PREDICTING MICROSTRUCTURE AND PERFORMANCE FOR OPTIMAL CELL FABRICATION

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Project ID # ES220

BYU

Overview

Timeline

- Project start date: Apr 2013
- Project end date: Mar 2017
- Percent complete: 25%

Budget

- Total project funding: $794,000
  - (DOE share 100%)
- Funding received in FY13: $99,250 (6 months)
- Funding for FY14: $198,500 (12 months)

Barriers

- Cell performance
  - 200 Wh/kg (EV requirement)
- Life
  - 3000 cycles (PHEV 40 mile requirement)
  - Calendar life: 15 years.
- Cost

Partners

- Industrial collaboration with A123
- Research collaborations with LBNL, ANL, and others

RELEVANCE

- Program Objectives:
  - Develop rapid and reliable tools for measuring and predicting electronic and ionic conductivities and 3D microstructures of particle-based electrodes
  - Understand tradeoffs and relationships between fabrication parameters and cell performance
- Current-Year Objectives:
  - Fabricate micro-four-line probe and assess conductivity variability in baseline electrodes
  - Characterize particle microstructures of baseline electrodes
- Impact on DOE Barriers for EVs/PHEVs:
  - This work addresses a longstanding unmet industry need to be able to conveniently quantify conductivity of thin-film electrodes and current collector contact resistance—solving this problem will accelerate process improvement.
  - This work remedies our poor understanding of the influence of fabrication parameters on heterogeneities in microstructure, which affect cell energy, power, and cycle life.

MILESTONES

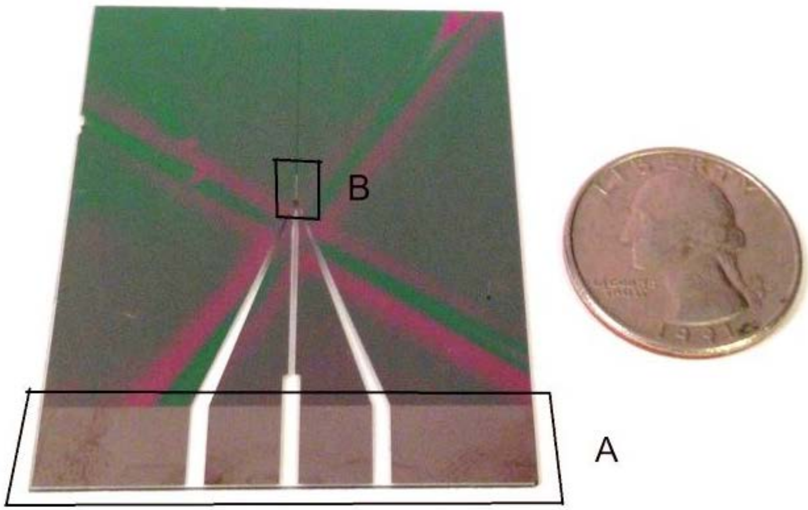
- **Sept 2013**: Fabricate first-generation micro-four-line probe to determine bulk electronic conductivity in non-delaminated battery films. *Complete*
- **Sept 2013**: Develop mathematical-model inversion technique to determine current collector contact resistance from film measurements. *Complete*
- **Dec 2013**: Measure variability and average electronic conductivity for 5 candidate electrodes using 4-line probe. *Complete*
- **Mar 2014**: Measure microstructure of 3 candidate electrodes using SEM/FIB. *Complete*
- **June 2014**: Determine appropriate set of descriptors or metrics that effectively characterize previously observed microstructures. *In progress*
- **Sept 2014**: (Go/No-Go) Discontinue current 4-line probe geometry if measurement variability is not significantly less than sample-to-sample variability. *Criterion is met as of Dec 2013*

APPROACH

- Construct a novel micro-N-line surface probe that can sample local conductivity of intact battery electrodes. Our apparatus overcomes multiple problems with previous methods, allowing reliable measurements of:
  - Bulk film conductivity while electrode still attached to metallic current collector
  - Contact resistance to current collector
  - Effects of pressure and presence of electrolyte
  - Spatial variations and anisotropy
- Construct a particle-dynamics model that can predict electrode microstructure and conductive pathways. Our model will be unique in that it:
  - Predicts effects of fabrication variables (slurry composition, calendering, etc.)
  - Is validated with extensive microstructure and transport experiments

Technical Accomplishment (Sep 2013): Fabrication of Four-Line-Probe

- Planar probes allow the surface of the probe to be placed directly upon electrode materials with an even pressure applied to the films, while remaining mechanically robust.



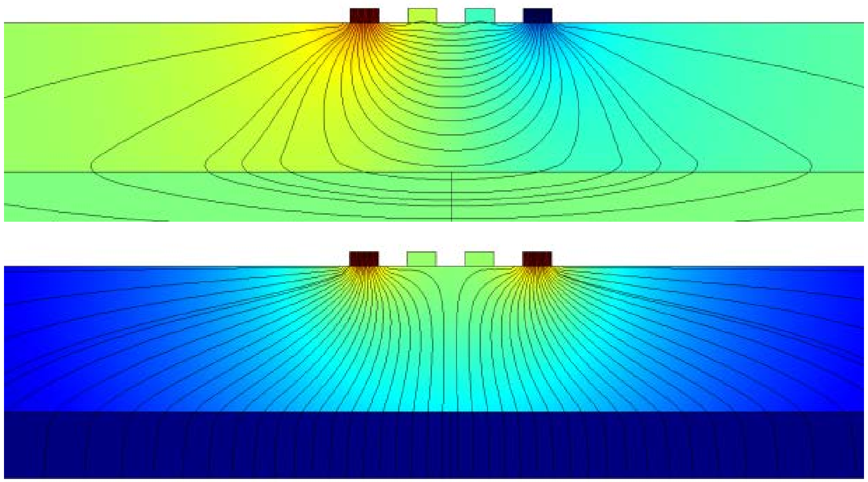
Completed micro-four-line-probe showing: (A) exposed connection pads, and (B) window for exposing the four contact lines.

- A micro-four-line-probe was fabricated in the BYU Cleanroom with inner conducting lines spaced 10 microns apart.
- Because the spacing of the contacts is on the order of the cathode material thickness, the probe current probes the cathode material conductivity properties without large amounts of shunt current passing through the current collector metal film.

A new device for measuring electronic properties was developed and fabricated.

TECHNICAL ACCOMPLISHMENT (SEP 2013): NUMERICAL INVERSION PROCEDURE

- To be able to properly interpret the micro-four-line probe measurements, a numerical inversion procedure was developed using simulations of the electrode conductivity as well as the current collector interface resistance.



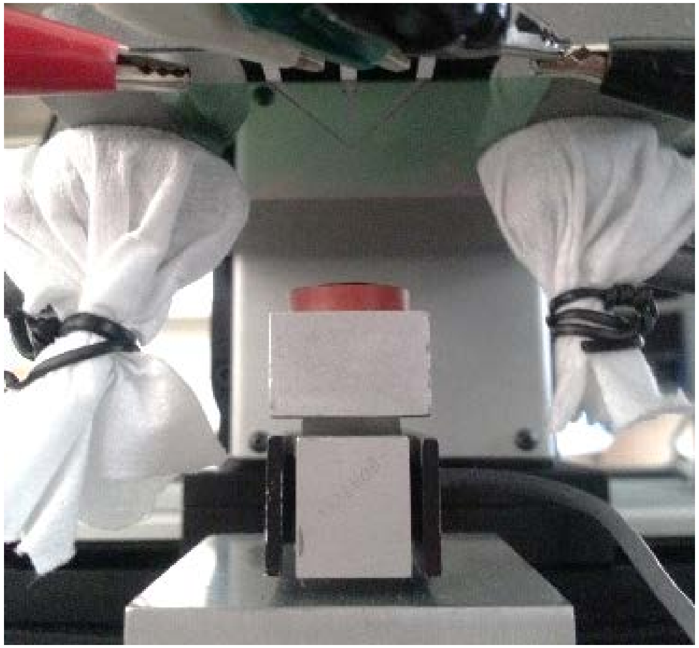
Finite element simulations of the two orthogonal electrical measurements of an intact electrode using the four-line probe.

- Inversion of two orthogonal electrical measurements allows near-simultaneous determination of both bulk electronic conductivity and contact resistance to the current collector.

Measurement data is interpreted using a numerical inversion method.

TECHNICAL ACCOMPLISHMENT (DEC 2013): AUTOMATED MEASUREMENT APPARATUS

- To be able to consistently make measurements with the fabricated four-line-probe, an apparatus was constructed to make automated measurements.



Measurement apparatus for electronic conductivity measurements. The probe wafer is clamped in an inverted orientation and descends upon the electrode sample.

- The electrode sample is mounted on an XYZ stage with a force gauge under the target position to control applied pressure with the probe. The entire measurement procedure with current source and multimeters is controlled using a computer with a custom data logging interface.

A high level of control and repeatability are achieved through automation.

TECHNICAL ACCOMPLISHMENT (MAR 2014): PROBE VALIDATION

- Validation of probe measurements of electrical properties were performed on a carbon-impregnated silicone sheet (Parker Chomerics) pressed against copper foil.

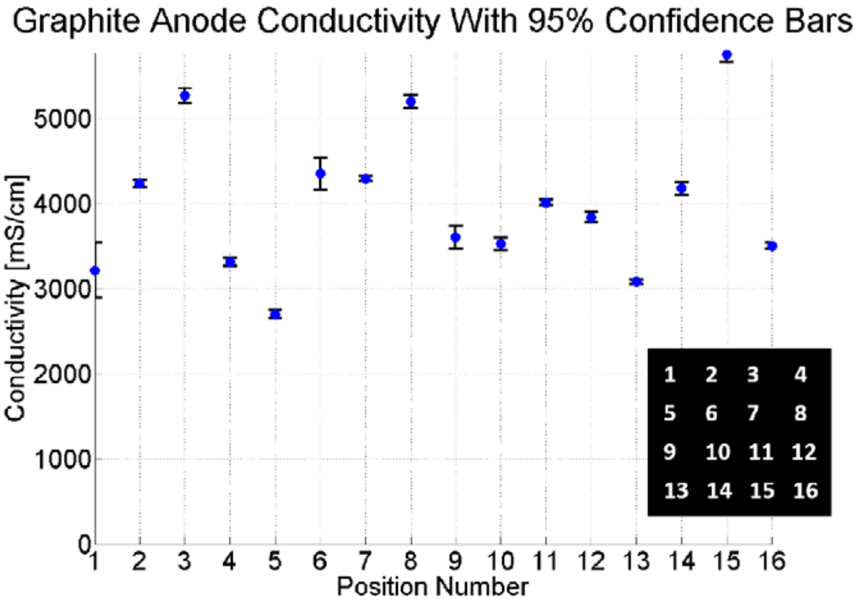
- Our probe produced bulk conductivity measurements within 4% and contact resistance measurements within 8% of standard techniques. Below are shown data with 95% confidence intervals.

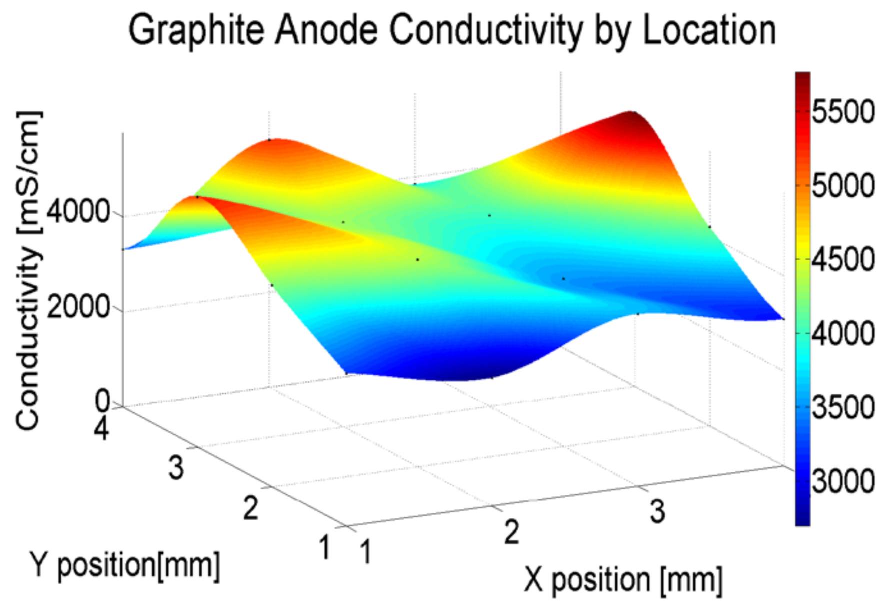
Method	**Bulk Electronic Conductivity (mS/cm)**
Van der Pauw	265.4 ± 1.1
Four-Line-Probe	276.5 ± 16.4

Method	**Current Collector contact R (Ω cm^2)**
Direct	0.134 ± 0.028
Four-Line-Probe	0.146 ± 0.008

New method is validated with a sample with electrical properties similar to those for battery electrodes.

TECHNICAL ACCOMPLISHMENT (DEC 2013): GRAPHITE ANODE (A123) RESULTS

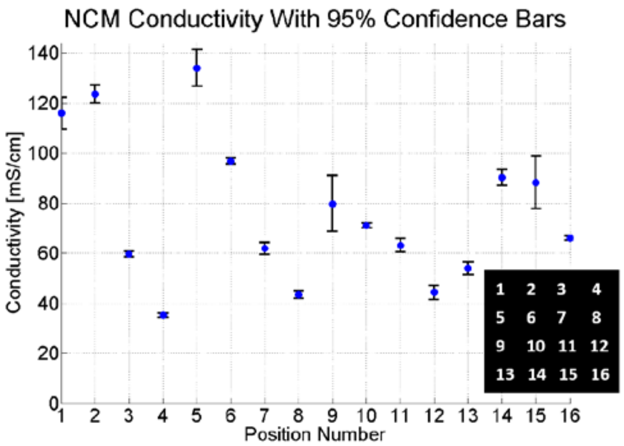


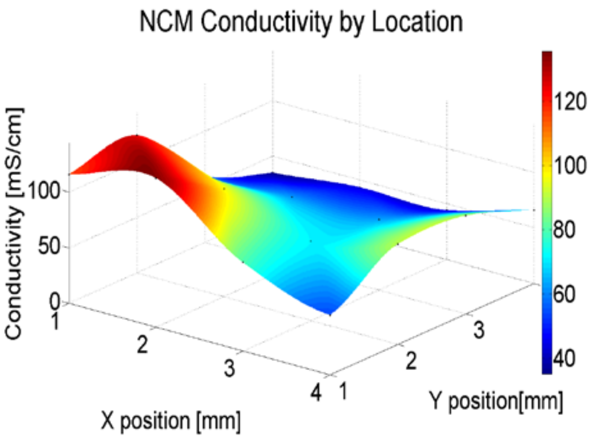


Probe is scanned across sample surface and multiple measurements are made at each location (1-16) allowing uncertainties in conductivity to be obtained at each location.

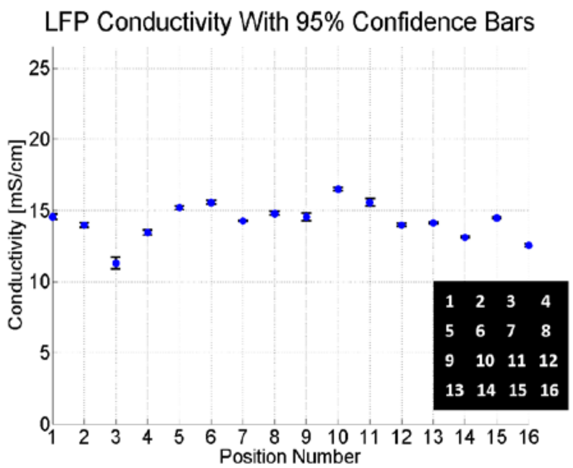
This and the three following slides show how probe apparatus can map local values of conductivity on different baseline electrodes.

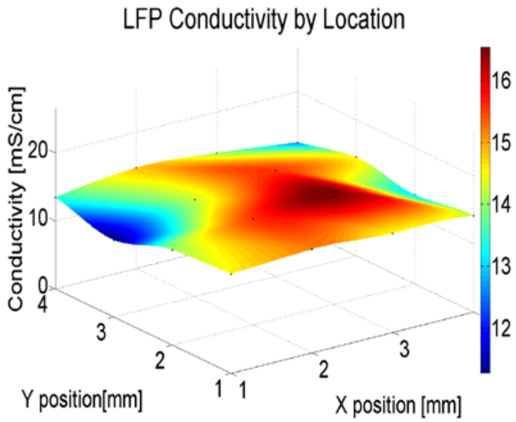
NCM (A123) Results





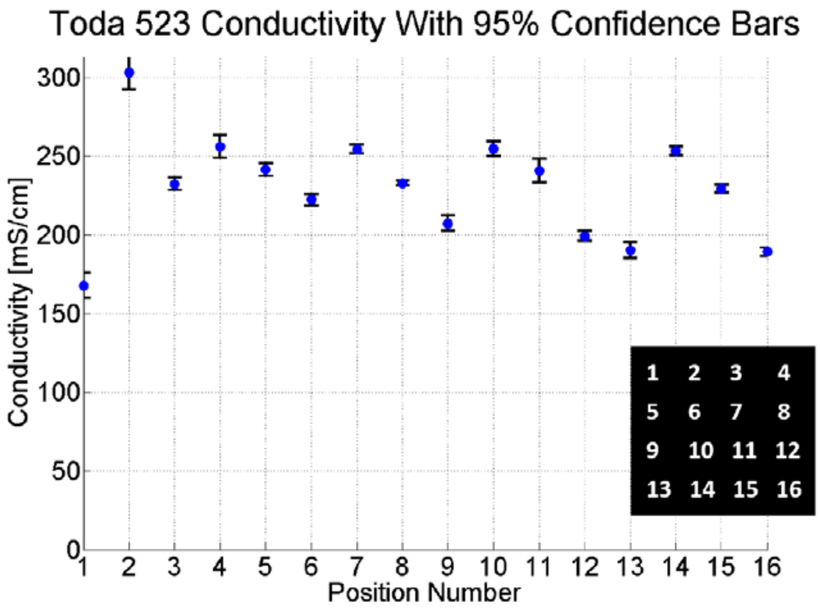
LFP (A123) Results

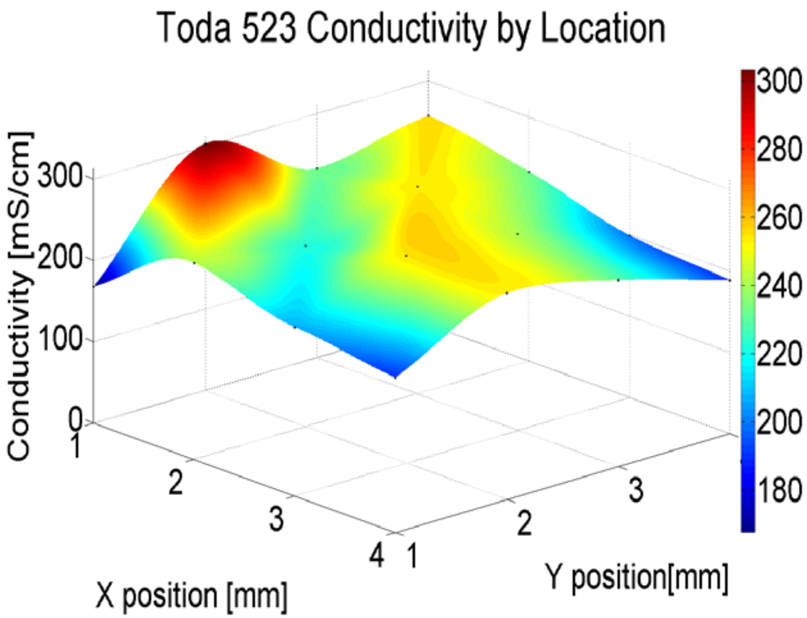


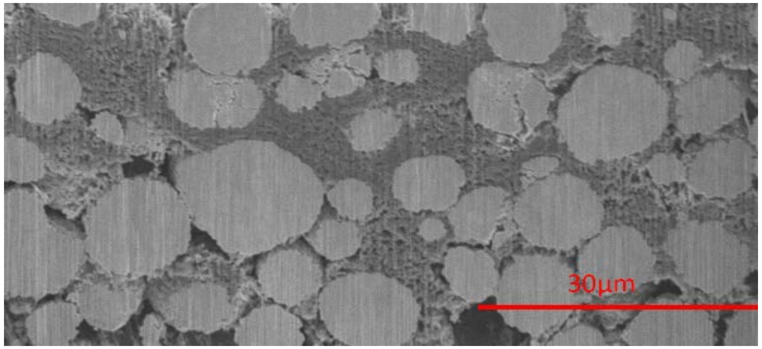


Even though LFP has lower average conductivity than other electrodes, it has the lowest relative variation in conductivity.

TODA 523 (ANL) RESULTS

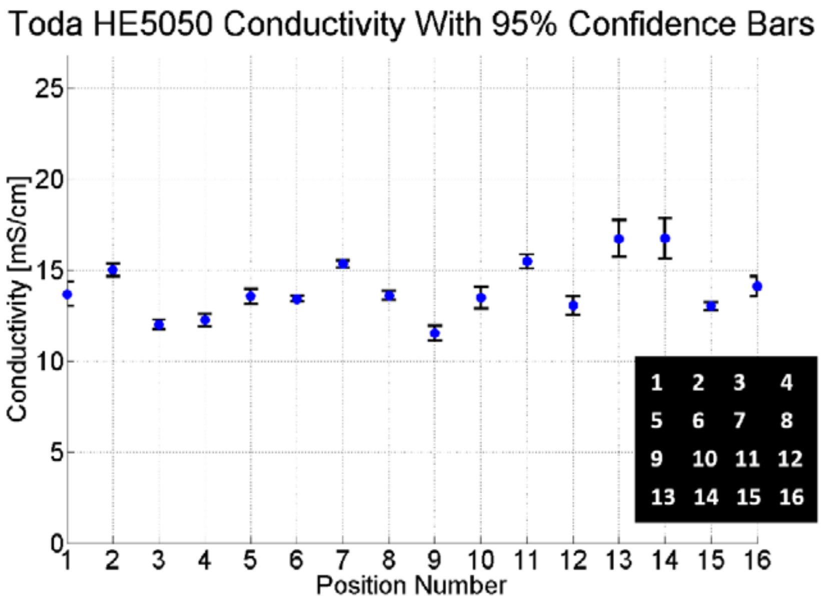


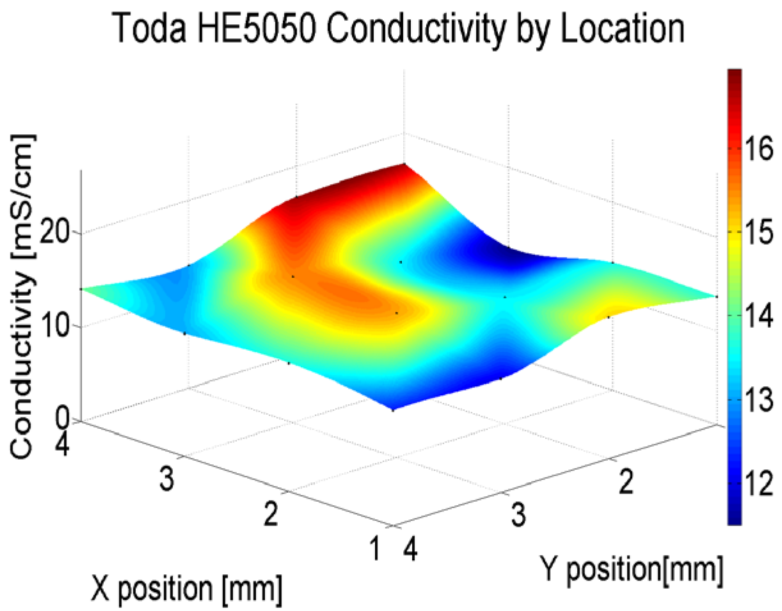


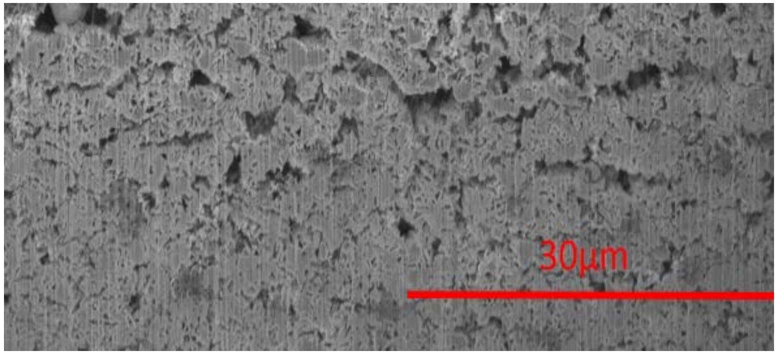


Microstructure determined by SEM/FIB as part of Mar 2014 milestone

TODA HE5050 (ANL) RESULTS







Microstructure determined by SEM/FIB as part of Mar 2014 milestone

Technical Accomplishment (Dec 2013, Mar 2014): Summary of Results on Baseline Electrodes

Electrode Sample	Bulk Electronic Conductivity (mS/cm)	Current collector interfacial contact resistance (Ω cm^2)
NCM (A123)	76.73 ± 29.47	0.0703 ± .0121
LFP (A123)	14.24 ± 1.26	
Graphite Anode (A123)	4009.76 ± 844.97	0.0474 ± 0.0017
Toda 523 (ANL)	229.66 ± 33.37	0.0448 ± 0.0033
Toda HE5050 (ANL)	13.95 ± 1.55	0.116 ± 0.011

- Uncertainties here indicate spatial variability across a 3mm x 3mm sample (see previous slides), not uncertainty in the probe measurements.
- Average values here are consistent with reported values for similar materials and alternative measurement techniques.

Responses to Previous Year Reviewers' Comments

Project has not been reviewed previously (began April 2013).

Collaborations and Coordination

- **A123** non-contract partnership
  - This project was initiated at A123's request for technology they needed but lacked.
  - A123 and BYU provide materials and expertise to each other.
  - A123 is purchasing BYU's conductivity probe technology to enable process improvement for their electrode fabrication process.
- Non-contract **research collaborations** within the battery research community, involving exchange of battery materials and expertise:
  - Andy Jansen, ANL
  - Vince Battaglia and Gao Liu, LBNL
  - Karim Zaghib, Hydro-Quebec
  - Claire Grey, Univ. of Cambridge
  - Simon Theile, Univ. of Freiburg / IMTEK
  - SAFT America

Remaining Challenges and Barriers

- Extend successful surface probe technique to measure additional parameters that determine cell power performance:
  - Anisotropic conductivity
  - Electronic conductivity while sample is wet (previous work suggests this is a significant effect)
  - Ionic conductivity
- Complete development of a predictive 3D microstructure model that is validated with
  - Experimental conductivity data
  - Experimental microstructure data

- Success in the above two areas will provide a suite of tools for optimizing fabrication processes of particle-based electrodes.

Proposed Future Work (Milestones)

- **June 2014:** Determine appropriate set of **descriptors or metrics** that effectively characterize previously observed microstructures. *Justification*: These descriptors will be used to assess accuracy of microstructure model and classify material and manufacturing differences.
- **Sept 2014:** (**Go/No-Go**) Discontinue current 4-line probe geometry if measurement variability is not significantly less than sample-to-sample variability. This criterion has already been met as of December 2013.
- **Dec 2014:** Measure localized **ionic conductivity** of two candidate electrode materials using micro-four-line probe and electrolyte solution. *Justification:* This measurement will provide another key performance parameter for understanding electrode structures and improving manufacturing processes.
- **Mar 2015:** Use **dynamic particle-packing (DPP) model** to predict electrode morphology of Toda 523 material. *Justification:* This Toda 523 material has a roughly spherical active component which makes it a preferred candidate for our initial particle simulations because it can accurately be represented by a distribution of different sphere sizes.
- **June 2015:** Develop fabrication process and demonstrate viability of **micro-N-line probe**. *Justification:* The additional lines on the probe will allow us to measure anisotropic effects and increase measurement robustness.
- **Sept 2015:** (**Go/No-Go**) Discontinue dynamic particle-packing (DPP) model if it cannot be used to predict electrode configurations of real electrode materials as analyzed by FIB/SEM. *Justification:* We must prove or disprove our hypothesis that aggregates of spheres can be used to predict electrode structures of relevance to battery research. As an alternative pathway, we can use automated segmentation techniques from FIB/SEM images in further simulations of battery performance, though this gives us less predictive capability than our preferred method of using DPP to predict initial structures.

- In addition to these milestones and decision points in FY14/FY15, we will pursue new collaborations and leverage our current collaborations to assess additional electrode materials of interest to DOE, using our unique diagnostic tools.

SUMMARY

- Deliverables after first year of project
  - First-generation electronic probe completed and tested. Transfer of technology to A123 in progress.
  - 3D microstructures for 3 candidate electrodes have been determined by SEM/FIB.

- How this will improve battery manufacturing
  - Commercial-grade electrodes have significant spatial differences in conductivity due to variability on the mm length scale.
  - Our technique can quantify these differences and increase real-time quality control in roll-to-roll processing. It is anticipated that this will improve electrode performance and cycle life.