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ADDRESSING HETEROGENEITY IN ELECTRODE FABRICATION PROCESSES

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Project ID # bat220

OVERVIEW

Timeline

- Project start date: Oct 2016
- Project end date: Sep 2019
- Percent complete: 50%

Budget

- Total project funding: $1,050,000
  (DOE share 100%)
- Funding received in FY17: $350,000
- Funding for FY18: $350,000 (12 months)

Barriers

XFC capable EV cells

- $75/kWh
- 80% ΔSOC in 15 min
- 275 Wh/kg @ C/3

Partners

- Industrial collaborations with Hydro-Québec, Bosch USA, K2, LG Chem
- Research collaborations with ANL, NREL, LBNL, Sandia, USU, and others

RELEVANCE

- Program Objectives:
  - Better understand connections between fabrication conditions and undesired heterogeneity of thin-film electrodes by means of new non-destructive inspection techniques and computer models

- Current-Year Objectives:
  - Complete prototypes for flexible conductivity probe and integrated positioning system
  - Use probe as well as other measurements to characterize effects of manufacturing heterogeneity and cell cycling
  - Further improve computer model for predicting mesoscale structure resulting from process steps
  - Complete proof of concept of acoustic probe

- Impact on DOE Barriers for EVs/XFC EVs:
  - This work addresses a longstanding unmet industry need to be able to conveniently measure conductive properties of thin-film electrodes and detect manufacturing variations and changes during cycling—solving this problem will accelerate process improvement
  - Extreme Fast Charging requires adequate transport of ions and electrons throughout the electrode—this work provides experimental and modeling tools to analyze the effect of processing on transport pathways
  - This work remedies our poor understanding of microstructural heterogeneities, which affect cell power, energy, and cycle life

Milestones

2017

- **3Q**: Demonstrate that microstructure model can match measured conductivities. *Complete*
- **4Q**: (Go/No-Go) Complete the proof of concept of acoustic probe that can detect variations in film mechanical properties. *Complete*

2018

- **1Q**: Build large-format integrated positioning system for flex probe. *Complete*
- **2Q**: Integrate flex probe with prototype rolling apparatus to enable interrogation of continuous-roll electrode films. *Complete*
- **3Q**: (Go/No-Go) Demonstrate that localized ionic conductivity probe has adequate reliability for continued development. *On track*
- **4Q**: Quantify the durability of flex probes to validate suitability for industrial use. *On track*

2019

- **1Q**: Predict effect of observed heterogeneity on extreme fast charging. *On track*
- **2Q**: (Go/No-Go) Complete proof of concept of laser interferometry apparatus to detect heterogeneity. *On track*
- **3Q**: Demonstrate ability of particle model to imitate drying and calendering processes. *On track*
- **4Q**: Quantify localized correlation between ionic and electronic pathways. *On track*

Any proposed future work is subject to change based on funding levels.

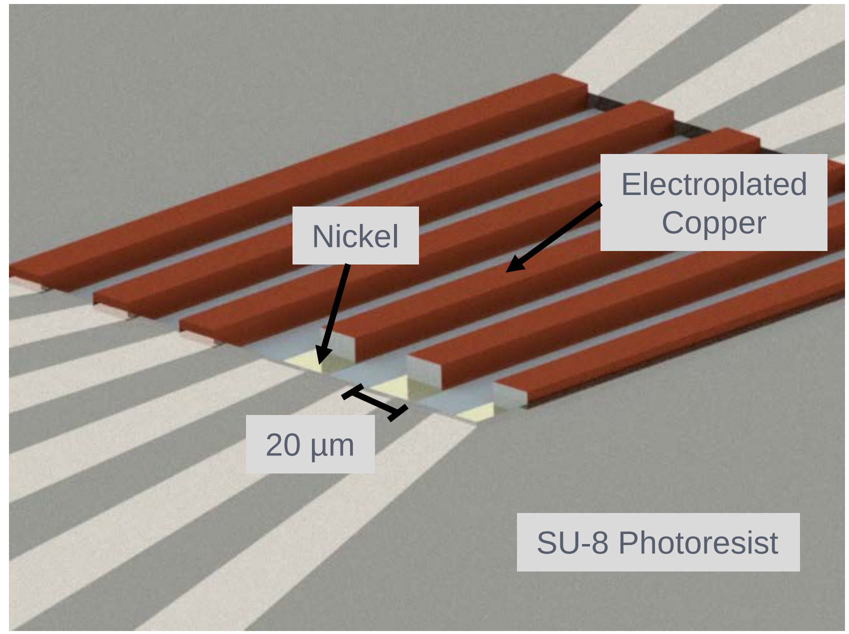
APPROACH

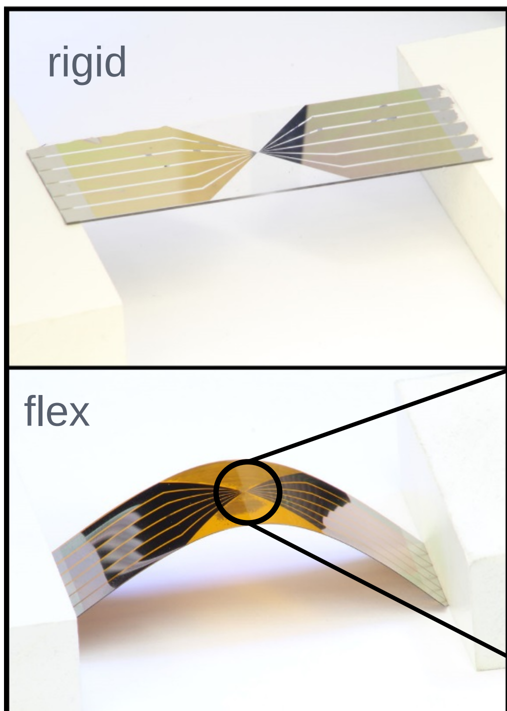
We propose to enable improved electrode manufacturing processes by rapid feedback on transport and mechanical problems associated with the microstructural arrangement of particles

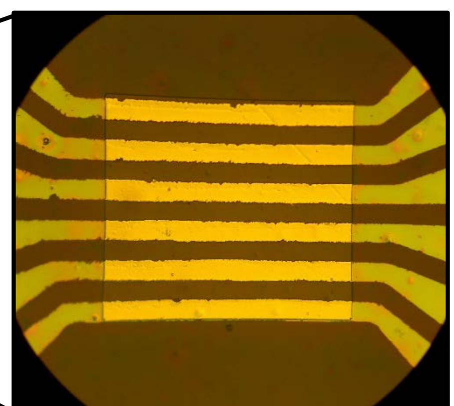
- Construct novel micro-N-line surface probes that can sample local conductivity of intact battery electrodes
- Experimentally compare tradeoffs of and effects on electronic and ionic transport (collaboration with NREL, ANL)
- Construct a first-principles particle-dynamics model that can predict electrode microstructure and conductive pathways (collaboration with Sandia)
- Construct a laser-based acoustic probe for rapidly determining mechanical properties of electrode films

Previous Technical Accomplishment (FY17): First Generation Flexible Micro-Line Probe

The flexible probe allows for an increased sampling area and a more robust measurement.

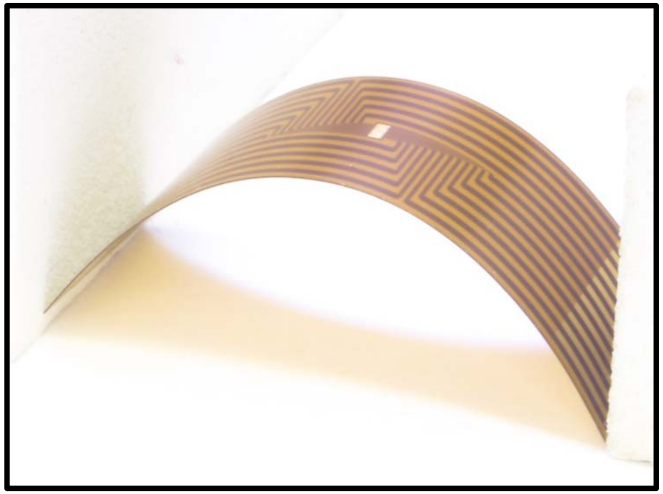




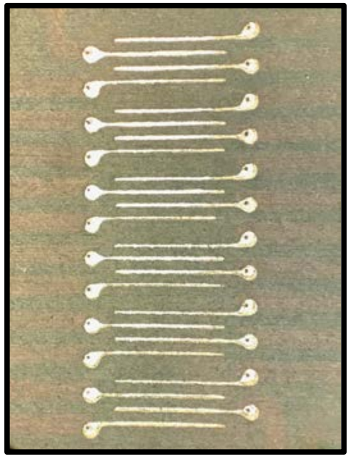


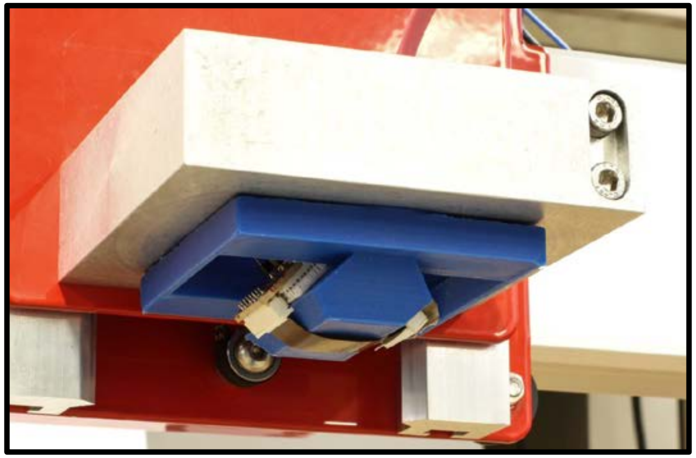
The flexible probe is built on a Kapton (polyimide) substrate and was successfully integrated into standard cleanroom fabrication procedures. Fabrication is repeatable and tolerances are close to that of the previous rigid probe design.

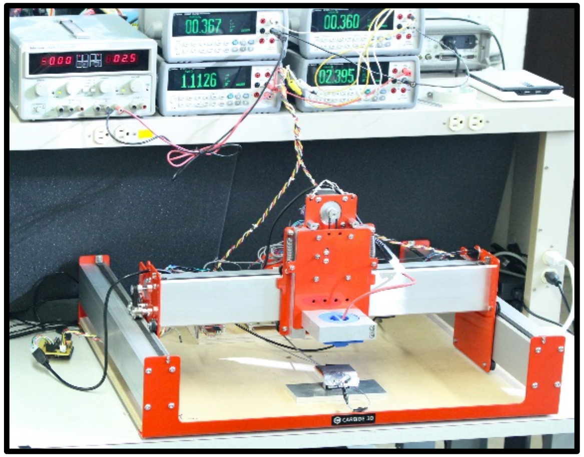
Technical Accomplishment (1Q18): Second Generation Flexible Probe



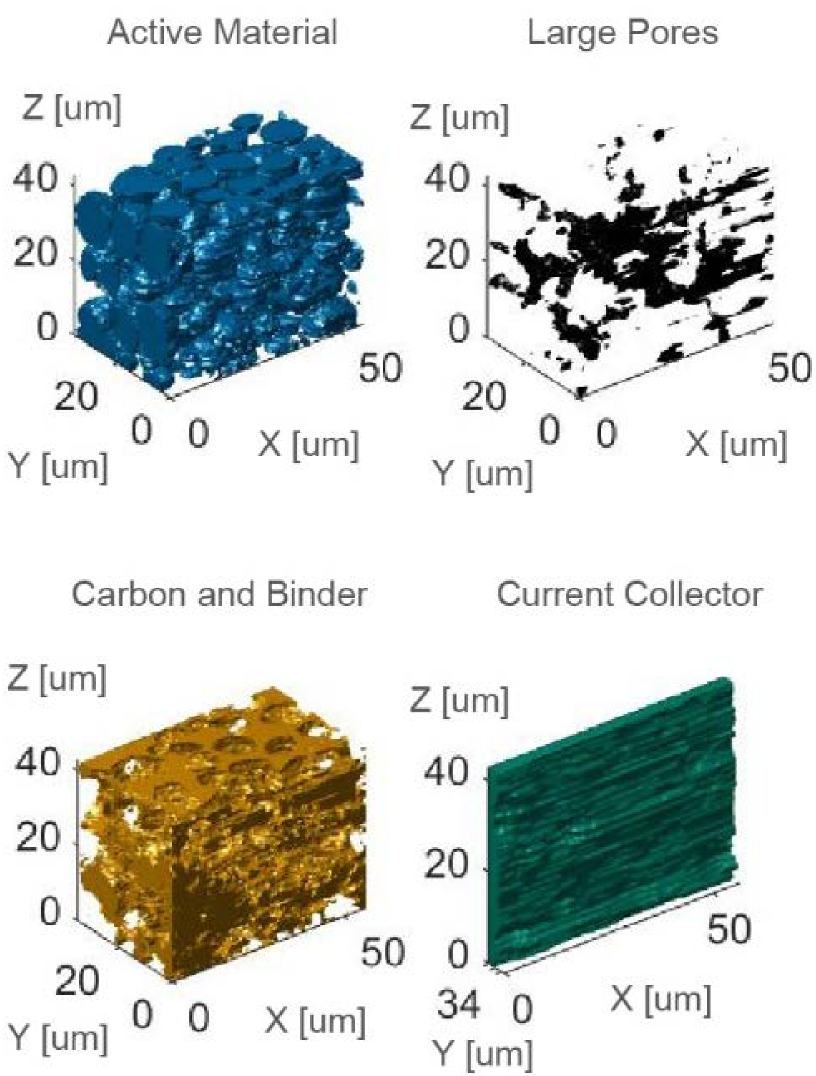
A second generation flexible micro-line probe was developed using a commercial flexible printed circuit board process (two-sided). This reduced fabrication costs considerably and increased yield. This probe was then incorporated into a low-cost, large-format stage to perform measurements on battery electrode materials, yielding similar results to the expensive, high-resolution stage and cleanroom-produced probes in previous experiments.







Technical Accomplishment (2Q18): Microstructure Controls Electronic Variation



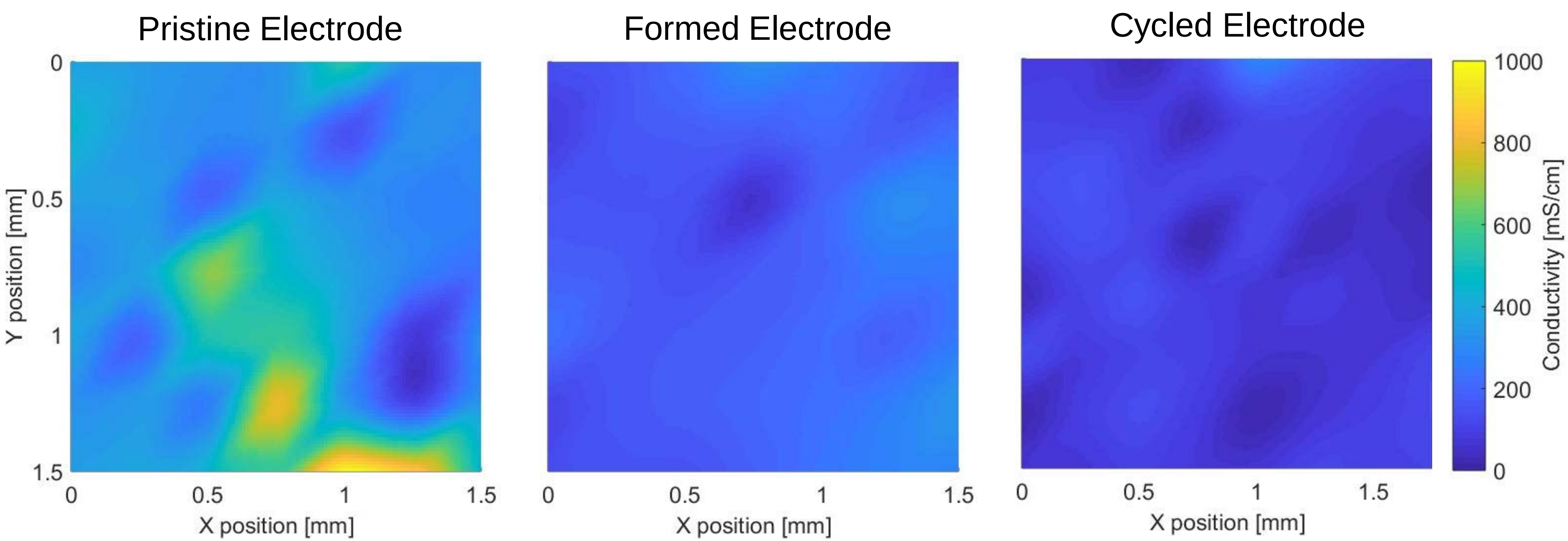
FIB-SEM was used to analyze different areas of area-specific electronic impedance (ASI) in a commercial Toda 523 electrode. Hand segmentation and 3D reconstruction techniques were used to create digital representations. Calculations of ASI and tortuosity were performed on these regions. For these regions, ionic tortuosity decreased with decreasing area-specific impedance, which indicates that naturally forming morphology can exhibit both beneficial electronic and ionic transport.

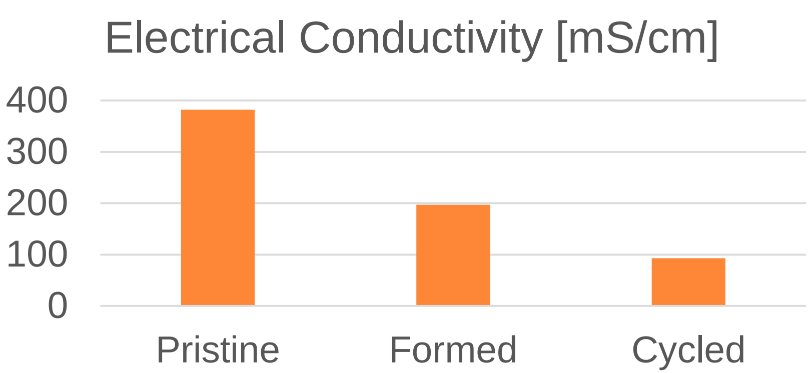
Measured ASI [Ω cm^2]	Calculated ASI* [Ω cm^2]	Calculated Ionic Tortuosity
0.024	0.027	3.35
0.030	0.030	3.40
0.038	0.045	3.64

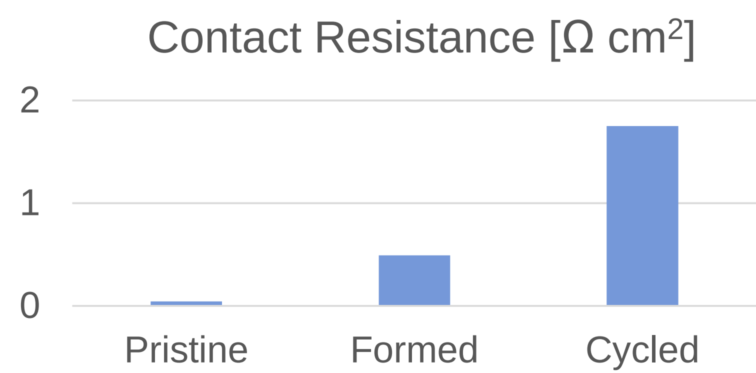
* Normalized

TECHNICAL ACCOMPLISHMENT (2Q18): EFFECT OF CYCLING ON ELECTRONIC PROPERTIES

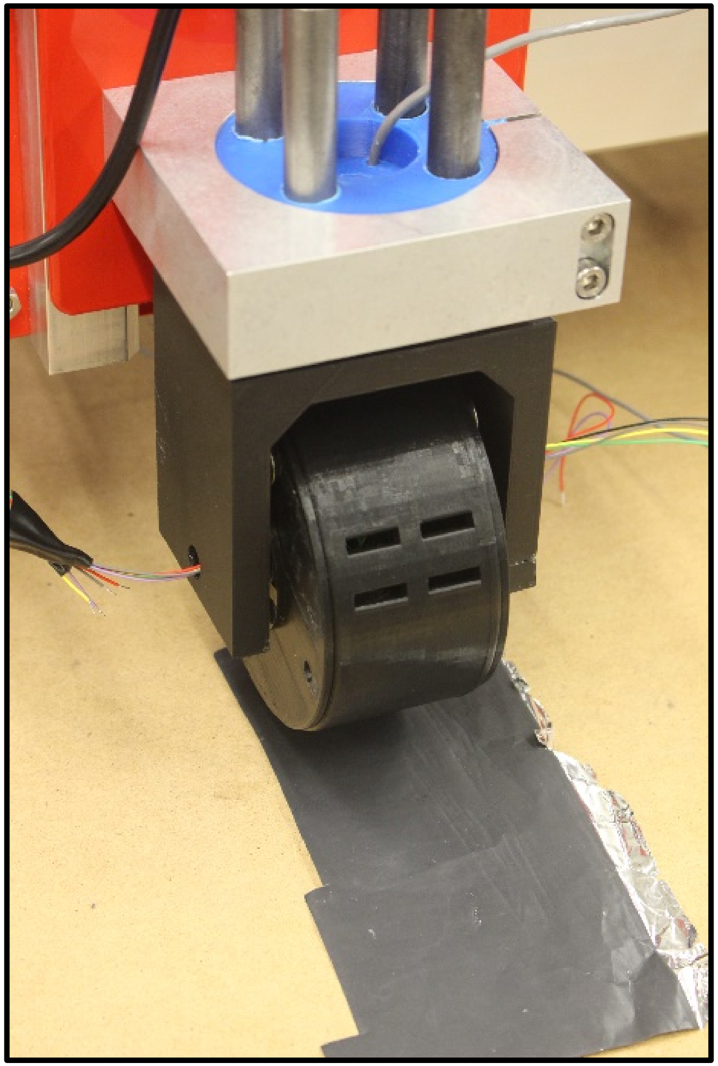
LCO cathodes from Hydro-Quebec were cycled to 80% capacity through accelerated life testing (55° C). Conductivity and contact resistance maps were obtained.



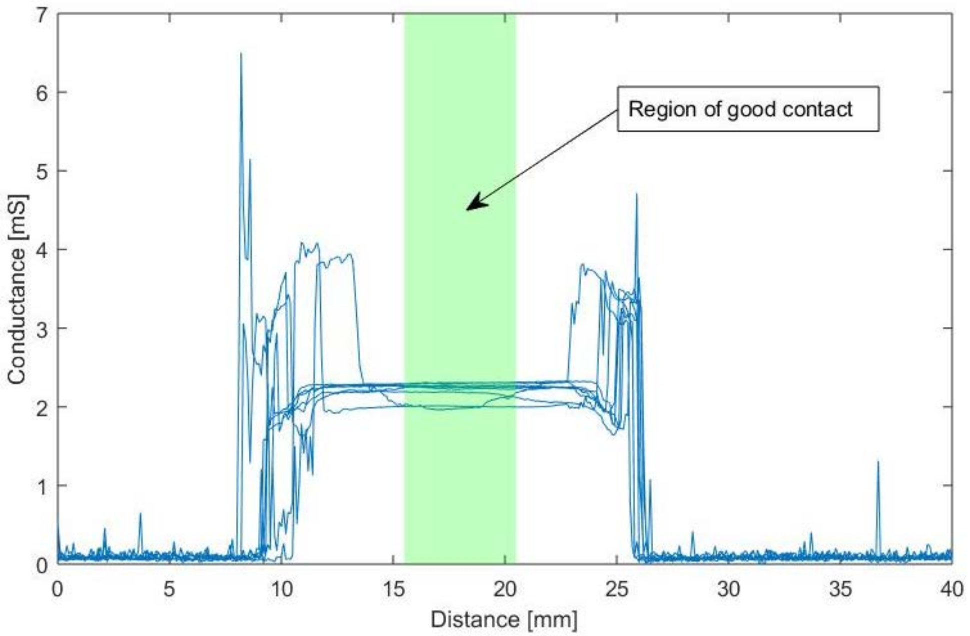




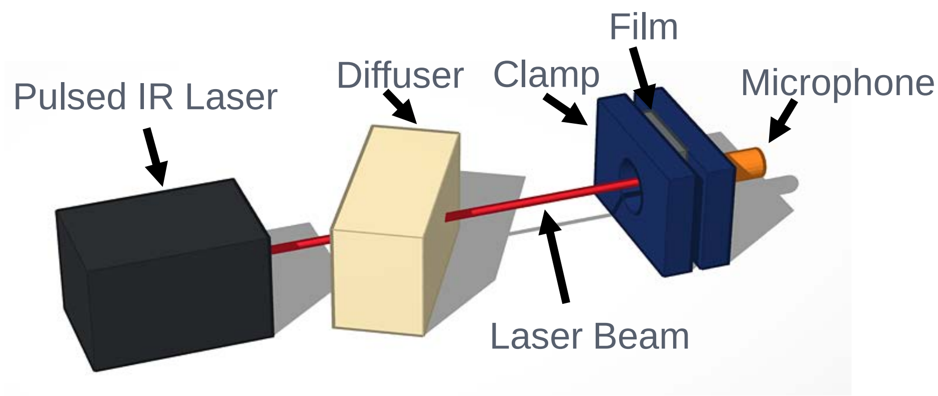
Technical Accomplishment (2Q18): Rolling Micro-N-Line Probe



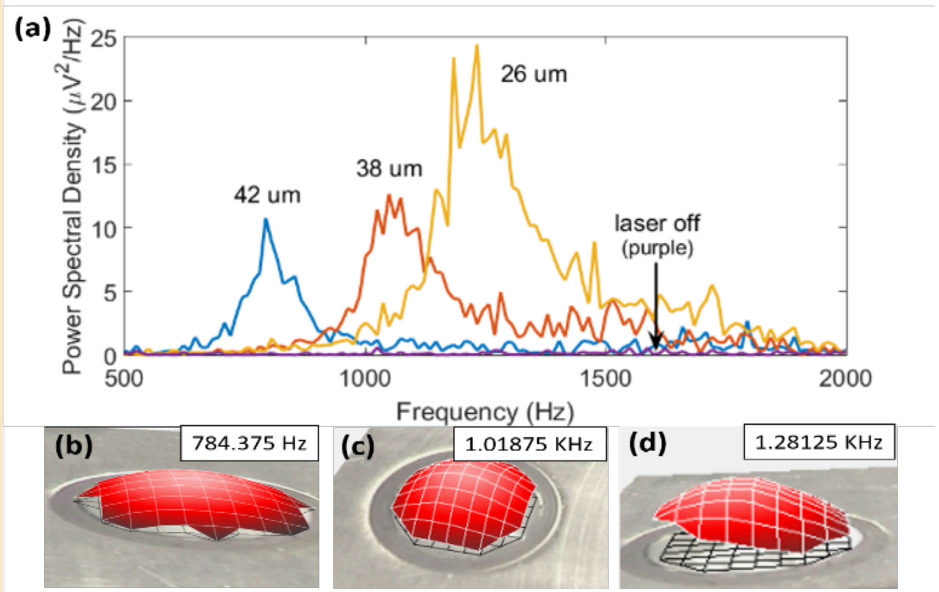
To address the need to make conductivity measurements over large areas of electrode films in-line during electrode fabrication, a rolling probe was developed. This design also took advantage of the flexibility of the newly fabricated flexible micro-N-line probes. To test the repeatability of measurements, the probe was rolled back and forth over a 40 mm segment of a commercial Toda 523 material.

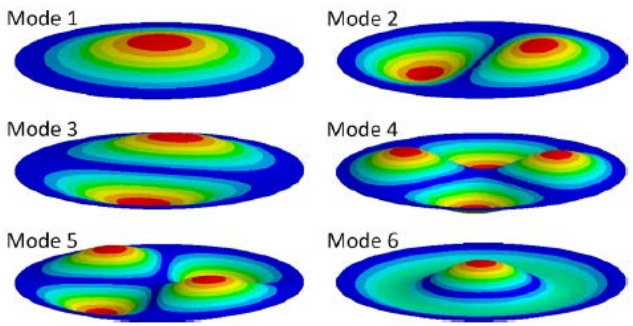


Technical Accomplishment (4Q17): Acoustic Measurement to Determine Modulus



Laser pulses excite mechanical resonances in commercially-coated battery films. By using a numerical model of the acoustic response, the Young's moduli of the cathode coatings were estimated.





Coating	h (μm)	ρ (g/cm^3)	E (GPa), SLDV	E (GPa), peaks	ν
1	42	2.760	0.344	0.412	0.3
2	38	3.055	1.71	2.01	0.3
3	26	2.479	5.04	4.13	0.3

K. Dallon et. al. "Characterization of mechanical properties of battery electrode films from acoustic resonance measurements," *Journal of Applied Physics* **123**, 135102 (2018).

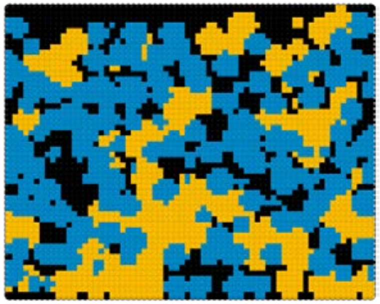
Technical Accomplishment (3Q17): Improvements to Microstructure Prediction Model

The previous generation particle model accurately predicted multiple physical and mechanical properties, but could not handle gas-liquid interfaces well. In order to better simulate coating and drying processes, the model was reformulated in FY17 using smoothed-particle hydrodynamics (SPH).

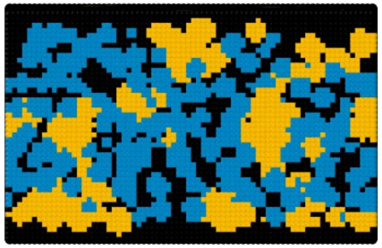
Preliminary SPH simulated ionic transport results, following drying and calendering steps, compared to experiment.

Electrode	Simulation		Experiment	
	Porosity (%)	Tortuosity	Porosity (%)	Tortuosity
CPG-A12	43.9	4.3	36.1	3.4
Toda 523	44.3	5.4	30.0	3.1
Toda HE5050	49.4	3.6	36.1	2.9

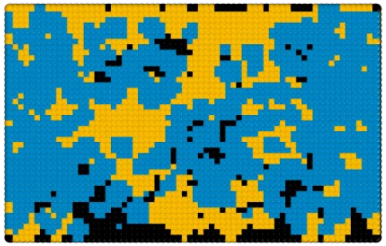
CPG-A12



Toda 523



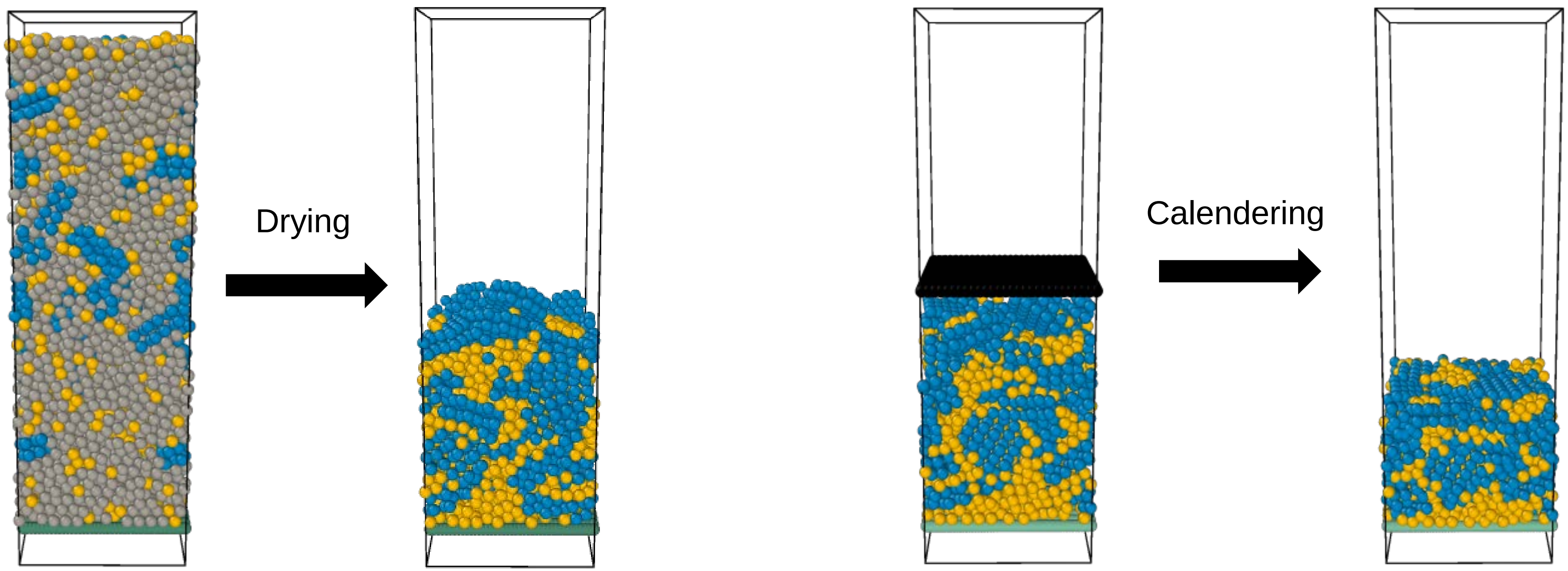
Toda HE5050



Active Material

Carbon-Binder

Future Technical Accomplishment (3Q19): Improved Microstructure Prediction of Drying and Calendering Processes

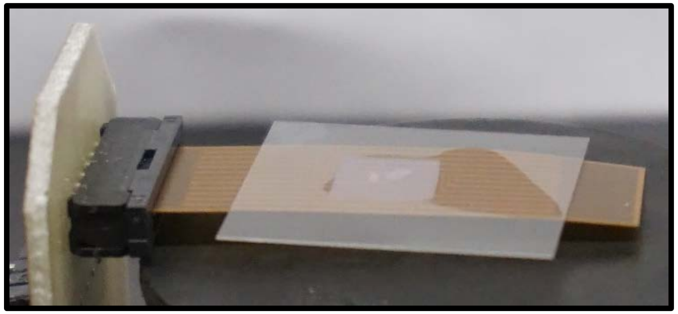


The model will continue to be improved in FY19 to give quantitative predictions of drying and calendering steps, including the effect of drying at different rates/temperatures.

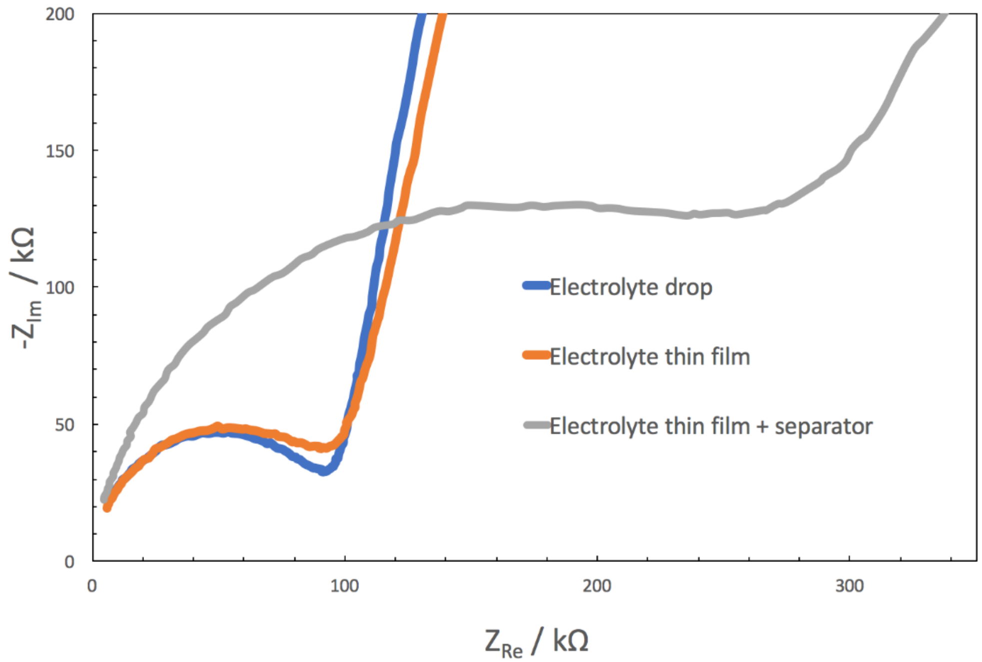
Future Technical Accomplishment (3Q18): Local Ionic Conductivity Measurements

The flexible probe is being adapted to map microscale ionic conductivity. Industry partners have expressed strong interest in being able to perform this measurement on complete electrodes. Proof of concept measurements are currently in progress.

Electrolyte drop



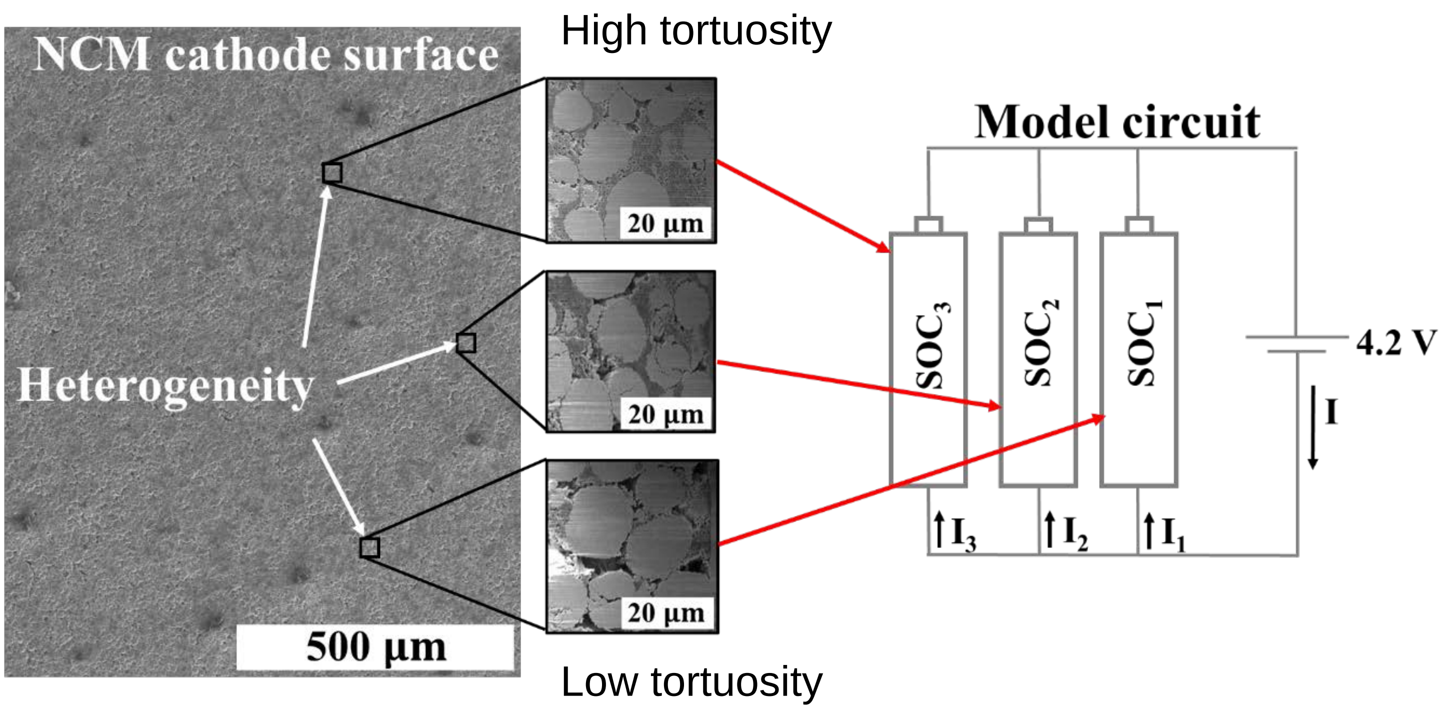
Electrolyte thin film + separator



Nyquist plot of “wet” micro-four-line probe experiments

Future Technical Accomplishment (1Q19): Predict Effect of Observed Heterogeneity on Extreme Fast Charging

A Newman-type model is being adapted to rapidly predict the effects of heterogeneity by placing dissimilar regions in parallel. The model will be able to show why lithium plating occurs preferentially in some regions.



Responses to Previous Year Reviewers' Comments

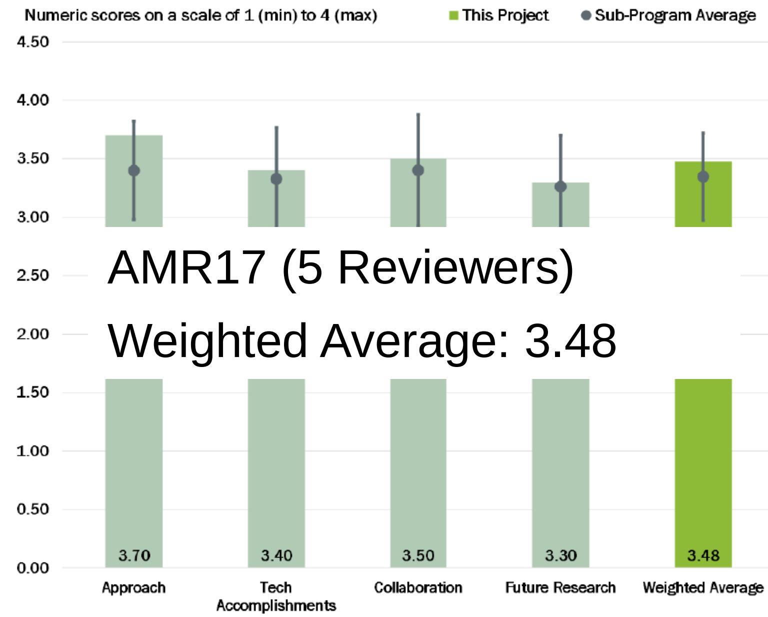
The project was favorably reviewed during AMR17 with generally positive comments, including, "The project is bringing deep understanding to electrode processing and developing tools that industry can use…this project was very good and has the right balance between the need to help industry versus not repeating what industry does best". Responses to the main concerns:

1. Limited measurement area compared to size of complete web:

   The ratio is indeed small. However, significant information can be obtained from the small areas and development of the rolling probe should address larger variations across the web.

2. Influence of pressure on measurements:

   Pressure is carefully controlled in the experiments. Indeed, this is a strength of the method.



3. Industrial collaboration:

   Measurements have been performed for a number of commercial partners. New collaborations are consistently sought to extend the reach of these methods. A new startup venture is being formed to commercialize this technology and provide services to industry.

Collaborations and Coordination

Non-contract partnerships and research collaborations involving exchange of battery materials and expertise

- NREL (Kandler Smith) – supplied materials for testing, joint publication with a large collaborative group
- Bosch USA – supplied materials for testing, joint publication
- Hydro-Québec (Chisu Kim) – supplied materials for testing
- ANL (Daniel Abraham and Bryant Polzin) – supplied materials for testing
- Sandia (Scott Roberts) – modeling collaboration
- Utah State University (Tianbiao Liu) – supplied materials for testing
- K2 – supplied materials for testing
- LG Chem – supplied materials for testing

Remaining Challenges and Barriers

- Continued development of new SPH microstructure model that is validated with
  - Experimental conductivity data
  - Experimental drying and microstructure data

- Continued measurements on commercial-grade electrodes to quantify
  - Natural spatial variations in pristine films
  - Effect of mixing and coating processes
  - Effects of cell formation and subsequent cycling

- Show that new acoustic probe can be used for rapid interrogation of film stiffness and/or thickness

- Demonstrate an appropriate electrolyte and measurement configuration to reliably conduct microscale ionic measurements

Proposed Future Research

2018

- **3Q**: (Go/No-Go) Demonstrate that localized ionic conductivity probe has adequate reliability for continued development. *Justification:* This milestone is important for fully quantifying the transport properties of electrodes due to the interest in fast charging and the recognition that **ionic transport limitations are critical** to many performance measures.
- **4Q**: Quantify the durability of flex probes to validate suitability for industrial use. *Justification:* This milestone is important to quantify the potential usage of the developed technology in industrial manufacturing environments. Results to date show that the second generation probes are much more durable than the rigid probes.

2019

- **1Q**: Predict effect of observed heterogeneity on extreme fast charging. *Justification:* This Newman-type modeling will quantify **how heterogeneity could limit fast charging**. Hot and cold spots are suspected to cause uneven performance across electrodes.
- **2Q**: (Go/No-Go) Complete proof of concept of laser interferometry apparatus to detect heterogeneity. *Justification:* This technique could potentially be used to estimate the heterogeneity of mechanical properties (e.g. Young's modulus) across battery electrodes. This decision point is important to determine if the sensitivity is adequate to perform estimation of these properties on commercial electrodes.
- **3Q**: Demonstrate ability of particle model to imitate drying and calendering processes. *Justification:* The fidelity of the model needs to be improved to better match commercial drying and calendaring steps. Achievement of this milestone will allow greater adoption of the simulation techniques to industry and academic development.
- **4Q**: Quantify localized correlation between ionic and electronic pathways. *Justification:* This culminating milestone will demonstrate the **combined use of our electronic and ionic mapping measurements, in conjunction with microstructure models**, to demonstrate how the microstructure controls important performance considerations in commercial electrode films.
- This project ends September 2019.

Any proposed future work is subject to change based on funding levels.

SUMMARY

- Deliverables after first half of project
  - Flex probe for conductivity measurements has been fabricated and validated. This probe has been used to better understand electrode spatial heterogeneities and property changes with cycling.
  - Significant progress has been made on other diagnostic tools (acoustic probe, ionic probe, and large-format positioning system), and refinement of microstructure prediction model.
- How this will improve battery manufacturing
  - Commercial-grade electrodes have significant spatial differences in conductivity due to variability on the mm and smaller length scales.
  - Our suite of tools can quantify these differences and enable real-time quality control in roll-to-roll processing. It is anticipated that this will improve electrode utilization, the ability to perform extreme fast charging, and cycle life.

Technical Back-up Slides