Scale-Bridging Simulations and Experiments of Electrode Materials in Li-ion Batteries

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Project ID: es_17_sastry

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acknowledgments

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leverage

- *General Motors*
- *Ford Motor Company*
- *Oak Ridge National Laboratory*
- *Army Research Office*
- *Air Force Office of Scientific Research*

purpose of work

OBJECTIVES: Determine optimal particle blends for high power and long lifetime for both energy- and power-dense systems via coupled multiphysics modeling and experiments on baseline materials. Identify and predict failure mechanisms in baseline cells, considering coupled electrochemical and mechanical effects. Determine fundamental properties of SEI layers, and model their effects on performance, in addition to self-assembly in particulate systems.

MILESTONES:

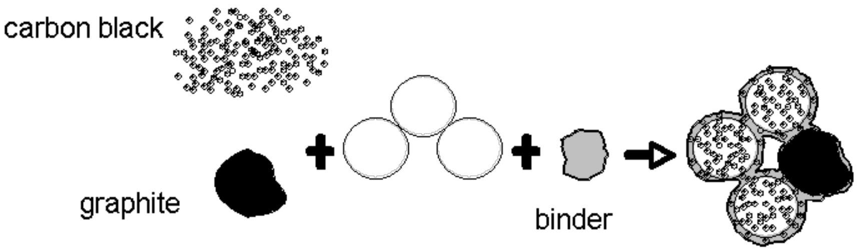
(a) implement 3D-FE model with layerwise SEI properties. (Feb. 09) (delayed; new in-situ AFM setup ready for SEI layer property study)

(b) model self-assembly of conductive additives and identify criticalities in volume fraction. (Mar. 09) (ahead of schedule: self-assembly modeling is ongoing; volume fraction optimization is complete)

(c) utilize measured diffusion coefficients in full 3D-FE simulations. (Jul. 09) (ahead of schedule: measurements at ORNL already complete)

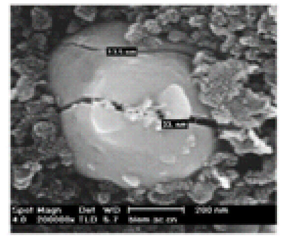
BARRIERS: Short lithium battery lifetimes, closely related to composition of electrode, processing conditions, and fracture of particles; inadequate power of lithium batteries, closely related to diffusion and conduction processes.

composition of the electrode

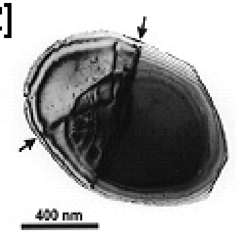


fracture due to intercalation and/or compression

[1]

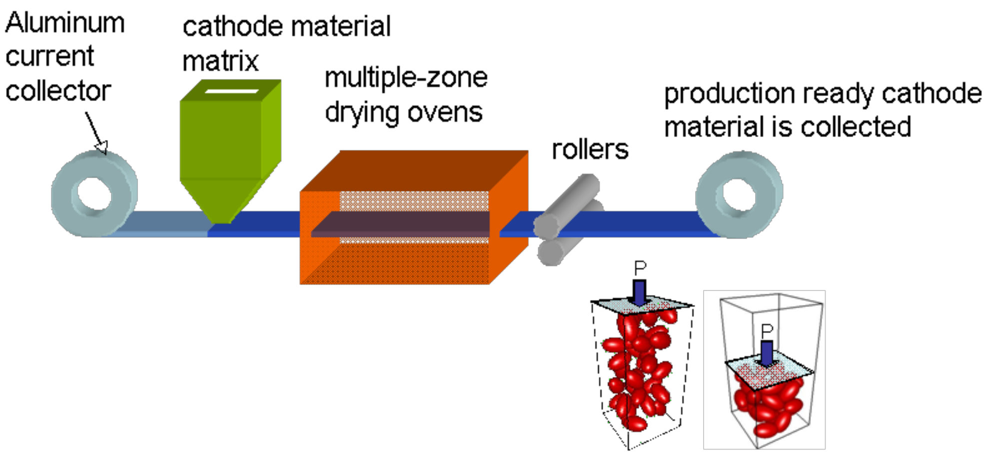


[2]

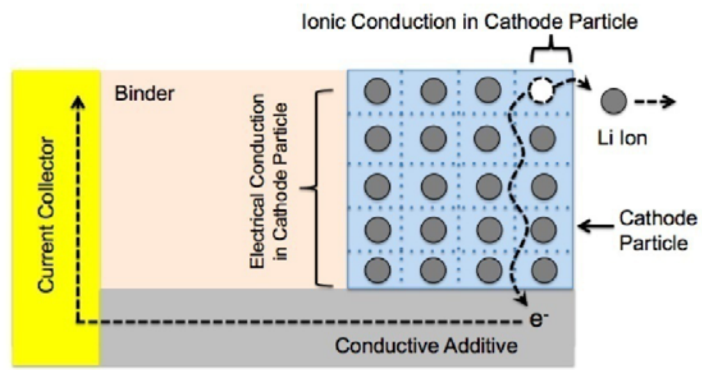


[1] D. Wang, X. Wu, Z. Wang, and L. Chen, "Cracking Causing Cyclic Instability of LiFePO4 Cathode Material", Journal of Power Sources, 140 125-128 (2005).
[2] H. Wang, Y. Jang, B. Huang, D. R. Sadoway, and Y.-M. Chiang, "TEM Study of Electrochemical Cycling-Induced Damage and Disorder in LiCoO2 Cathodes for Rechargeable Lithium Batteries", Journal of the Electrochemical Society, 146(2) 473-480 (1999).

processing conditions



conduction and diffusion processes



FY09

our approach

1) build finite element simulations, in collaboration with continuum modeling (with V. Srinivasan, LBNL), to understand critical failure mechanisms and their interactions;

2) optimize electrode design and fabrication (with V. Battaglia, LBNL) using developed simulation tools;

3) consider self-assembly of conductive additives as a mechanism in simulations of conduction and in order to reduce inactive mass;

4) measure conductivity and diffusivity in cathodes experimentally (with N. Dudney, ORNL);

5) study SEI layer material properties using our in-situ AFM to provide inputs for 3D finite element modeling.

overview / lab efforts

A • M • S • L

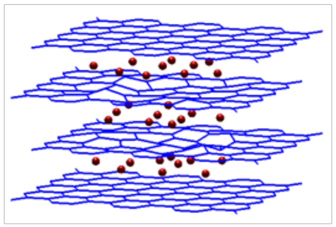
modeling

DoE: particle multiphysics simulations (08); aggregation (09)

GM: ongoing

GM: ongoing

atomic/molecular: understand chemistry



particle-scale: understand physics

micro-scale: understand mechanics

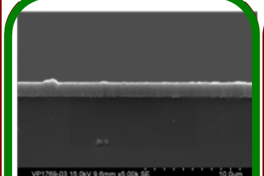
macro-scale: battery optimization

GM: collaboration with A. Van der Ven

experiments

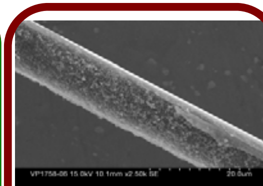
materials synthesis

DoE/ORNL (08-09)

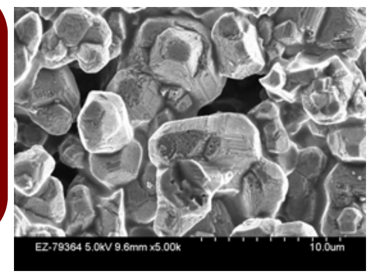


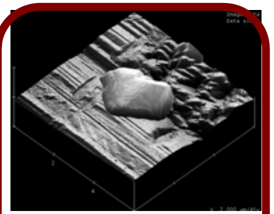
• thin film

ARO (06-09)



• fiber





• particle

GM (08-09)

battery performance testing

modeling of single particles - (FY08)

A • M • S • L

objectives

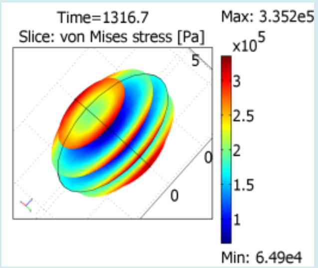
• understand the physical mechanism of intercalation-induced stress generation
• understand the interplay between thermal, kinetic and mechanical effects
• optimize electrode particle shape for stress and heat generation reduction

approach

• model intercalation-induced stress via analogy to thermal stress
• apply a surrogate-based approach to systematically study the effect of particle morphology and cycling rate on stress and heat generation

findings/results

• thermal, kinetic and mechanical effect amplify each other
• electrode particle with larger aspect ratios are preferred to reduce stress and heat generation

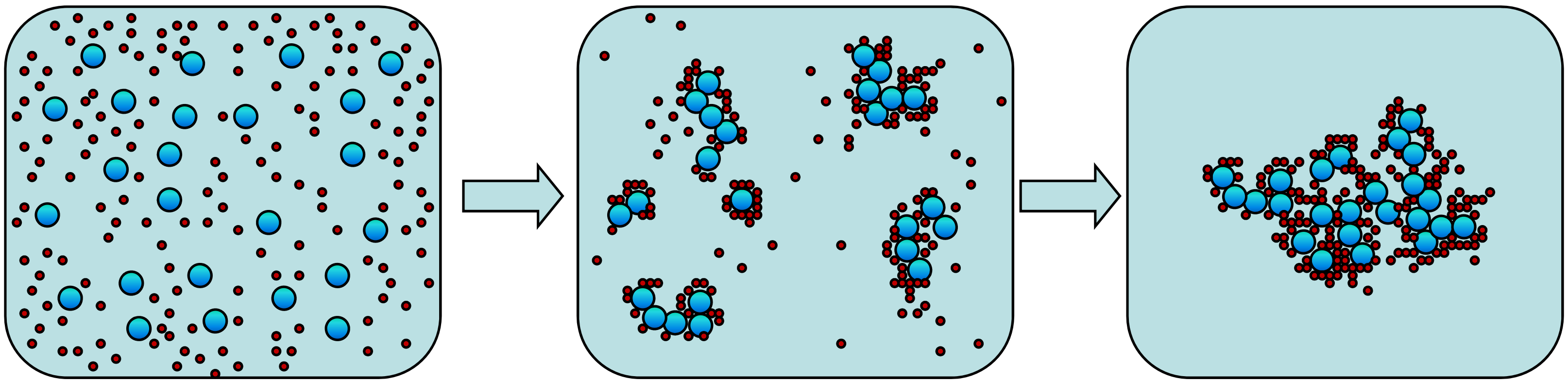


publications

• Zhang, X.C., Sastry, A.M. and Shyy,W., 2008, "Intercalation-induced stress and heat generation within single lithium-ion battery cathode," Journal of the Electrochemical Society, v.155(7), pp.A542-A552.

electrode construction: FY09

- Brownian dynamic simulation for cluster formation
- start from randomly distributed particles, moving under the influence of inter-particle forces (van der Waals and Columbic) and random Brownian forces
- particles aggregate to form small clusters, than larger clusters
- generate multi-physics models for FE analysis based on the obtained aggregates



a schematic for Brownian dynamic simulation of a binary system

electrode construction: FY09

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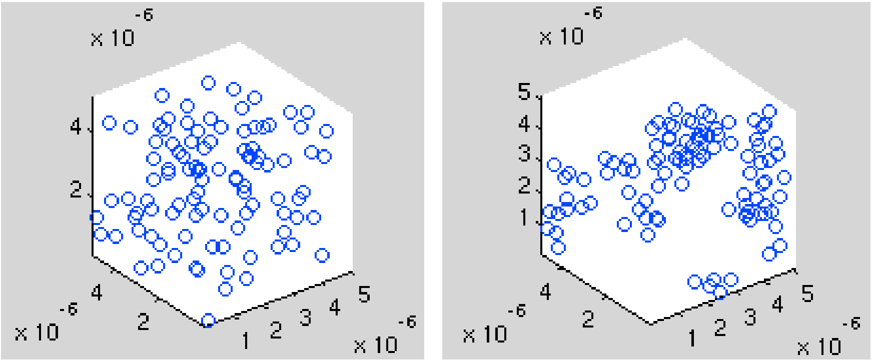
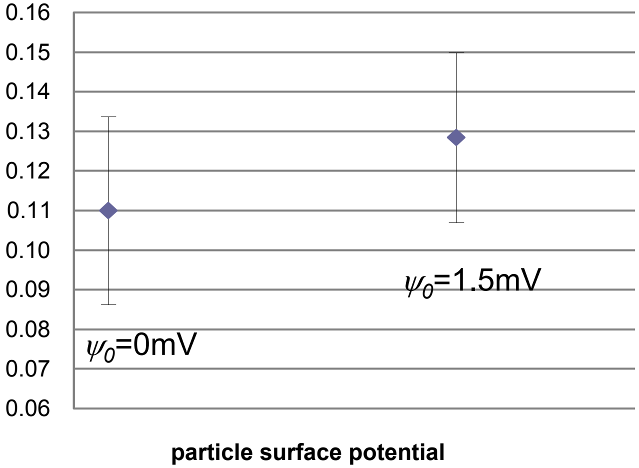
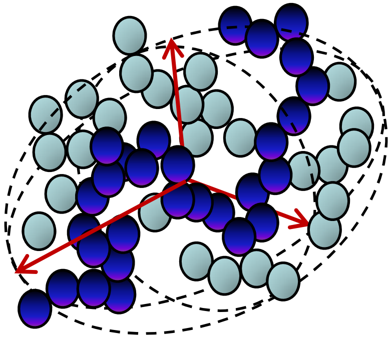
- simulation of monodisperse systems
  - inter-particle forces are adjusted by changing particle surface potential from 0mV to 1.5mV
  - particle geometry characterized by radius of gyration R_g and main chain length L_m, which increase by 16.8% and 6.20%, respectively, due to increase of particle surface potential



(a) original configuration (b) aggregated configuration

aggregation process simulation

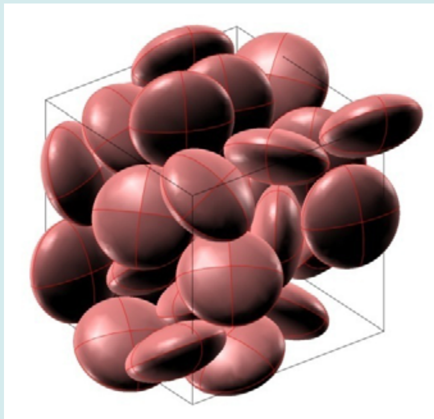




microscopic modeling: FY09

- electrode microstructural geometry modeling

  - use a dynamic packing algorithm



a demonstration of 30 particle packing;
aspect ratio 0.5, volume fraction 0.7

  - model two phases in electrode

liquid electrolyte phase

solid active material phase

- governing equations
  - Li ion transport in liquid electrolyte and solid active material
  - electric potential equation in both phases
  - Butler-Volmer equation on the phase interface
- governing equations are implemented in COMSOL Multiphysics

microscopic modeling results: FY09

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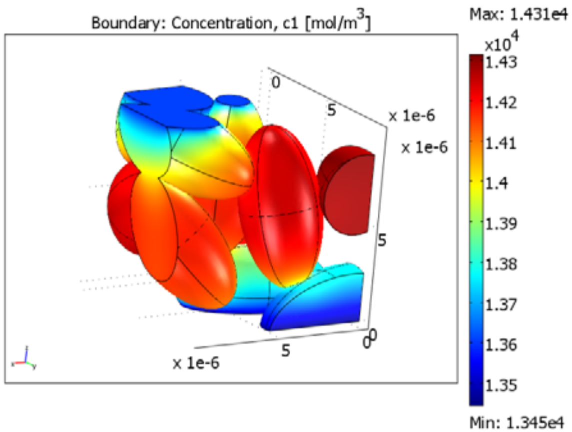
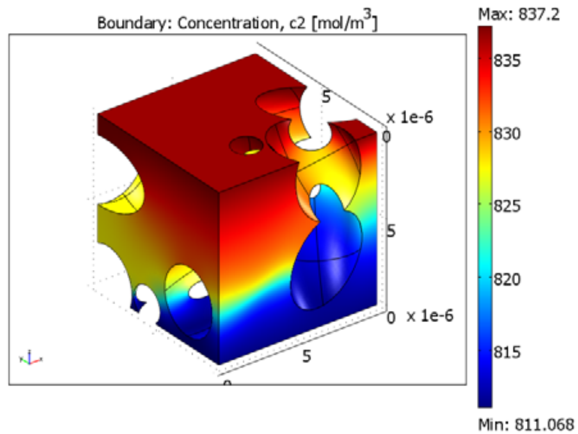
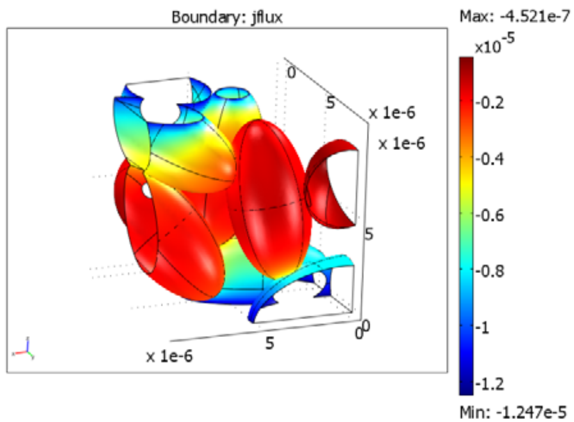


Li-ion concentration in solid phase



Li-ion concentration in liquid phase



flux on the interface

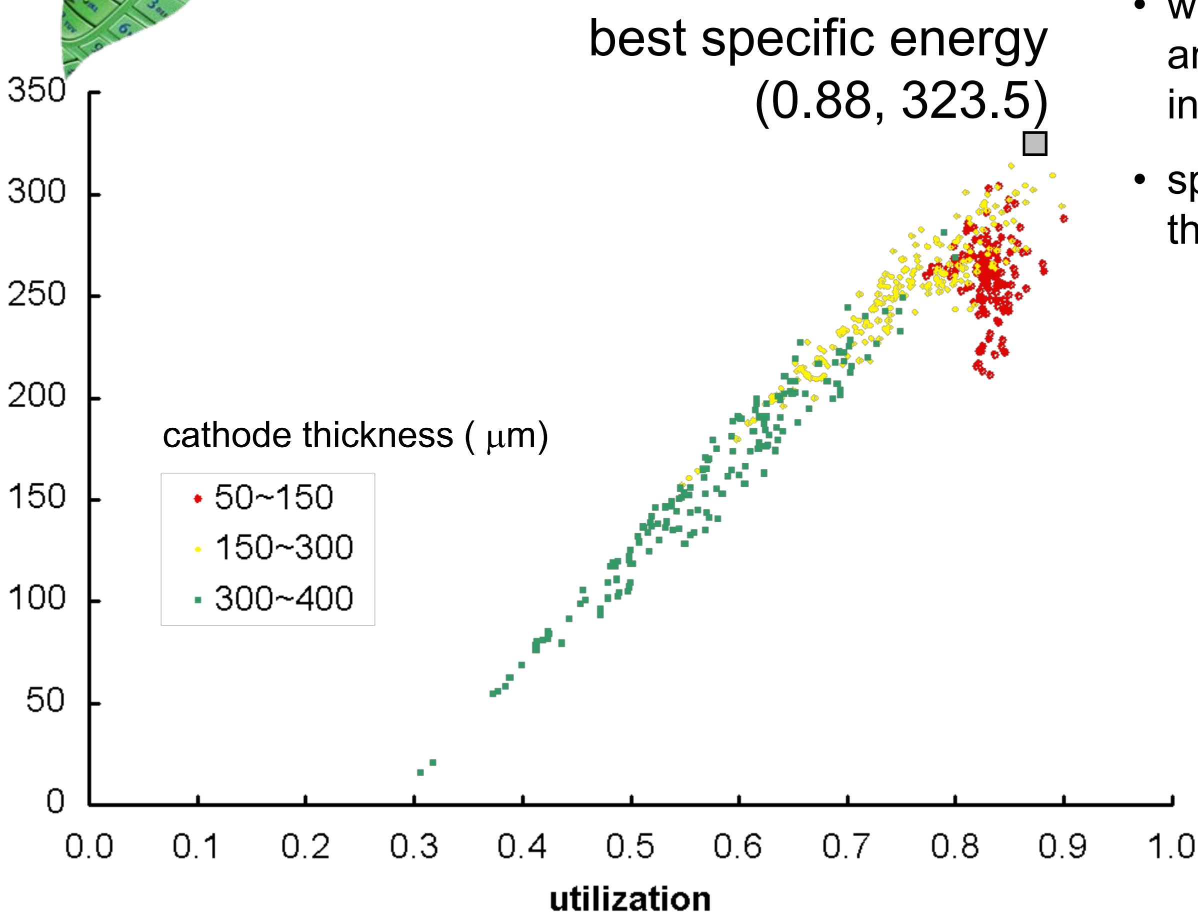
- comparison of reaction electric current (A/m^2) of 3D microscopic and pseudo 2D simulations

simulation domain	pseudo 2D model	3D particle cluster model	
		realization 1	realization 2
165 ~ 175 mm	-2.08	-1.59	-1.62
125 ~ 135 mm	-1.16	-1.12	-1.15
215 ~ 225 mm	-2.82	-2.16	-2.12

- results from 3D and pseudo 2D models are largely different

- high fidelity 3D microscopic modeling and simulations are necessary

electrode design optimization: FY09 A • M • S • L



specific energy vs. utilization

- when cathode is 150 to 400 μm, utilization and specific energy increase with decrease in cathode thickness
- specific energy drops when cathode is small than 150 μm due to mass balance effect

optimized properties:
- active material: 36.2%
- PVDF/C: 10% • graphite: 0
- thickness: 192.5 μm

- electronic conductivity: 20.5 S/m
- normalized ionic conductivity: 0.4

- specific energy: 323.5Wh/kg
- specific power: 1614 W/kg
- utilization: 0.88

experimental diffusion study: FY09

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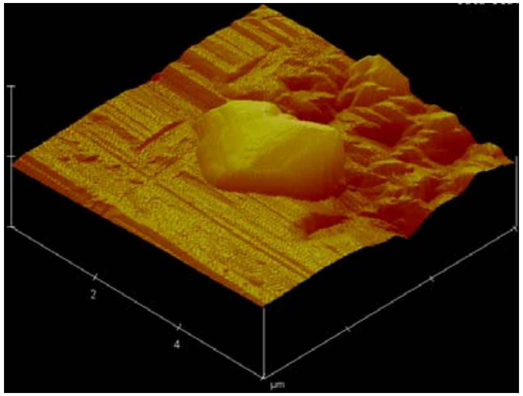
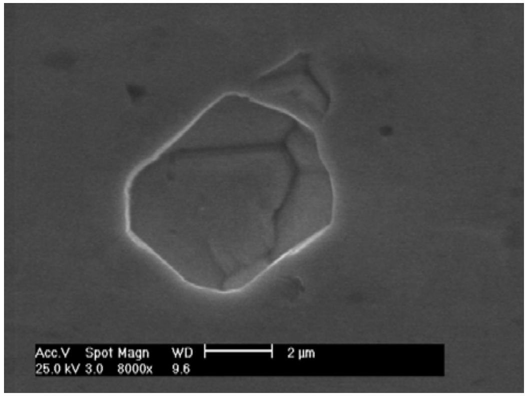
• use of thin film / particle based electrode models for Li-ion diffusion study, also for materials characterization

• performing various electrochemical testing including cyclic voltammetry (CV) and potentiostatic intermittent titration technique (PITT)

• developing experimental models to validate the modeling and simulation



AFM image of $LiMn_2O_4$ particle on gold substrate; sample 052-83-02

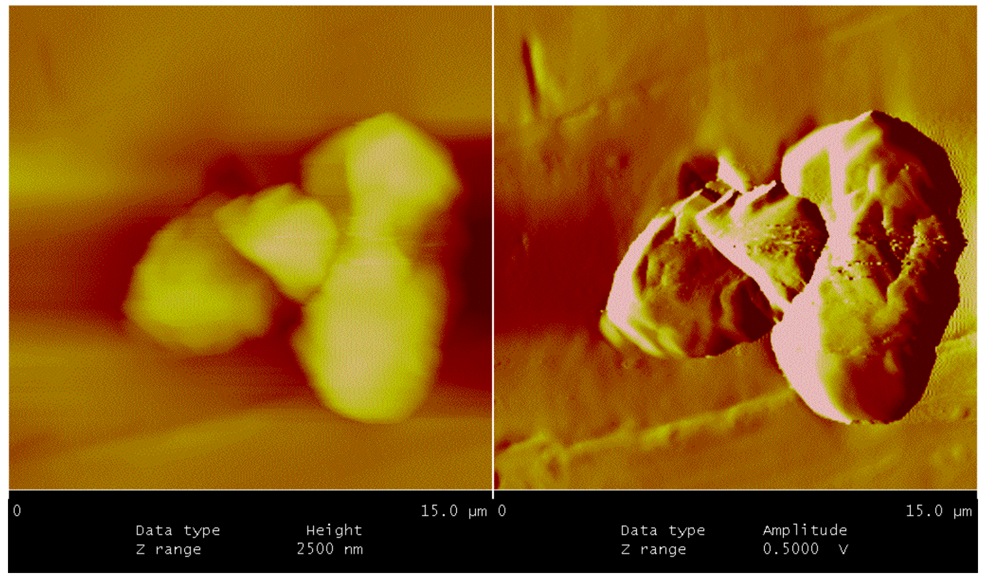


SEM image of $LiMn_2O_4$ particle on gold substrate; sample 052-42-01

in-situ AFM study w/ GM: FY09

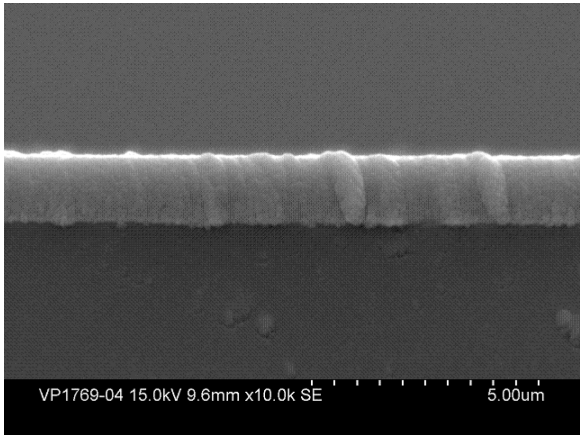
- Veeco Multimode AFM in Golvebox
  - O_2 and H_2O level < 1 ppm
  - surface morphology in nm scale
  - electrical resistance in femto amp
  - electrochemical AFM mode

the setup is proposed to be used for SEI layer property study

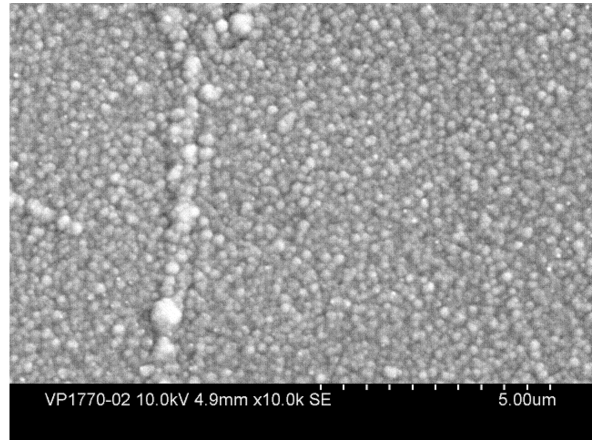


AFM image of $LiMn_2O_4$ particles on gold substrate; sample 052-42-02

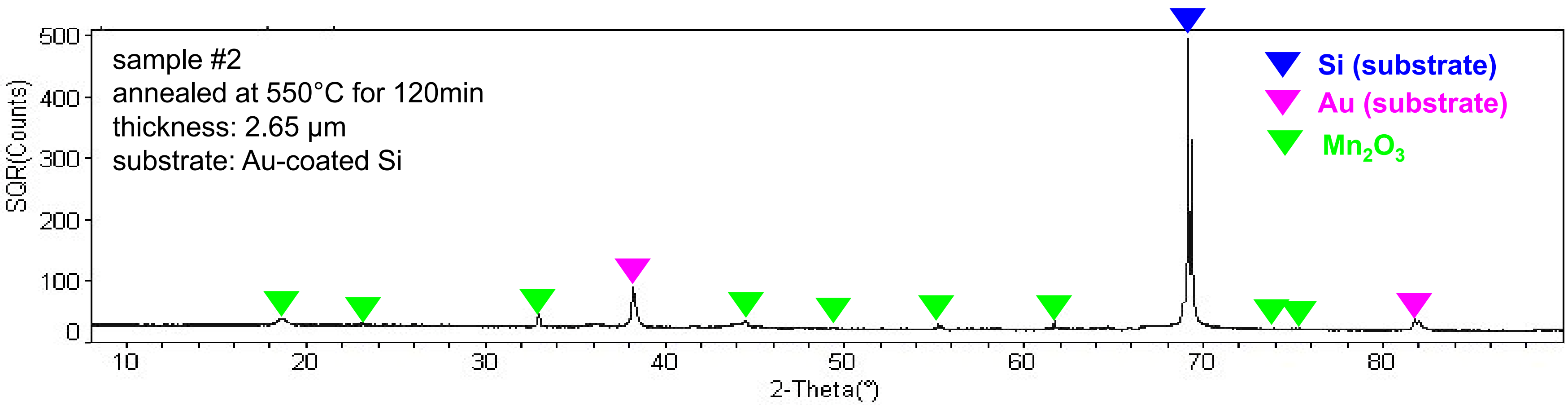
thin film characterization: FY09



sample #17 (side view)
condition: unannealed
thickness: 0.9 μm, substrate: silicon (Au/Ti/Si)



sample #2 (top view)
condition: annealed at 550°C for 120min
thickness: 2.65 μm, substrate: silicon (Au/Ti coated)



accomplishments and status

- **FY08 - Fundamental:** particle morphology affects the generation of intercalation stress and heat. **Practical:** electrode particles of larger aspect ratios are preferred to reduce stress and heat generation

- **Fundamental:** diffusion process for three basic schema (particle, film, fiber) presumed to be different but relatable via closed-form approaches. **Practical:** measured diffusion coefficients can be used as inputs for 3D finite element models .

- **FY08 - FY09 - Fundamental:** electrode architectures were constructed using both dynamic packing algorithms and Brownian dynamic aggregation, and investigated for robustness. **Practical:** generated microstructures can be used as inputs for electrochemical modeling and structural failure analysis of electrode materials .

- **Fundamental:** a surrogate-based approach was applied for the design optimization of Li-ion cathodes for baseline materials. **Practical:** optimal solutions were identified for best specific capacity which suggests the material and structure choices for battery electrode design. **NEW LEVERAGE - GM ongoing R&D in different cathode architectures.**

future work

- SEI formation and consideration of its effects on kinetic performance will be sought. Both experimental and numerical tools will be developed.

- Anode materials and their optimization are important, and several materials systems will be considered, including novel architectures.

- Particle aggregation will be studied in the context of manufacturing conditions, using fundamental models to explore manufacturing approaches which produce superior electrodes.

- Cumulative effects of intercalation stresses and heat generation are being studied at multiple scales. We will continue to refine models based on base-set architectures: particles, fibers and films, and consider novel architectures as well (LEVERAGE: ORNL, FORD).

- We will continue to explore progressive damage in the context of multiple scales in particle aggregates (primary and secondary) and couple these to kinetic and thermal effects (LEVERAGE: GM).