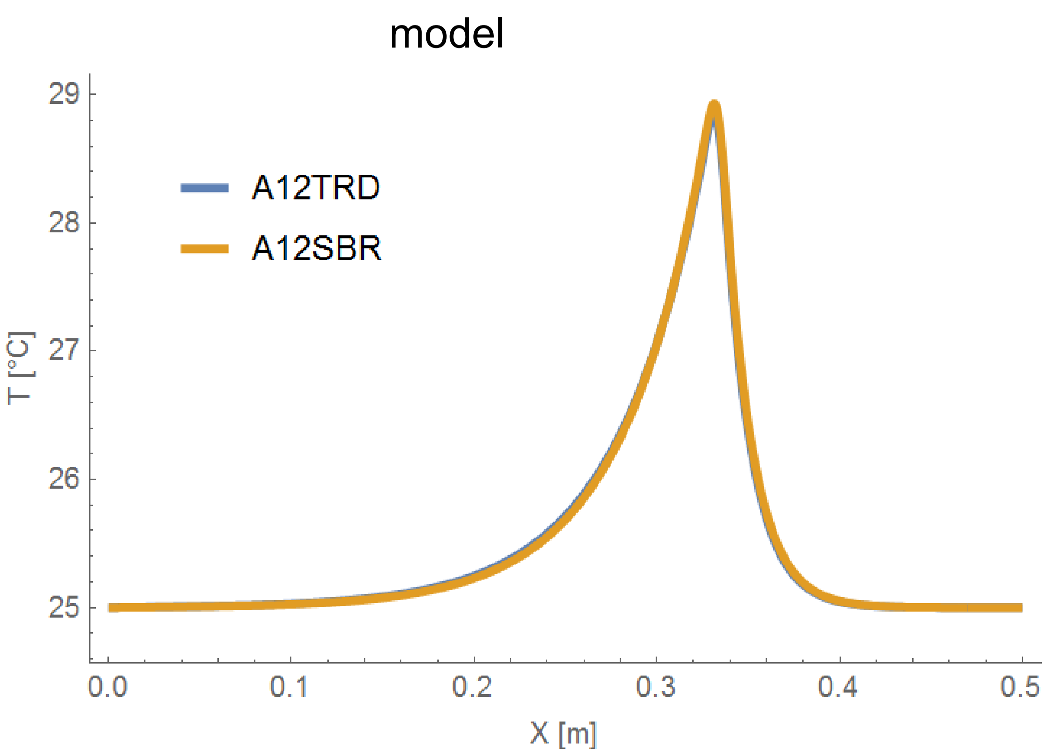


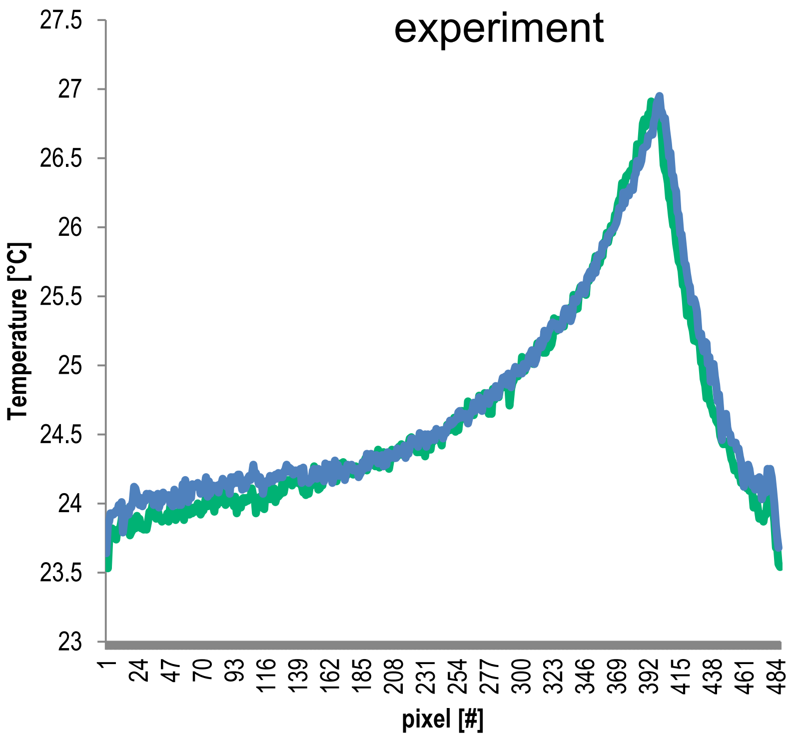


- **Exactly the same effect was found with the model as in the experimental IR thermography measurements.**
- **The difference between the maximum temperature is about two times larger in the experiment than in the model.**

Technical Accomplishments – Standing Wave Comparison with Experiment (Anodes)

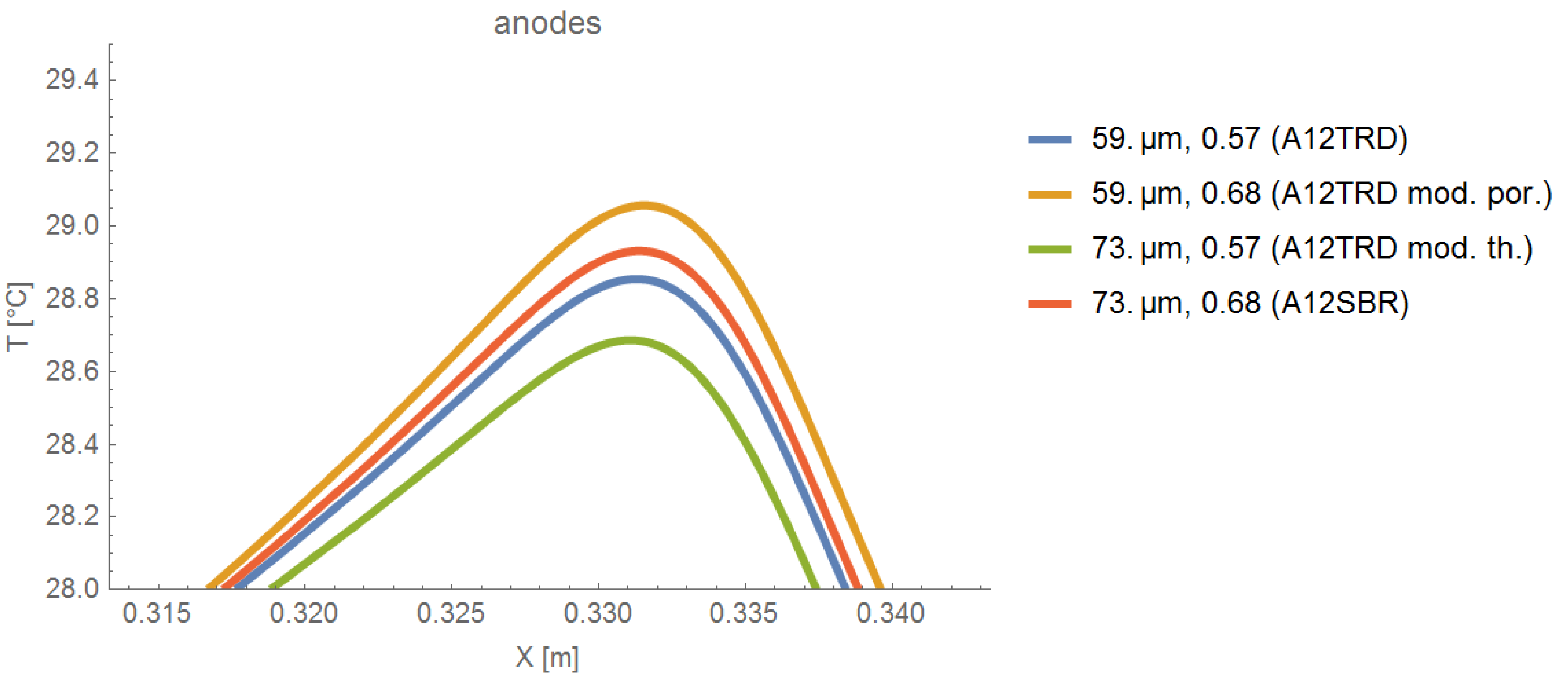
- Speed 0.5 ft/min
- Steady-state distribution of temperature was analyzed





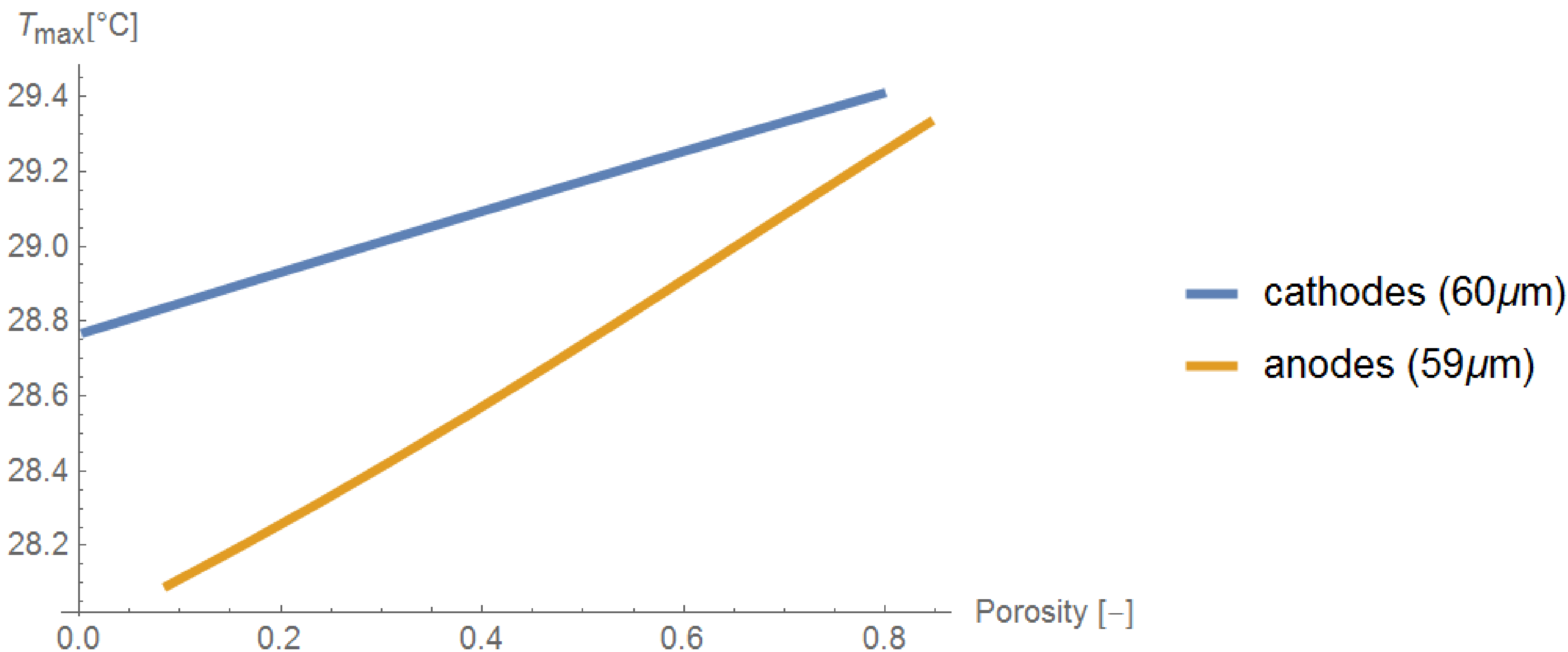
- **For the two anodes, the same T profiles were obtained with the model despite the fact that the samples had different thickness and porosity.**
- **The same behavior was observed in the experiment.**

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_{max}; however, increase in thickness reduces T_{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_{max} to Electrode Porosity Range



- The model shows that for the two considered cases T_{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_{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

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

- 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:
  - Guido Bender
  - Seong Jin An
  - Ralph Dinwiddie

Technical Collaborators

- Mike Wixom
- Fabio Albano
- David Telep
- Jerry Forbes

Information Dissemination and Commercialization

- Refereed Journal Paper
  1. D. Mohanty, J. Li, C. Daniel, and D. L. Wood, "Effect of electrode defects on electrochemical performance of a lithium ion battery; from non-destructive evaluation to microstructural investigation," *ACS Applied Materials and Interfaces*, In Preparation, 2015.
  2. 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).
- Presentations
  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. Wood, J. Li, D. Mohanty, S. Nagpure, and C. Daniel, "Aqueous Colloidal Chemistry and Coating Technology for Low-Cost Green Manufacturing of Lithium Ion Battery Electrodes," ASM Educational Symposium – Electrochemical Energy Storage, Knoxville, Tennessee, April 16, 2014 **(Invited)**.

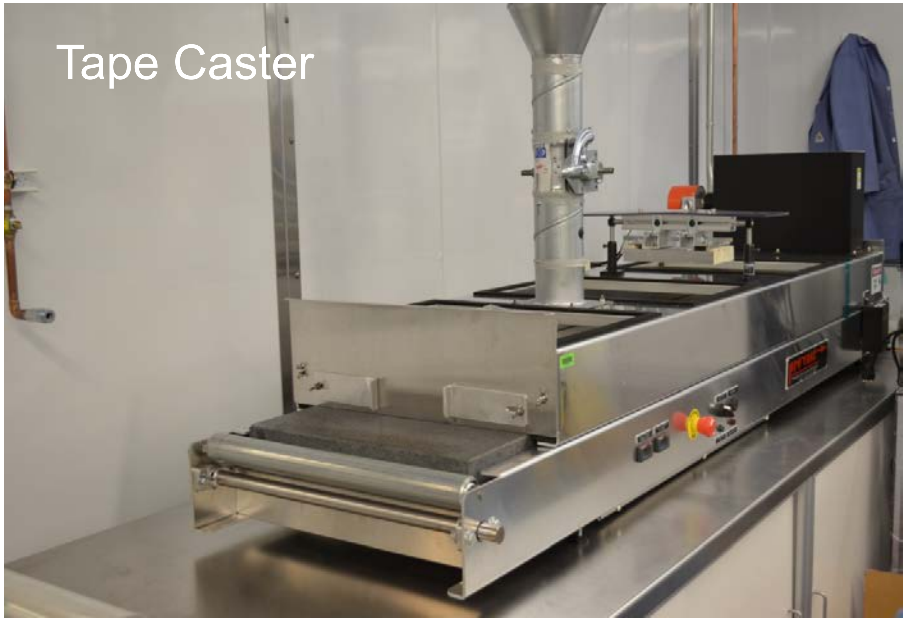
Thank you for your attention!

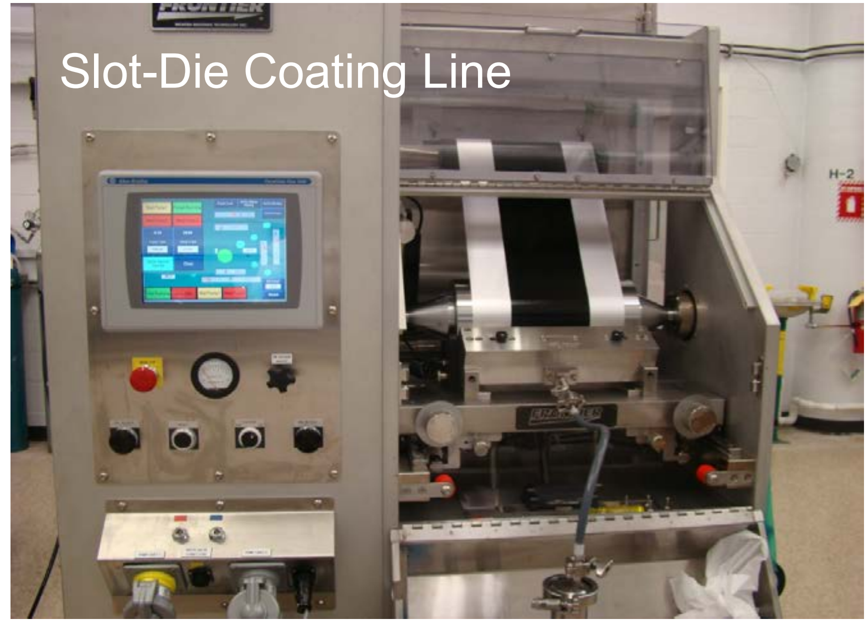
Technical Back-Up Slides

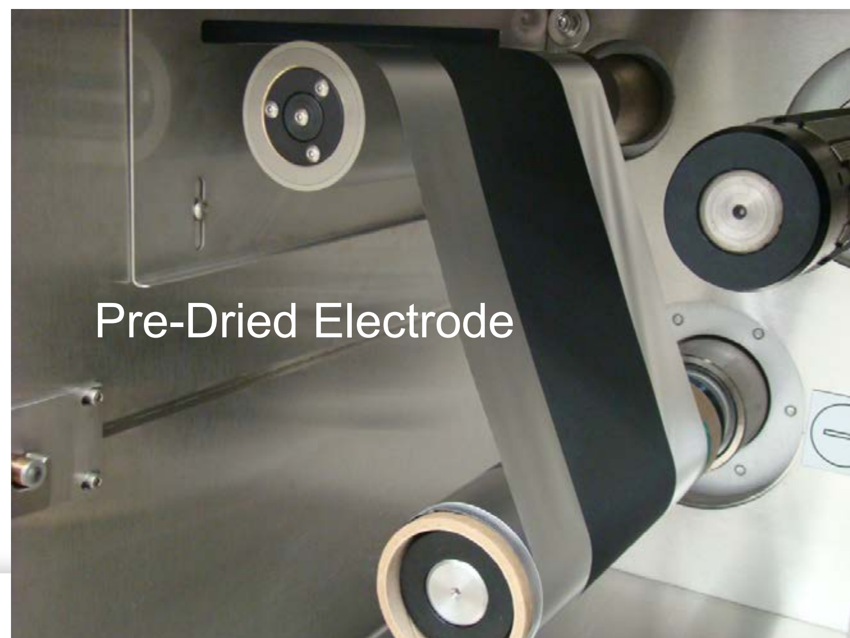
Overview of Lithium Ion Electrode QC State-of-the-Art

- 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).
- Raman microscopy – Panitz and Novák, *J. Power Sources*, **97-98**, 174 (2001).
- 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







Thermal Conductivity of Electrode

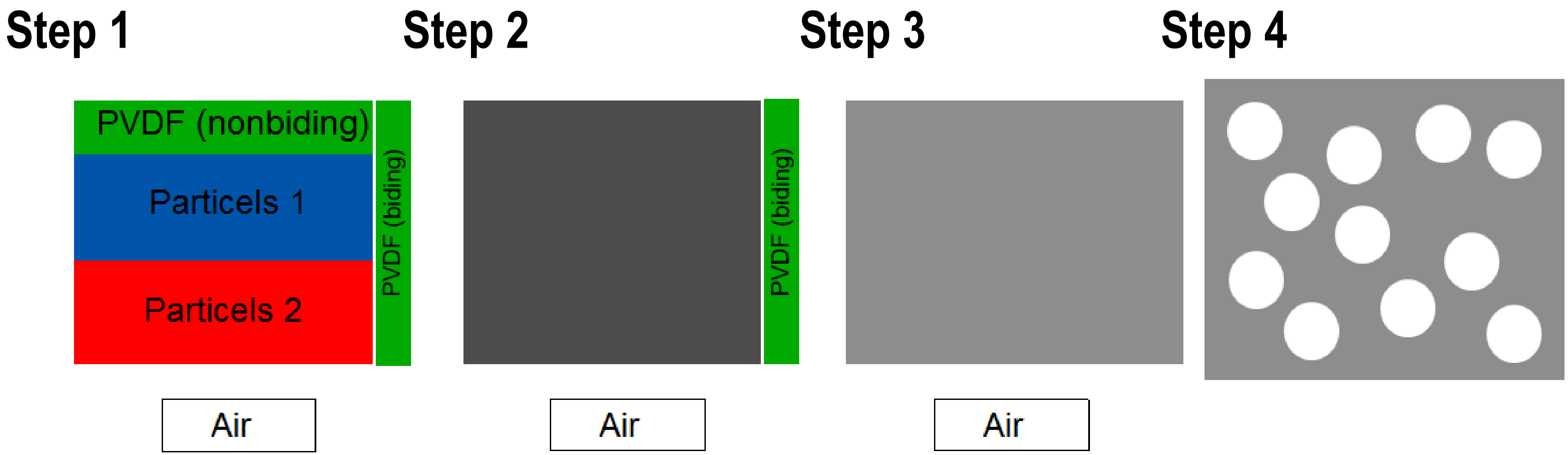
- Based on the literature the expected value for cathode's top layer is 5 W/(m K)
- A few Eshelby based approaches were considered:

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

- Model #4 gives the best estimate and was chosen for all subsequent calculations

Thermal Conductivity of Electrode

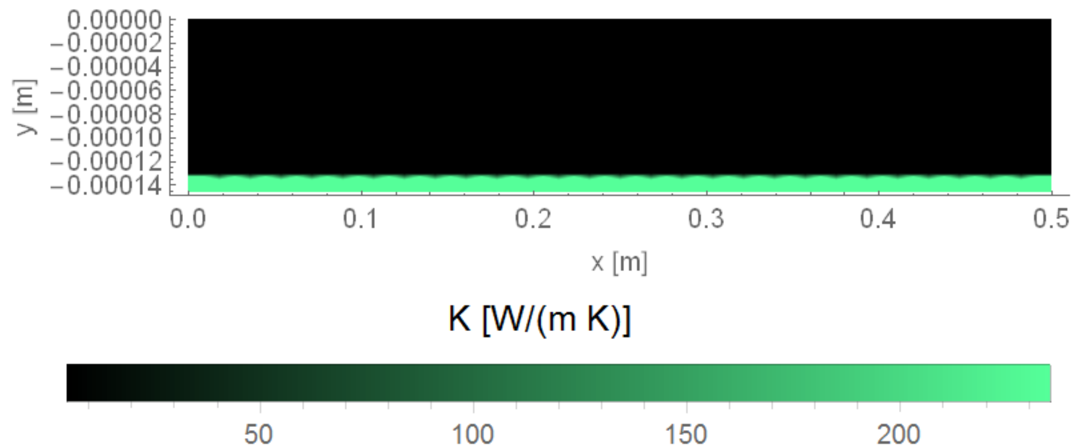
Graphical representation of the micro-scale modeling procedure #4:



- 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 consist 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: