



Microscale Electrode Design Using Coupled Kinetic, Thermal and Mechanical Modeling

Ann Marie Sastry, PI

Project ID: ES082

Arthur F. Thurnau Professor, Mechanical, Biomedical and Materials Science and Engineering University of Michigan, and
Director, Energy Systems Engineering Program, University of Michigan,
Ann Arbor, MI 48109-2125

**CONTRIBUTORS: Dr. Yen-Hung Chen, Dr. Xiangchun Zhang,
Dr. Myoungdo Chung, Prof. Wei Shyy, Dr. Jeong Hun Seo,
Dr. Jonghyun Park, Dr. Myounggu Park, Mr. Min Zhu**

*2010 DOE Annual Merit Review Meeting
Washington D.C. | June 7, 2010*

This presentation does not contain any proprietary or confidential information

Advanced Materials Systems Laboratory

Departments of Mechanical, Biomedical and Materials Science and Engineering



acknowledgements

Advanced Materials Systems Laboratory

sponsor

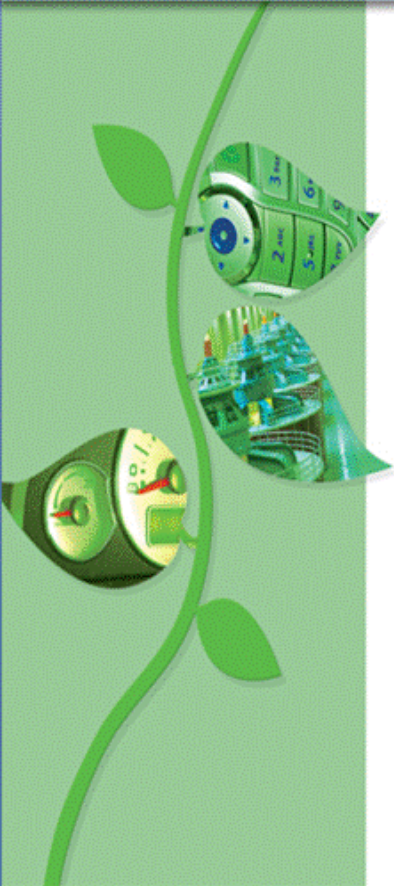
DOE

Sastry group members

*Dr. Greg Less
Dr. Joseph Gallogos
Mr. Sang Woo Han
Mr. Dong Hoon Song
Mr. Ho Sop Shin
Mr. Yoon Koo Lee*

leverage

*-General Motors
-Ford Motor Company
-Oak Ridge National Laboratory
-Army Research Office*



OBJECTIVES: Determine battery performance for high-power systems via multiscale modeling of thermo-electrochemistry. Model SEI film formation as a precipitation process including a nucleation and a phase growth. Determine SEI layer properties depending on cycling, charge/discharge rate and temperature

MILESTONES:

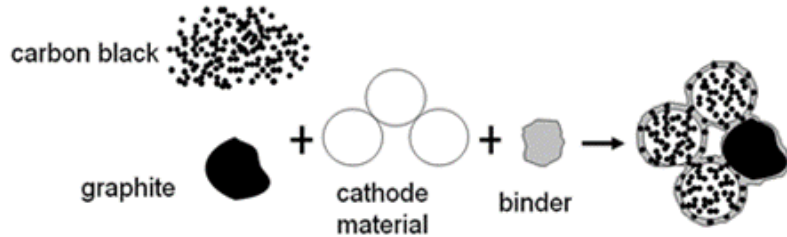
- (a) Implement multiscale thermo-electrochemistry model (Mar. 10) (implemented)
- (b) Implement SEI formation modeling (May 10) (phase-field modeling is ongoing)
- (c) Measure SEI layer properties to inform these models (Aug. 10) (experiment setup is designed and ORNL collaboration in place)

barriers

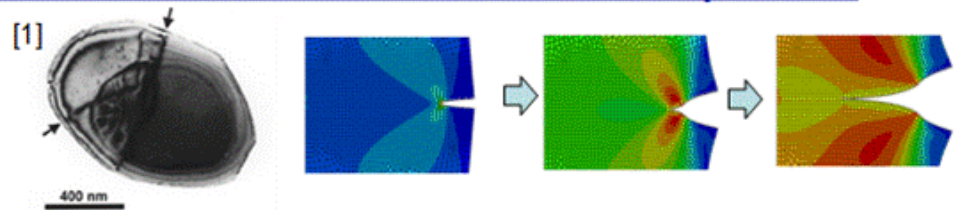
A • M • S • L

BARRIERS: Short lithium battery lifetimes, closely related to composition of electrode, particle aggregates and fracture of particles; closely related to SEI layer formation on electrodes

electrode configuration (e.g., composition)

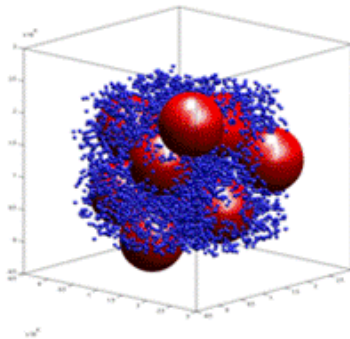
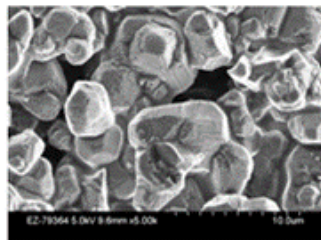


fracture due to intercalation and/or compression

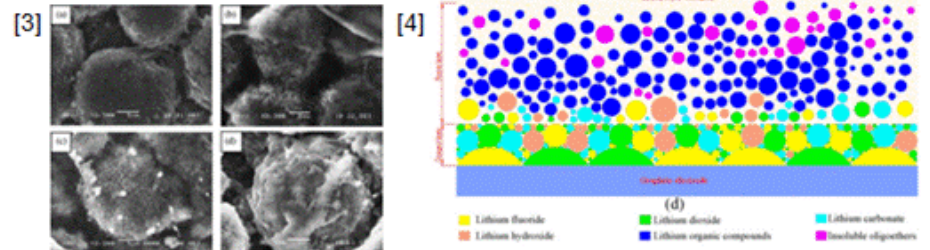


[1] H. Wang, Y.-I. Jang, B. Huang, D. R. Sadoway, and Y.-M. Chiang, "TEM Study of Electrochemical Cycling-Induced Damage and Disorder in LiCoO_2 Cathodes for Rechargeable Lithium Batteries", *Journal of The Electrochemical Society*, Vol. 146 (2), pp. 473-480, 1999

particle aggregates (active material & additives)



SEI layer formation



[3] P.L. Moss, G. Au, E.J. Plichta and J.P. Zheng, "Investigation of solid electrolyte interfacial layer development during continuous cycling using ac impedance spectra and micro-structural analysis," *Journal of Power Sources*, Vol. 189 (1), 2009

[4] J. Yana, B.-J. Xia, Y.-C. Su, X.-Z. Zhou, J. Zhang, X.-G. Zhang, "Phenomenologically modeling the formation and evolution of the solid electrolyte interface on the graphite electrode for lithium-ion batteries," *Electrochimica Acta*, Vol. 53, pp.7069-7078, 2008

overview / lab efforts

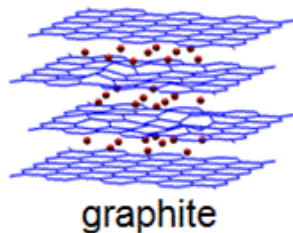
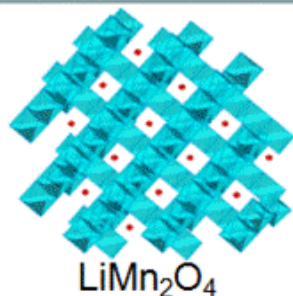
A • M • S • L

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

GM: ongoing

GM: ongoing

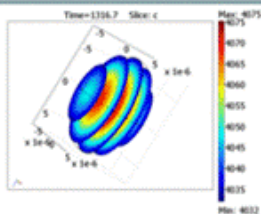
atomic/molecular:
understand chemistry



GM: collaboration
with A. Van der Ven
& B. Bartlett

↓
materials
synthesis

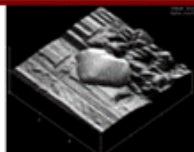
particle-scale:
understand physics



DoE/ORNL (08-09)



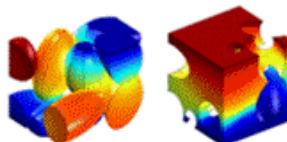
thin film



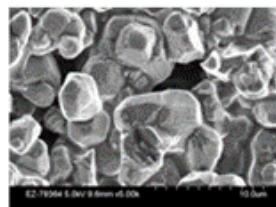
particle

GM (08-09)

micro-scale:
understand mechanics



reaction current

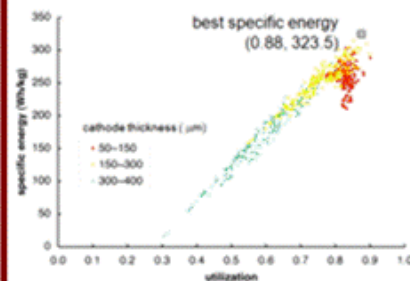


particle aggregates

performance
testing



macro-scale:
battery optimization



objectives

- map relationship between the ionic and electronic conductivities
- correlate conductivities to performance
- Identify optimal schema for high energy cells

approach

- model 3D porous electrode and evaluate effective material properties
- simulate 1D electrochemical model for battery performance
- apply surrogate modeling to correlate conductivities and battery performance

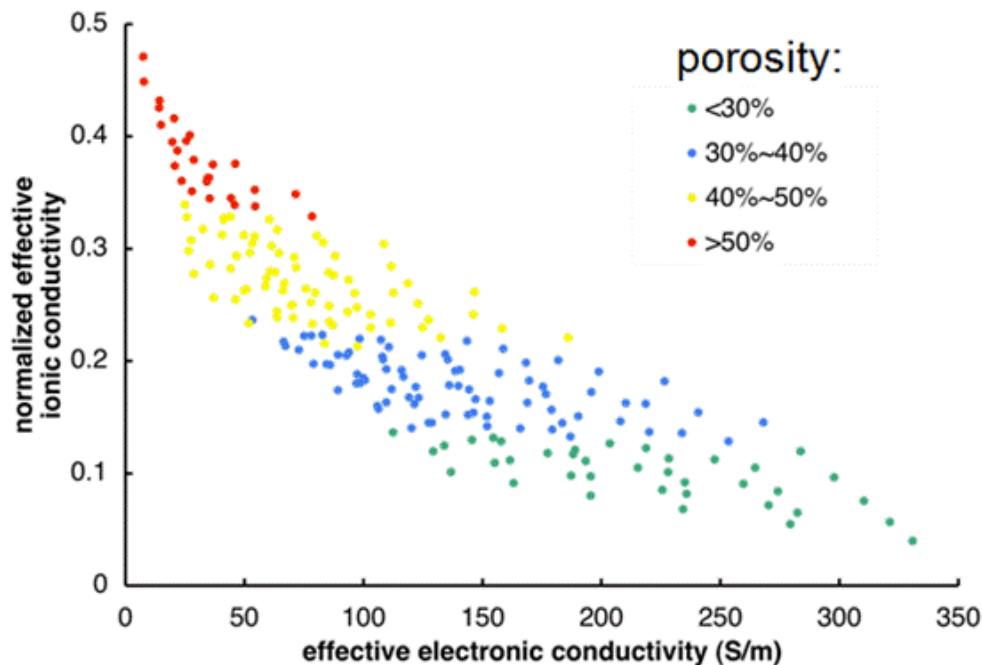
finding/results

- trade off between ionic conductivity and electronic conductivity
- quantitative guidance for the design of high energy density and guidelines for the design of cathode systems

publications

- Chen, Y.-H., Wang, C.-W., Zhang, X., Sastry, A.M., 2010, "Porous cathode optimization for lithium cells: Ionic and electronic conductivity, capacity, and selection of materials", Journal of Power Sources, v.195, pp.2851-2862.

ionic vs. electronic conductivity



$$\frac{\sigma_{l,overall}}{\sigma_{l,bulk}} = \sigma_{e,ionic}$$

$\sigma_{l,overall}$: overall liquid phase conductivity

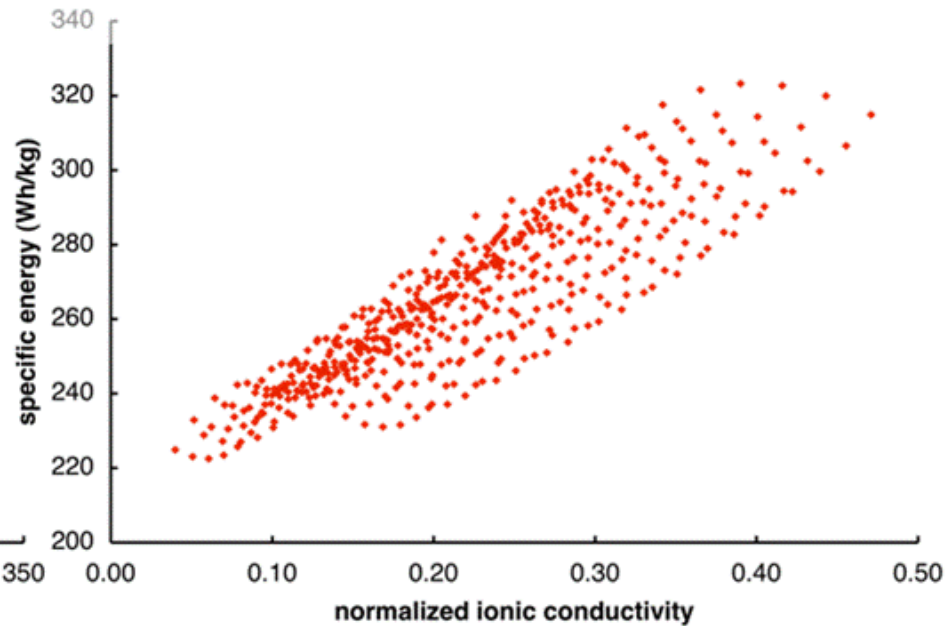
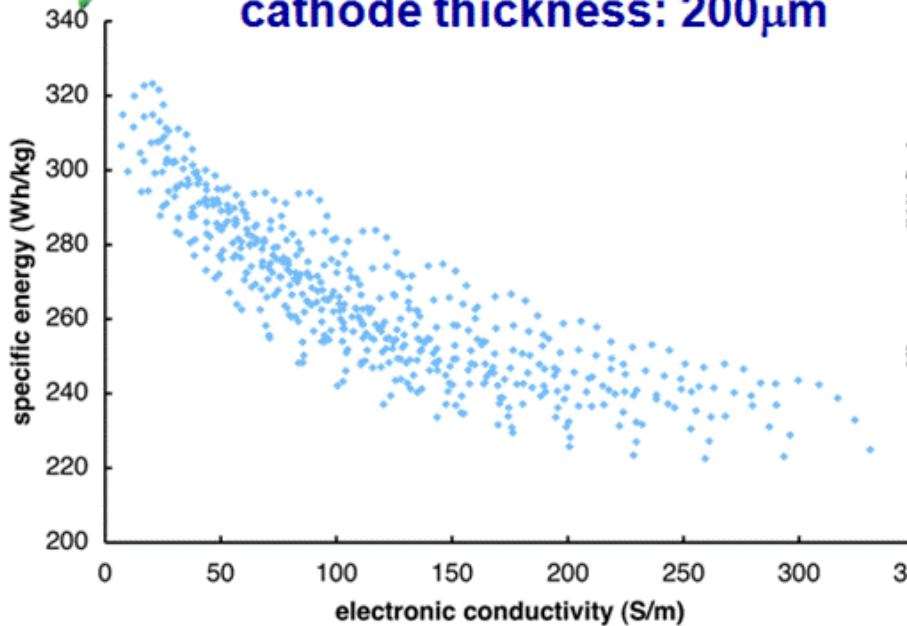
$\sigma_{l,bulk}$: bulk electrolyte conductivity

$\sigma_{e,ionic}$: normalized effective ionic conductivity

- there is a trade-off between ionic and electronic conductivity
- ionic conductivity increases with increase in porosity

conductivity vs. specific energy

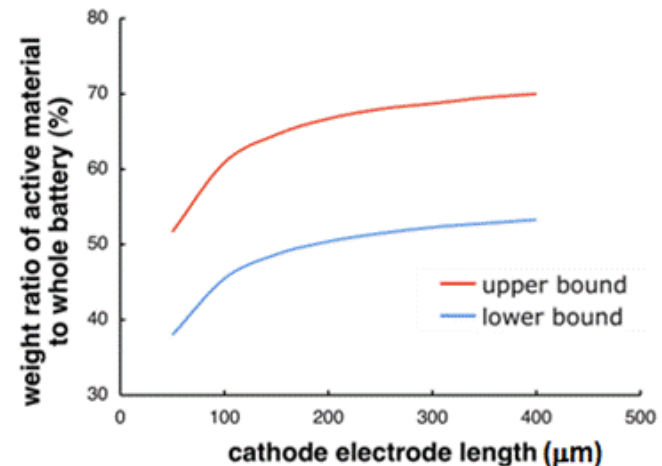
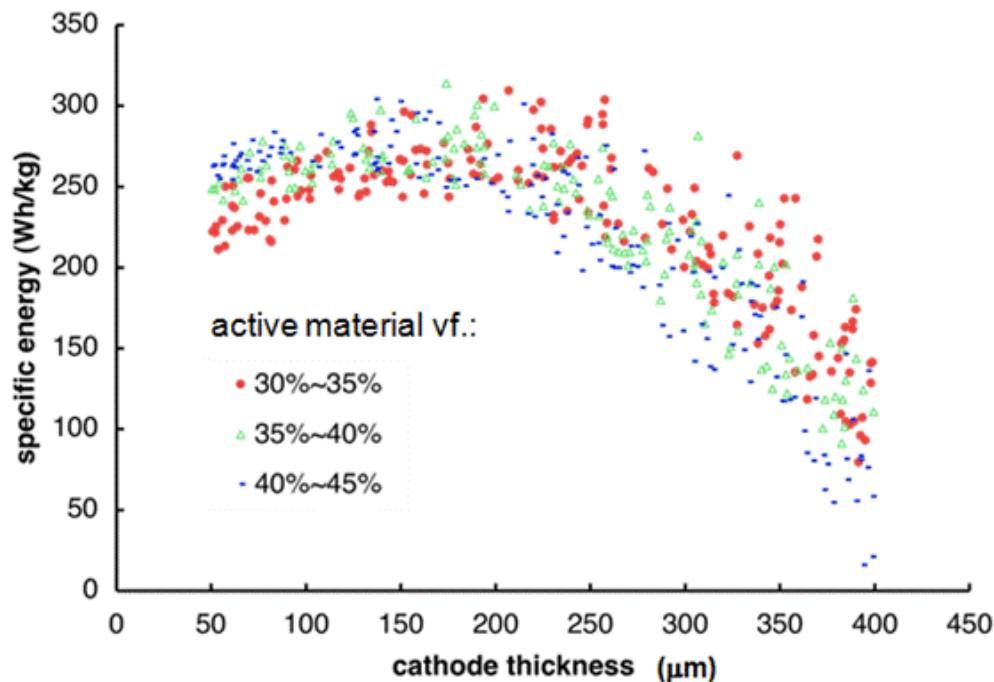
cathode thickness: 200 μ m



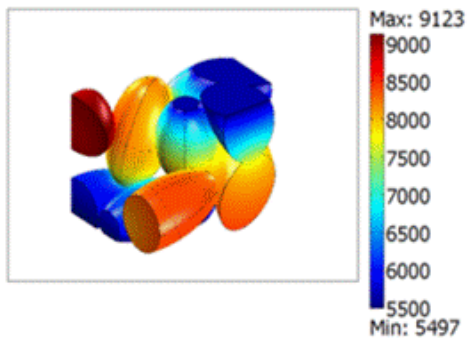
- best electronic conductivity or ionic conductivity doesn't ensure best specific energy

effect of thickness and active material vf.

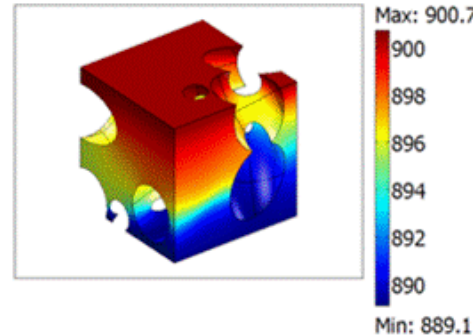
- thicker electrode or more active material vf.:
larger theoretical capacity but slow in ion transport
- thinner electrode or less active material:
fast in ion transportation but less theoretical capacity
- relatively lower capacity due to mass balance effect of active material also results in lower specific energy



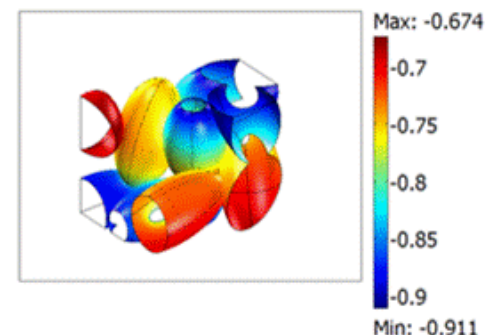
- 3-D microstructure characterization parameters
 - volume fraction: active material in the electrode
 - aspect ratio: interfacial area available for reactions
 - equivalent particle radius: characteristic time for diffusion
- geometry modeling
 - microstructure characteristics: 10 ellipsoidal particles, aspect ratio 2, solid volume fraction 0.6, equivalent radius $5.34\mu\text{m}$
 - particles are packed using a collision-driven molecular dynamics algorithm [1]



Li ion concentration in solid phase
(mol/m^3)



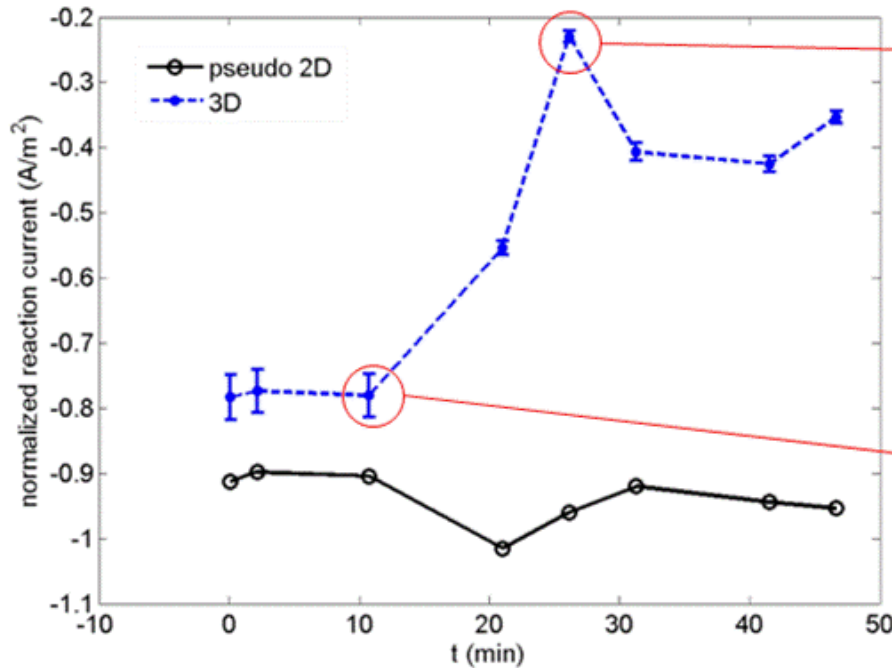
Li ion concentration in liquid phase
(mol/m^3)



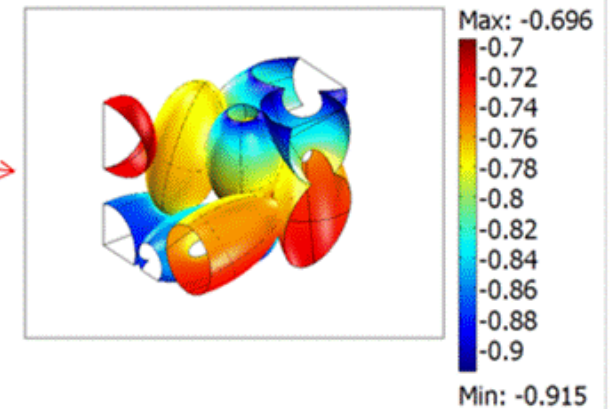
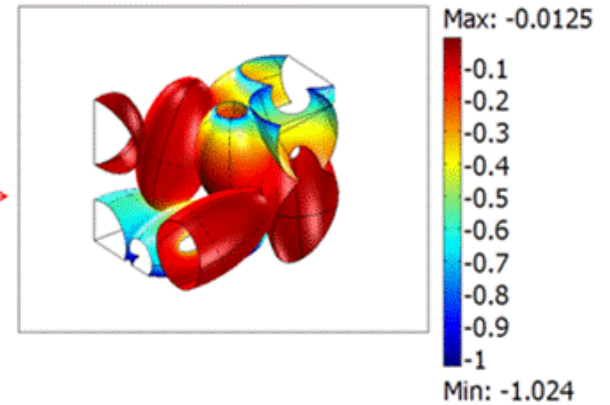
reaction current density at interface
(A/m^2)

[1] A. Donev, F. H. Stillinger, and S. Torquato, Neighbor List Collision-Driven Molecular Dynamics Simulation for Nonspherical Particles. I. Algorithmic Details II. Applications to Ellipses and Ellipsoids, *Journal of Computational Physics*, 202, 737-764 (part I) and 765-793 (part II) (2005).

comparison: reaction current density



time history of normalized reaction current density



- local distribution of variables is important for normalized reaction current density
- detailed 3-D microscopic modeling reveals distribution of local variables

microscopic scale
3-D electrode microstructure

liquid phase
(electrolyte)



solid phase
(active material)



both phase



interface



$$\frac{\partial c_2}{\partial t} = \nabla \cdot (D_2 \nabla c_2)$$

$$\nabla \cdot [\kappa \nabla V_2 + \kappa_D \nabla (\ln c_2)] = 0$$

$$\frac{\partial c_1}{\partial t} = \nabla \cdot (D_1 \nabla c_1)$$

$$\nabla \cdot \mathbf{i}_1 = \nabla \cdot (\sigma \nabla V_1) = 0$$

$$\rho c_p \frac{\partial T_k}{\partial t} = \nabla \cdot (\lambda_k \nabla T_k) + i_k \cdot \nabla V_k$$

Butler-Volmer equation

$$J = \frac{i_n}{F} = i_0 \left\{ \exp \left[\frac{(1-\beta)F}{RT} \eta \right] - \exp \left[-\frac{\beta F}{RT} \eta \right] \right\}$$

volume
averaging
→

macroscopic scale
1-D Li-ion cell

anode | separator | cathode

$$\frac{\partial \bar{c}_2}{\partial t} = \nabla \cdot (D_2^{\text{eff}} \nabla \bar{c}_2) + J_{c_2}$$

$$\nabla \cdot [\kappa^{\text{eff}} \nabla \bar{V}_2 + \varepsilon_2 \kappa_D^{\text{eff}} \nabla (\ln \bar{c}_2)] + J_{V_2} = 0$$

$$\frac{\partial \bar{c}_1}{\partial t} = \nabla \cdot (D_1^{\text{eff}} \nabla \bar{c}_1) + J_{c_1}$$

$$\sigma^{\text{eff}} \nabla \bar{V}_1 + J_{V_1} = 0$$

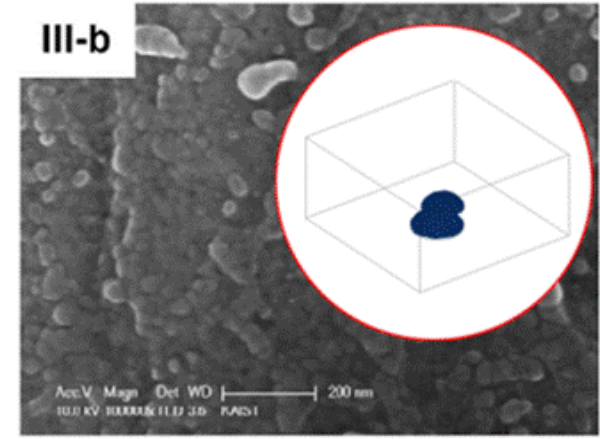
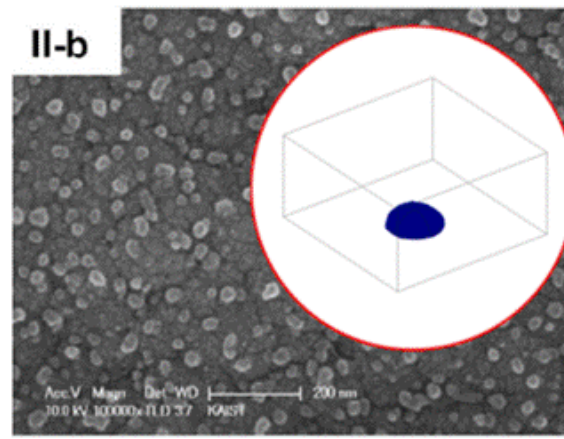
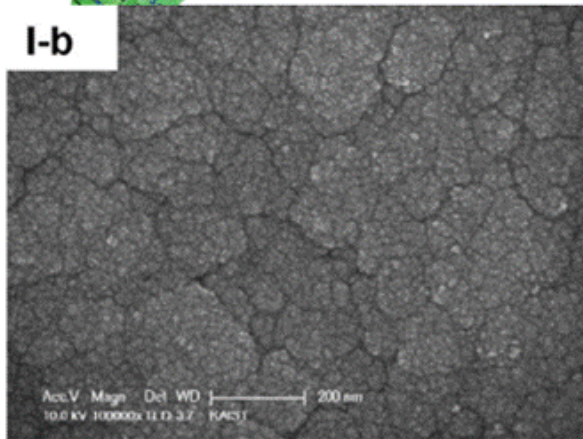
$$\rho^{\text{eff}} c_p^{\text{eff}} \frac{\partial \bar{T}}{\partial t} = \nabla \cdot (\lambda^{\text{eff}} \nabla \bar{T}) + \bar{Q}$$

closure terms

- effective material properties
- volumetric reaction rate
- heat generation

nucleation process

growth process



SEM images for the surface of the Si thin electrode [1]

free energy of the system

$$G = \int_{\Omega} \left(f(c) + \frac{1}{2} h(\nabla c)^2 \right) dV + \int_{\partial\Omega} [\sigma_{SD} + (\sigma_{SM} - \sigma_{SD})\rho(c)] dA$$

kinematics + kinetics

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad \mathbf{J} = \mathbf{M}\mathbf{F}$$



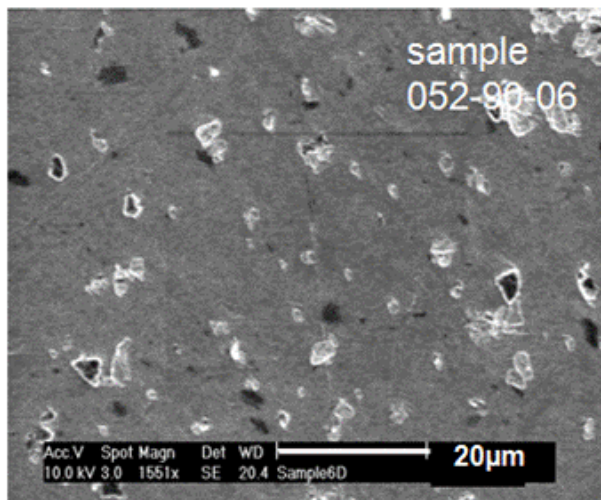
$$\left(\frac{\partial c}{\partial t} = \nabla(\mathbf{M} \cdot \nabla \mu) \right) \Big|_{\Omega}$$

$$\left(\mu = f'(c) - h\nabla^2 c \right) \Big|_{\Omega}$$

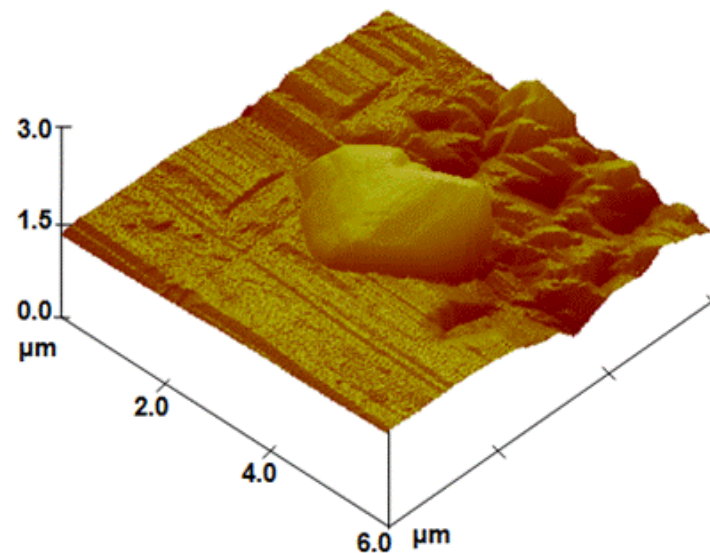
$$\left(\mathbf{n} \cdot \nabla \mu = 0 \right) \Big|_{\partial\Omega}, \left(h\mathbf{n} \cdot \nabla c + (\sigma_{SM} - \sigma_{SL})\rho'(c) = 0 \right) \Big|_{\partial\Omega}$$

[1] Yong Min et al., SEI Layer formation on amorphous Si thin electrode during pre cycling, *Journal of The Electrochemical Society*, 154 6 A515-A519 2007

- use of dispersed 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)



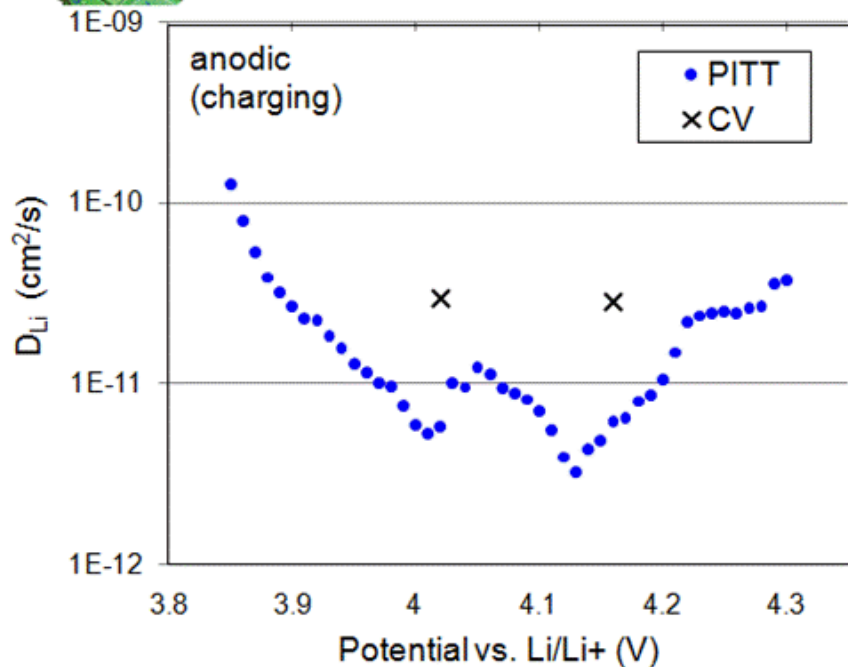
highly dispersed particles on a gold foil substrate



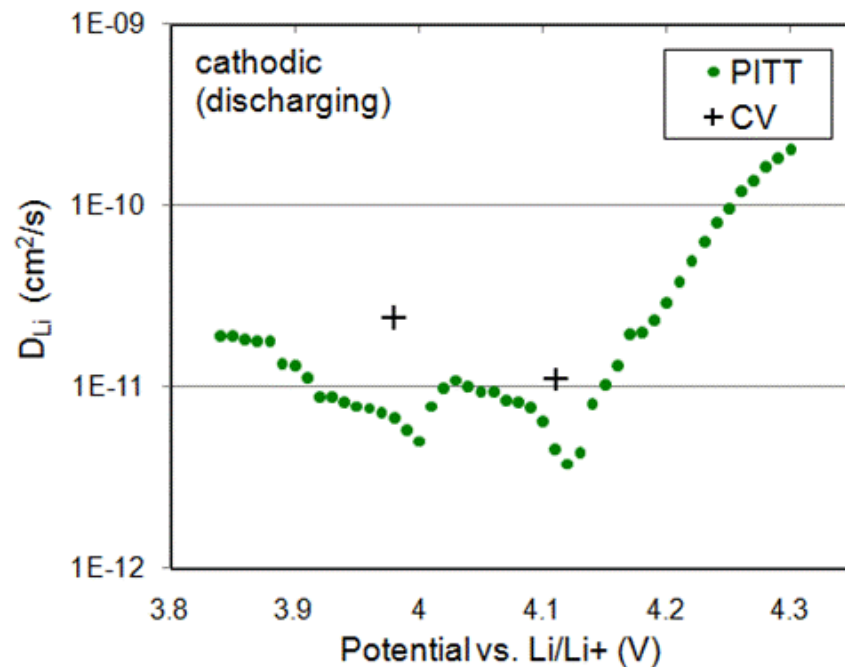
AFM image of LiMn_2O_4 particle on gold substrate; sample 052-83-02

Li-ion diffusion in LiMn_2O_4 : FY10

A • M • S • L

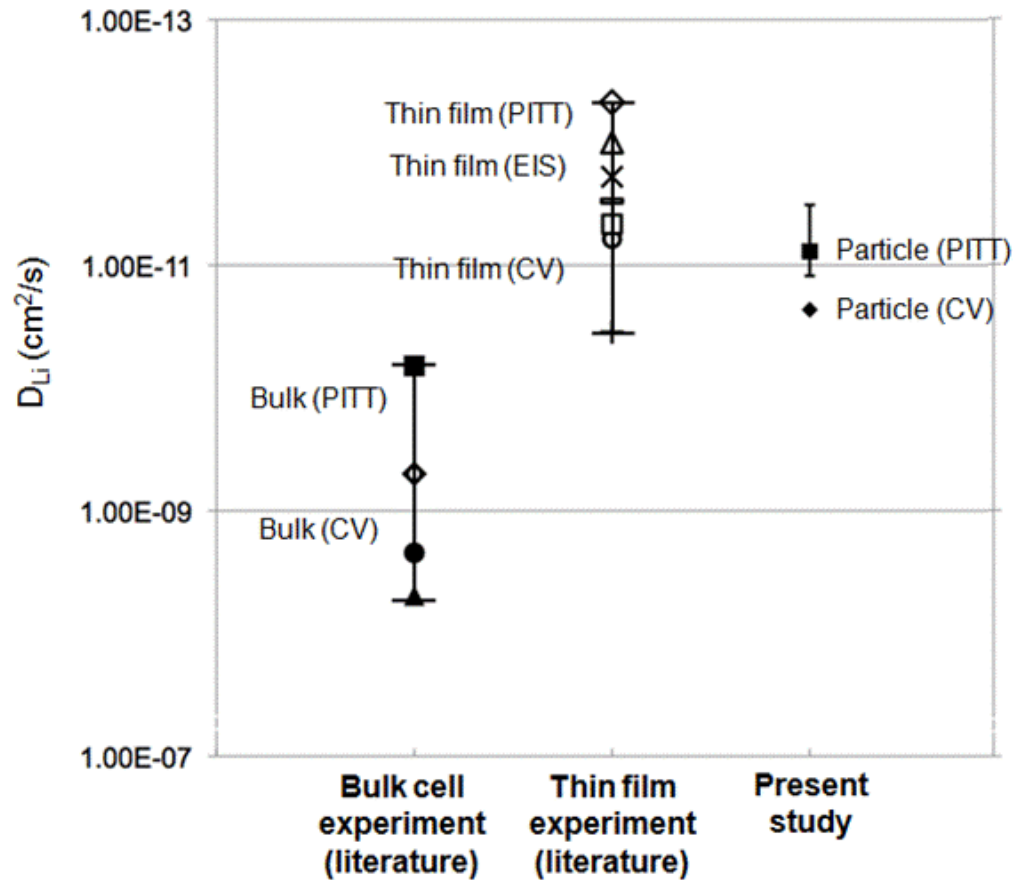
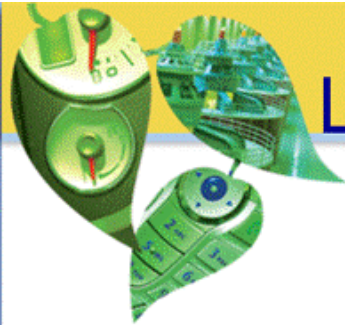


Cell : 052-90-04
Scanning range: 3.84~4.30 V
Scanning rate: 10mV/s



cell: 052-90-04
Scanning range: 3.84~4.30 V
Scanning rate: 10mV/s

[1] M.D. Chung, X.C. Zhang and A.M. Sastry, Experimental Study of Diffusion Coefficients in Single LiMn_2O_4 Particles, ECS 215th Meeting, San Francisco, CA, May 28, 2009



Literature value vs. present study result

- ◆ bulk A (PITT)
- bulk B (PITT)
- ▲ bulk C (CV)
- bulk D (CV)
- bulk E (CV)
- + thin film A (CV/PLD)
- thin film B (PITT/ESD)
- thin film C (PITT/ESD)
- ◇ thin film D (PITT/sol-gel)
- thin film E (CV/PLD)
- △ thin film E (EIS/PLD)
- × thin film E (PITT/PLD)
- ◆ particle (CV)
- particle (PITT)

- **SEI (solid electrolyte interphase) layer**

- SEI layer is formed both cathode and anode during cycling
- SEI layer prevents direct reduction of the electrolyte
- Reduction of energy density of Li ion battery is unavoidable
- It is important to understand mechanism of its formation and microstructure
- Challenges: very thin and complex microstructure

- **available characterization techniques**

- TEM (transmission electron microscopy): thickness of SEI layer, local variation of atomic structure
- AFM (atomic force microscopy): observation of surface morphology, local stiffness (modulus) and conductivity
- XPS (X-ray photoelectron spectroscopy) and AES (Auger electron spectroscopy): elemental identification and bonding state determination
- IR (infrared) and Raman spectroscopy: identification of surface/interface species, defects, and structure change



Figure 1. TEM at ORNL

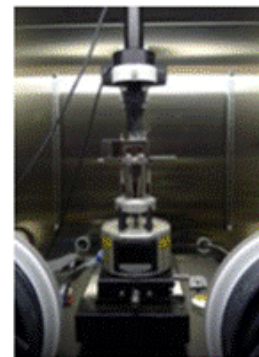


Figure 2. AFM at ABCD

preliminary results : TEM image of SEI layer formed on the LMO particle in composite electrode and modulus mapping of LCO thin film electrode using Veeco iCon system.

- Thickness of SEI layer: 3 to 4 nm, amorphous phase
- RMS roughness (Figure 2): 11.5 nm
- Mean value of Young's modulus (Figure 3): 1.94 ± 0.71 GPa

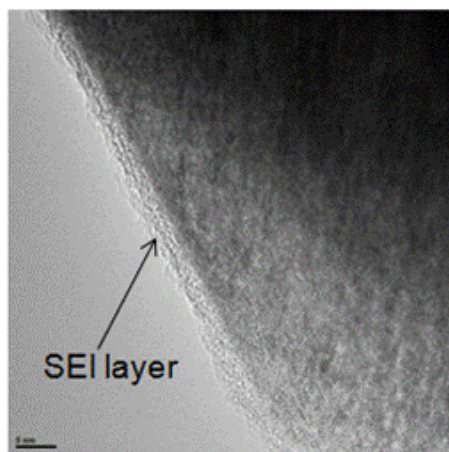


Figure 1. SEI layer formed on LMO surface

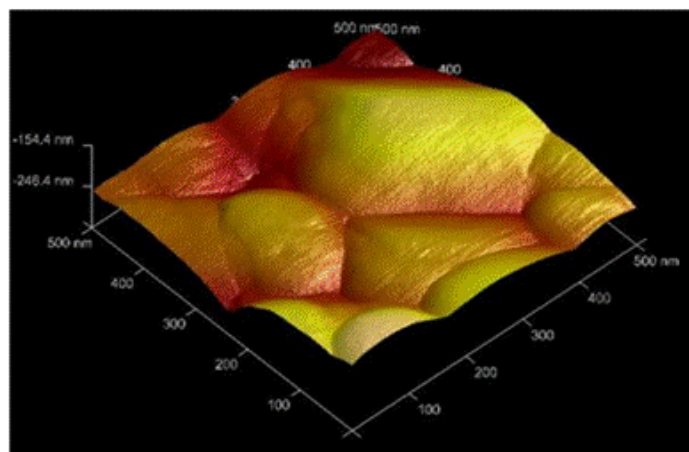


Figure 2. Surface morphology of LCO thin film annealed at 700° C (before cycling)

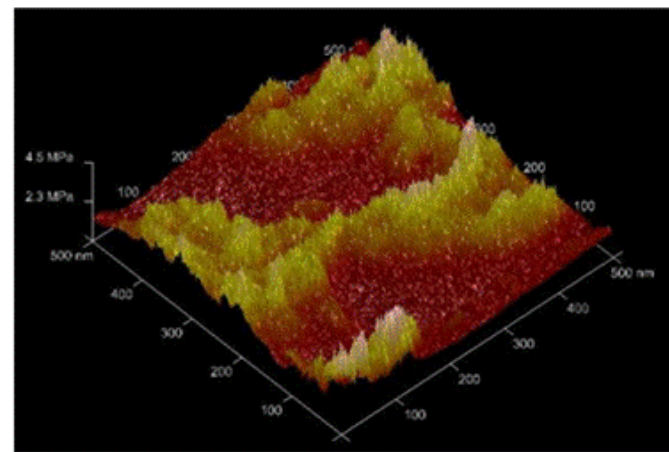


Figure 3. Modulus mapping of LCO thin film surface annealed at 700° C (before cycling)

- **FY09–10 Fundamental:** ionic/electronic conductivities were studied in a 3D porous composite electrode. Surrogate modeling was applied to correlate effective conductivities and battery performance. **Practical:** A trade off between ionic conductivity and electronic conductivity was revealed and a quantitative guidance is proposed for the design of high energy density and for the design of cathode systems.
- **FY10 Fundamental:** A multiscale framework was proposed to include the electrode microstructure information in battery scale modeling. **Practical:** the constructed surrogate models fit the training data very well and give good prediction of the closure term (i.e., reaction current density).
- **Fundamental:** electrochemical technique (e.g., CV and PITT) was applied for the experimental study of Li-ion diffusion in dispersed single particles. **Practical:** measured diffusion coefficient can be used as a SOC-dependent input for electrochemical modeling of cathode systems.
- **Fundamental:** TEM and AFM study characterized SEI layer and surface morphology. **Practical:** measured thickness and elastic modulus of SEI layer can be used as inputs for modeling SEI layer



future work

A • M • S • L

- SEI formation and consideration of its effects on kinetics and thermo-electrochemical performance will be sought. Both experimental and numerical tools will be sought as well.
- We will continue to refine numerical models based on findings from simulated performance and experiments: particle structures, film formations, and temperature dependence as well.
- We will continue to explore progressive capacity degradation in electrodes in the context of multiple scales and multiphysics coupling electrochemical kinetics and thermal effects.