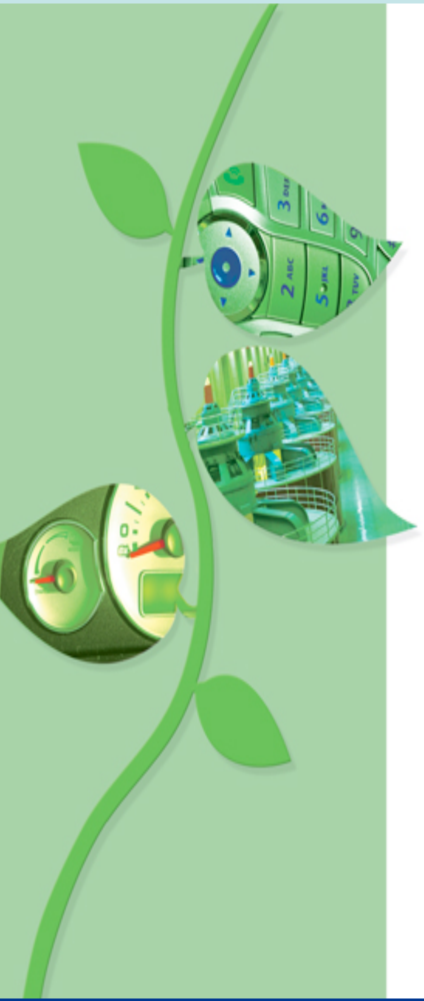
Modeling - Scale-Bridging Simulation Active Materials in Li-ion Batteries, an Validation in BATT Electrodes



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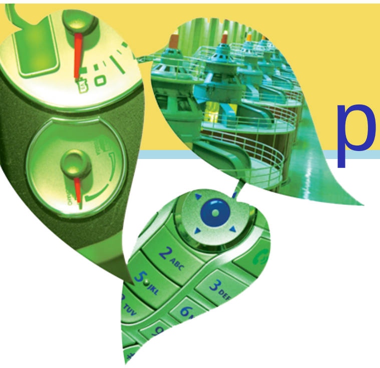


purpose of work

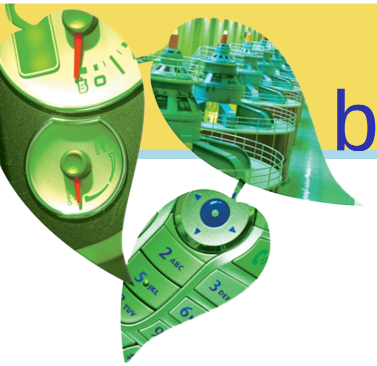
OBJECTIVES: Determine superior composition and processing conditions of electrodes for cond enhancement, especially for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode. Develop scale-bridging simulatio will allow identification of the best particle morphologies for both energy- and power-dense sy Develop superior anodes and cathodes by altering the content and morphologies of cond materials.

MILESTONES:

(a) Implement 3D finite element (FE) model with coupled mechanical/electrochemical effects. (Feb. 07

(b) Identify specific blends for manufacture, which reduce unnecessary mass but m conductivity/capacity, in collaboration with Battaglia, Srinivasan and Doeff. (Mar. 08)

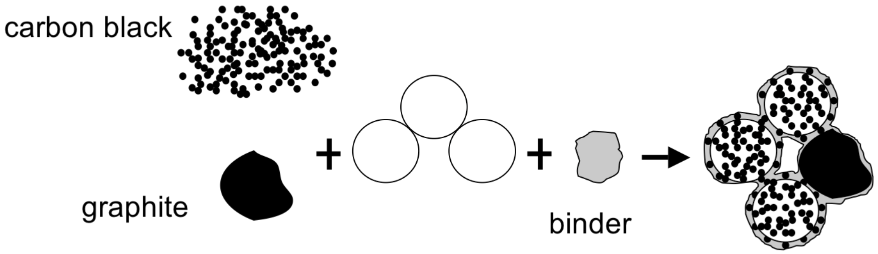
(c) Use *ab initio* predictions of conductivities based on atomistic calculations (collaborati Grey/Ceder) to perform large-scale FE modeling of lifetime. (Jul. 08)



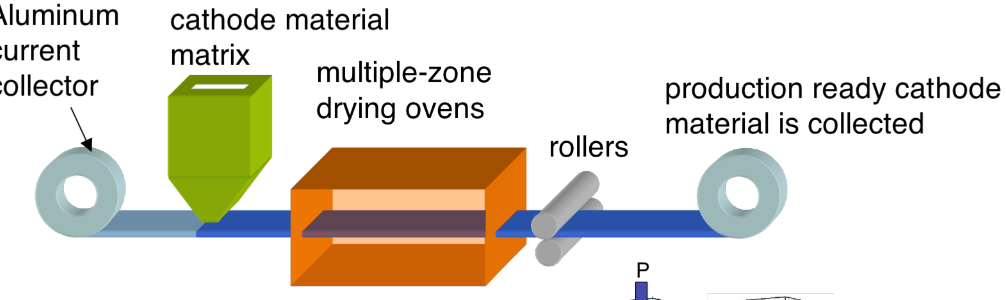
barriers

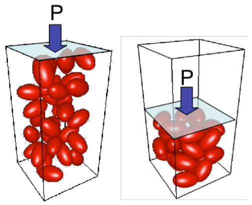
BARRIERS: Short lithium battery lifetimes, closely related to compositio electrode, processing conditions, and fracture of particles.

composition of the electrode

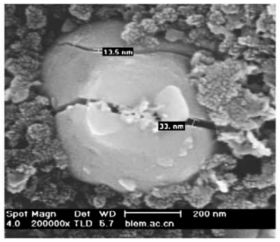


processing conditions

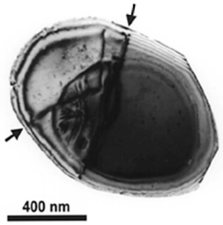




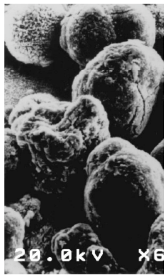
fracture due to intercalation and/or compression



LiFePO$_4$ particle after 60 cycles between 2.0 and 4.5V under the current density of 30mAg^{-1} (around 1/5 to 1/4C) [1]



LiCoO$_2$ particles after 50 cycles between 2.5 and 4.35 V under the current density of 0.4 mA/cm^2 (C/5 rate) [2]

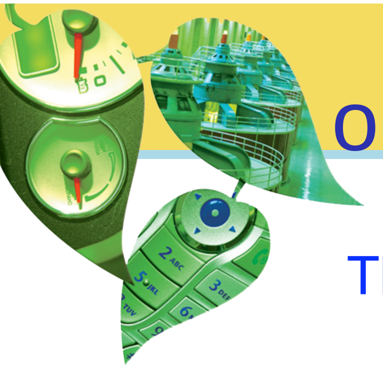


LiMn$_2$O$_4$ particles between 3.5 and 4. Li/Li$^+$ at a scan rate C) (particle diamet

[1] D. Wang, X. Wu, Z. Wang, and L. Chen, "Cracking Causing Cyclic Instal LiFePO4 Cathode Material", Journal of Power Sources, 140 125-128 (20

[2] H. Wang, Y. Jang, B. Huang, D. R. Sadoway, and Y.-M. Chiang, "TEM Electrochemical Cycling-Induced Damage and Disorder in LiCoO2 Cath Rechargeable Lithium Batteries", Journal of the Electrochemical Society 480 (1999).

[3] M.-R. Lim, W.-I. Cho, and K.-B. Kim, "Preparation and Characterization Codeposited LiMn2O4 Electrodes", Journal of Power Sources 92 168-17



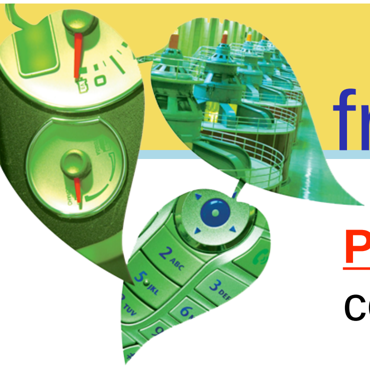
our approach

Three major thrusts to identify superior composition and processing conditions of electrodes for conductivity enhancement :

1) modeling—packing, conductivity, electrochemistry and mechanics;

2) electrode design;

3) experimental measurement of conductivity in cathodes. Realistic microstructu of porous electrodes have been built, based on results of image analysis of re electrodes (V. Battaglia, LBNL). Porosities and dimensions for candidate cells were used as input (V. Battaglia, LBNL) to identify optimal combinations of materials from simulations. We have tested electrodes prepared at LBNL to minimize resistivity and density.



fracture of particles

PROBLEM: minimize battery failure due to intercalation-induced and compression stresses. Requires modeling to determine the magnitude of ea

Li-ion battery modeling difficulties

- multiscale: battery pack ➡ cell ➡ electrode/separator layers ➡ particles
  1~10 cm ~1mm ~100µm ~1µm
- multi-physics: ionic diffusion; electrochemical reaction and side reactions; electronic conduction; strain/stres generation

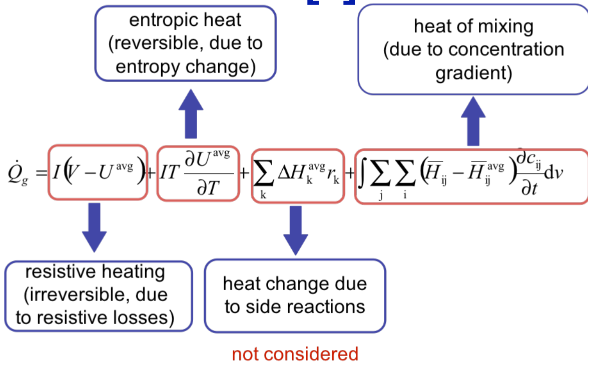
APPROACH: model single (cathode) particles; then extend to larger scale simulat Apply surrogate-base analysis to determine the effect of particle morphology and operating conditions, and stress and heat generation inside a single particle

intercalation induced stress [1]

$$\varepsilon_{ij} = \frac{1}{E}\left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}\right] + \boxed{\frac{\tilde{c}\Omega}{3}\delta_{ij}} \longleftrightarrow \alpha T\delta_{ij}$$

Ω partial molar volume (m^3/mol)

intercalation induced heat [2]



entropic heat (reversible, due to entropy change)

heat of mixing (due to concentration gradient)

$$\dot{Q}_g = \boxed{I\left(V - U^{\mathrm{avg}}\right)} + \boxed{IT\frac{\partial U^{\mathrm{avg}}}{\partial T}} + \boxed{\sum_{\mathrm{k}} \Delta H_{\mathrm{k}}^{\mathrm{avg}} r_{\mathrm{k}}} + \boxed{\int \sum_{\mathrm{j}} \sum_{\mathrm{i}} \left(\overline{H}_{\mathrm{ij}} - \overline{H}_{\mathrm{ij}}^{\mathrm{avg}}\right)\frac{\partial c_{\mathrm{ij}}}{\partial t}\mathrm{d}v}$$

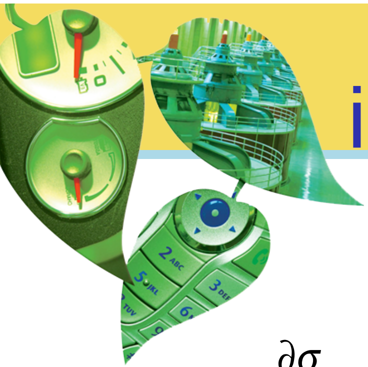
resistive heating (irreversible, due to resistive losses)

heat change due to side reactions

not considered

[1] X. Zhang, W. Shyy and A.M. Sastry, Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles, *Journal of the Electrochemical Society*, 154, A910-A916 (2007).

[2] K.E. Thomas and J. Newman, Thermal Modeling of Porous Insertion Electrodes, *Journal of the Electrochemical Society*, 150 (2003), A176-A192



intercalation induced stress

FINDINGS: trends in **maximum von mises stress, σ_{max},** obtained by surrogate-base analysis.

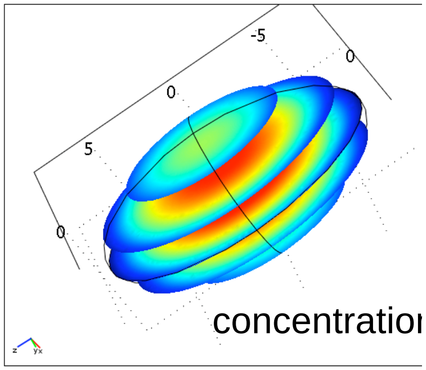
$$\frac{\partial \sigma_{\max}}{\partial R} > 4.73, \quad \frac{\partial \sigma_{\max}}{\partial v} > 12.41, \quad -5.61 < \frac{\partial \sigma_{\max}}{\partial \alpha} < 2.95$$

- equivalent radius ***R*** increases → stress increases
- potential sweep rate **ν** increases → stress increases
- aspect ratio **α** increases → stress increases first; then decreases

why?

intercalation-induced stress depends on concentration distribution

- *R* increases → wider range of concentration distribution
- ν increases → larger concentration gradient
- α increases → shorter semi-axis decreases; longer semi-axis increases



intercalation induced heat

FINDINGS: trends in **resistive heating, Q_r**, obtained by surrogate-base a

$$\frac{\partial Q_r}{\partial R} > 0.89\,, \quad \frac{\partial Q_r}{\partial \nu} > 1.48\,, \quad \frac{\partial Q_r}{\partial \alpha} < -0.016$$

- equivalent radius R increases ➡ resistive heating increases
- potential sweep rate ν increases ➡ resistive heating increases
- aspect ratio α increases ➡ resistive heating decreases

why?

resistive heating depends on the total flux over the particle surface and polari

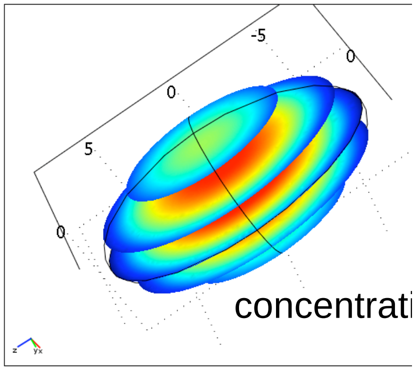
$$Q_r = I\left(V - U^{\text{avg}}\right)$$

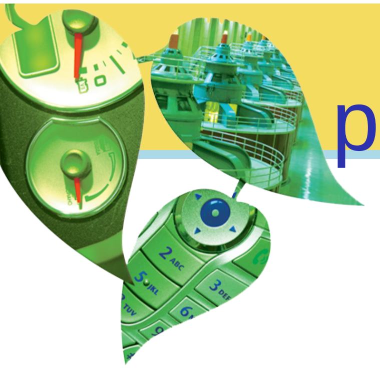
I current

V potential

U^{avg} averaged open circuit potential

- R increases ➡ larger current
- ν increases ➡ larger polarization due to larger concentration gradient
- α increases ➡ smaller polarization due to shorter diffusion path along the shorter axis

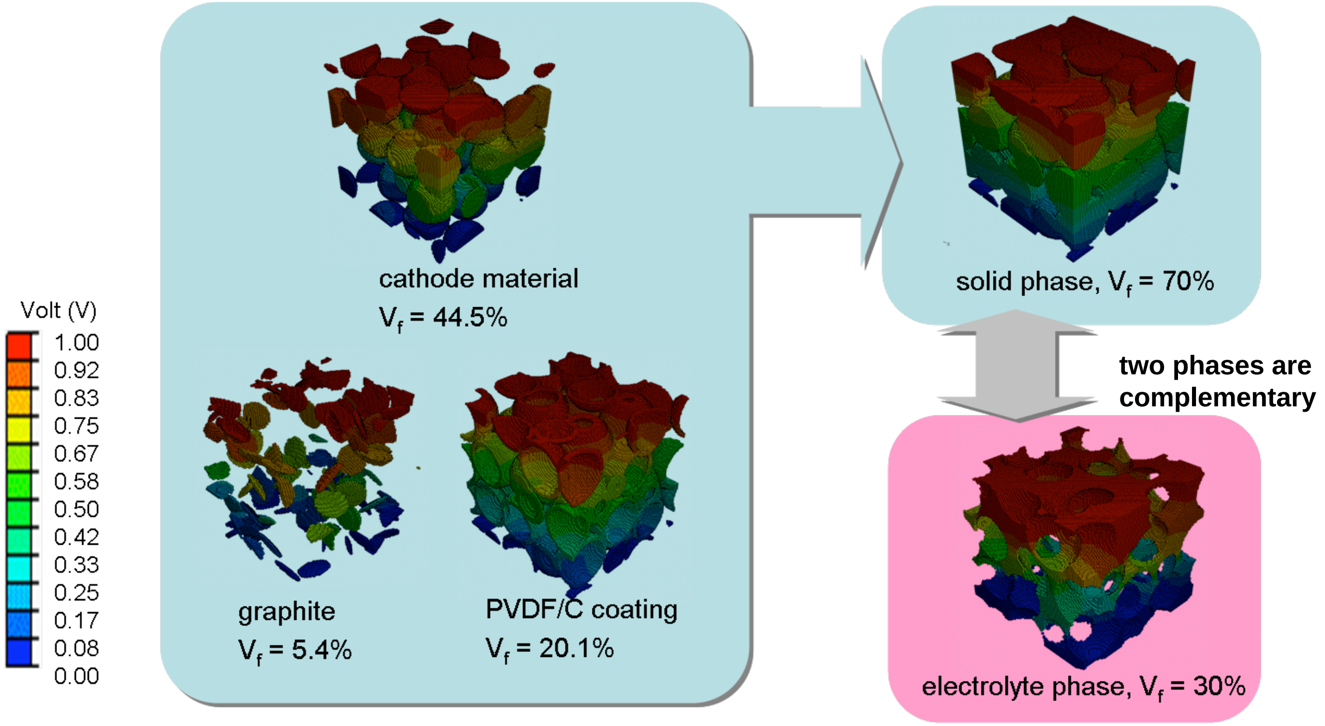




packing

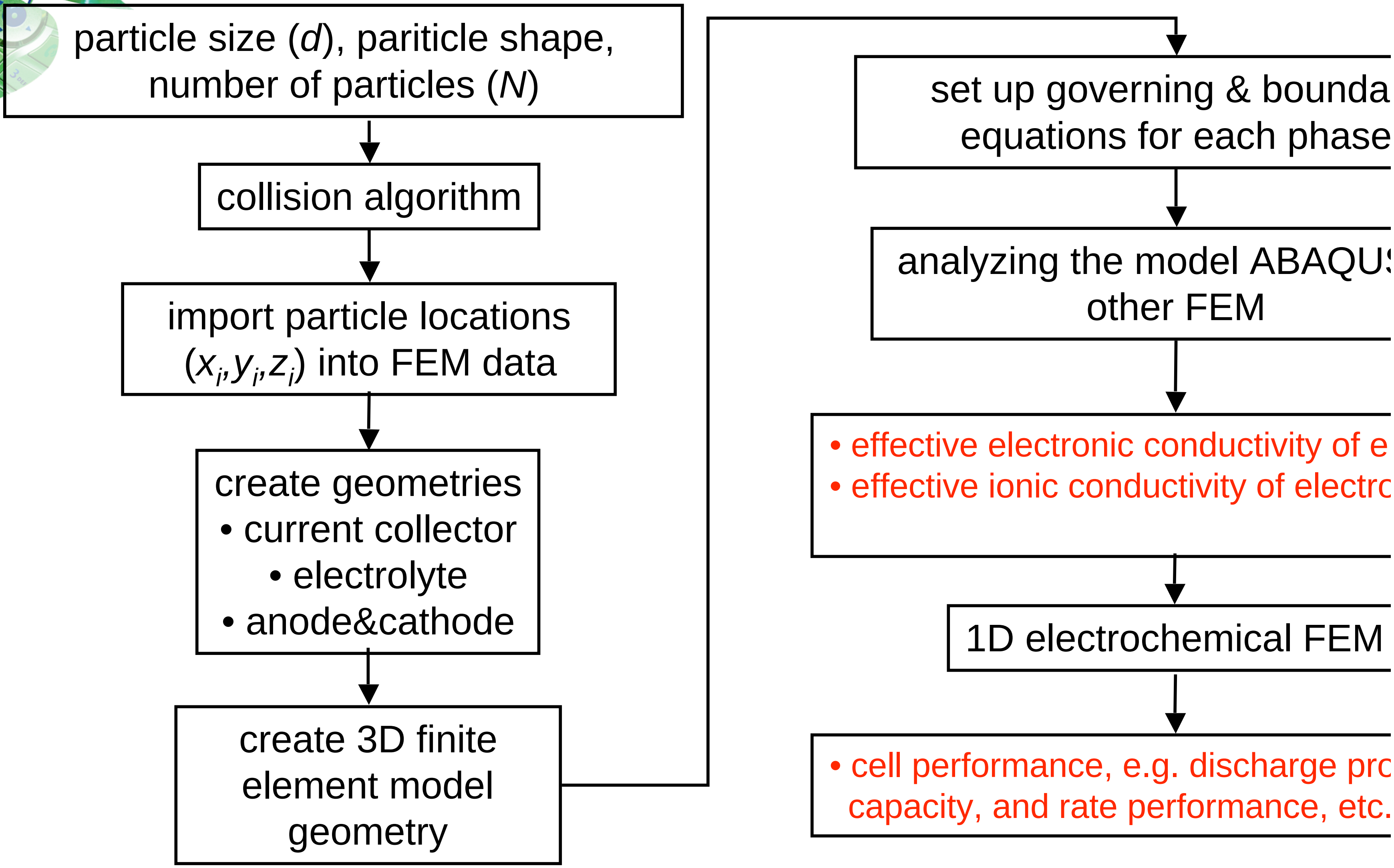
A • M •

PROBLEM: the life of the Li-ion battery depends on composition, morph
and processing conditions. Models are required for correlation of these.



APPROACH: integrate our packing model with 1D electrochemical model, to determine th
whole cell performance, and suggest superior composition and processing conditions.

flow chart for packing



particle size (*d*), pariticle shape, number of particles (*N*)

collision algorithm

import particle locations (x_i,y_i,z_i) into FEM data

create geometries
- current collector
- electrolyte
- anode&cathode

create 3D finite element model geometry

set up governing & bounda equations for each phase

analyzing the model ABAQU: other FEM

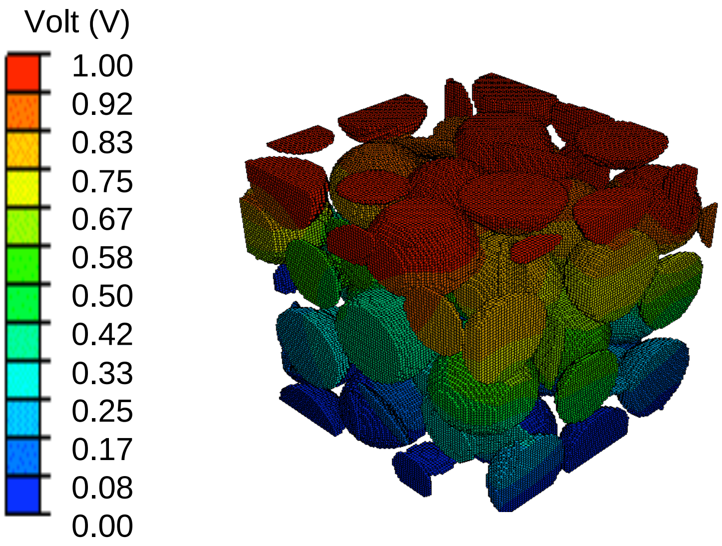
- effective electronic conductivity of e
- effective ionic conductivity of electro

1D electrochemical FEM

- cell performance, e.g. discharge pro capacity, and rate performance, etc.

effective conductivity (packing)

we developed a 3D finite element model to determine the effective conductivity of the composite electrode



current density: $J = - \sigma_1 \nabla V$ (1)

heat flux: $F = - \sigma_2 \nabla T$ (2)

σ_1: electrical conductivity (S*m)

J: current density (A/m^2)

V: electrical potential drop (V)

σ_2: thermal conductivity (W/m*K)

F: heat flux (W/m^2)

T: temperature drop (K)

boundary conditions:

x=0: T = 1 K

x=1: T = 0 K

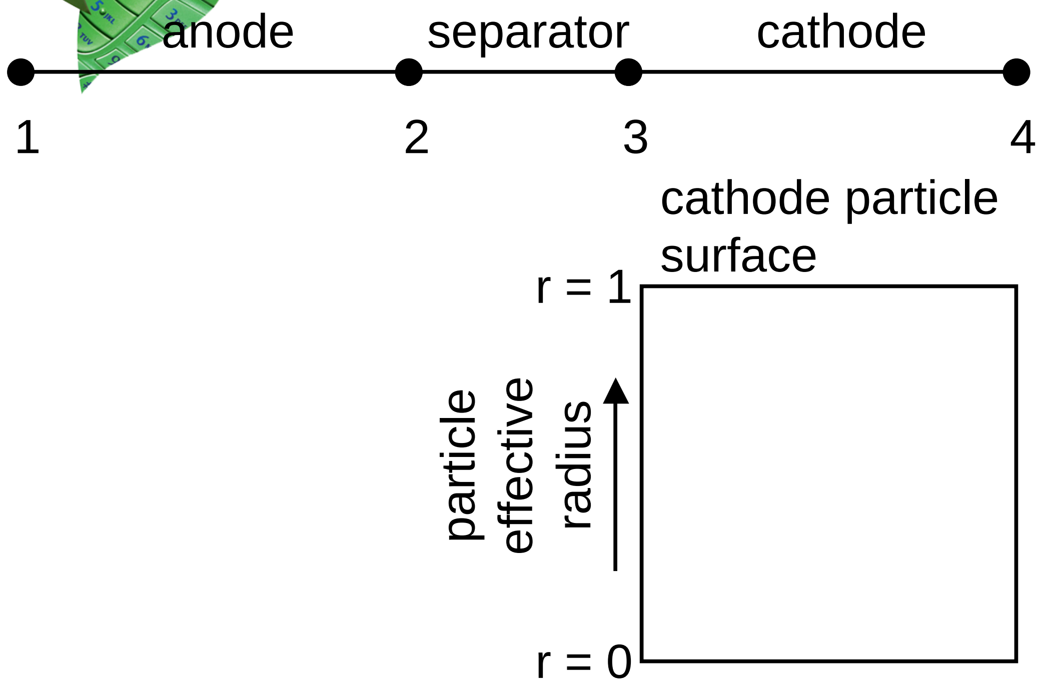
initial condition:

particle temperature: 0 K

at steady state, total flux calculated using FE analy
ABAQUS/Standard

effective σ of the porous structure found via Eq. (2)

1D electrochemical FEM (packing)

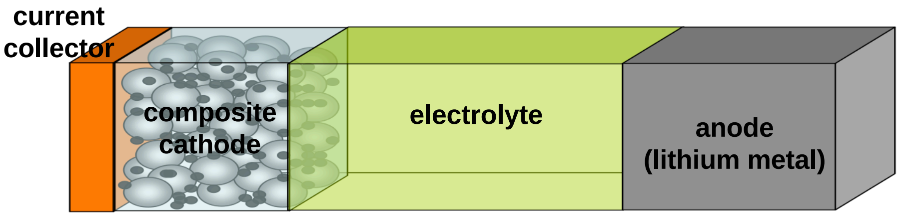


- 1D electrochemical finite element model (FEM) was modified from porous electrode model coupled 2D spherical particle diffusion modeling[1,2]
- effective material properties calc from 3D finite element model wer introduced
- this model couples ionic diffusion electrical conduction in solid phas with ionic conduction and diffusio electrolyte phase.

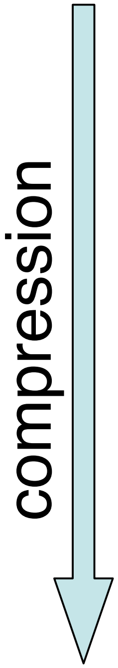
[1] M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, and J. –M. Tarascon, Comparison of modeling predictions with experimental data from plastic lithium ion cells he Electrochemical Society, 143 (6), 1890-1903 (1996).
2] COMSOL 3.3a, COMSOL Inc., Stockholm, SWEDEN

studied system (packing)

$Li/LiPF_6$:(EC and DMC; 2:1 v/v)/$Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2/Al$



composition of composite cathode



porosity (vf%)	active material (vf%)	graphite (vf%)	carbon black (vf%)	PVDF (vf%)
50	31.8	3.8	6.1	8.3
40	38.2	4.6	7.2	10.0
30	44.5	5.3	8.6	11.6
20	50.9	6.1	9.7	13.3
10	57.2	6.8	11.0	15.0

material properties (packing)

A · M ·

material	$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	graphite	PVDF/C=1.36	electrolyte
particle size (µm)	11.04	7.45	-	-
mass density (g/cm^3)	4.75	1.95	1.86	1.32
bulk conductivity (S/m)	1.06×10^{-3}	1.67×10^{4}	760	as Fig. 1
diffusion coefficient (m^2/s)	as Fig. 2	-	-	3.06×10^{-10}
reference	[1,2]	[3]	[1]	[4]

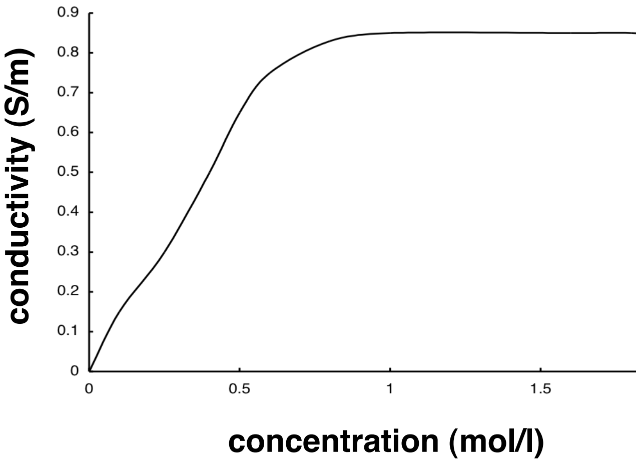


Fig. 1, ionic conductiv

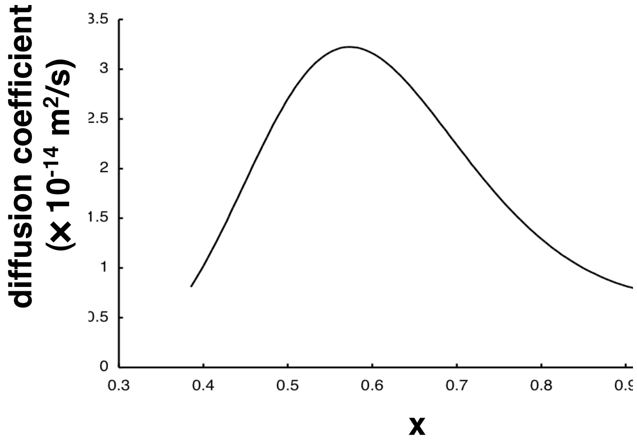


Fig. 2, Li333 diffusion coe

1] Y. -H. Chen, C. -W. Wang, G. Liu, X.-Y. Song, V. S. Battaglia, and A. M. Sastry, Selection of conductive additives in Li-ion battery cathodes: a numerical study, Journal of the Electrochemical Society, **154** (10), A978-A986 (2007)

2] Kevin Eberman and Larry Krause, Diffusion coefficient of lithium in $Li_x(Co_y(NiMn)_{(1-y)/2})O_2$ cathode powders, The 204th Electrochemical Society Meeting, Orlando, FL (2003).

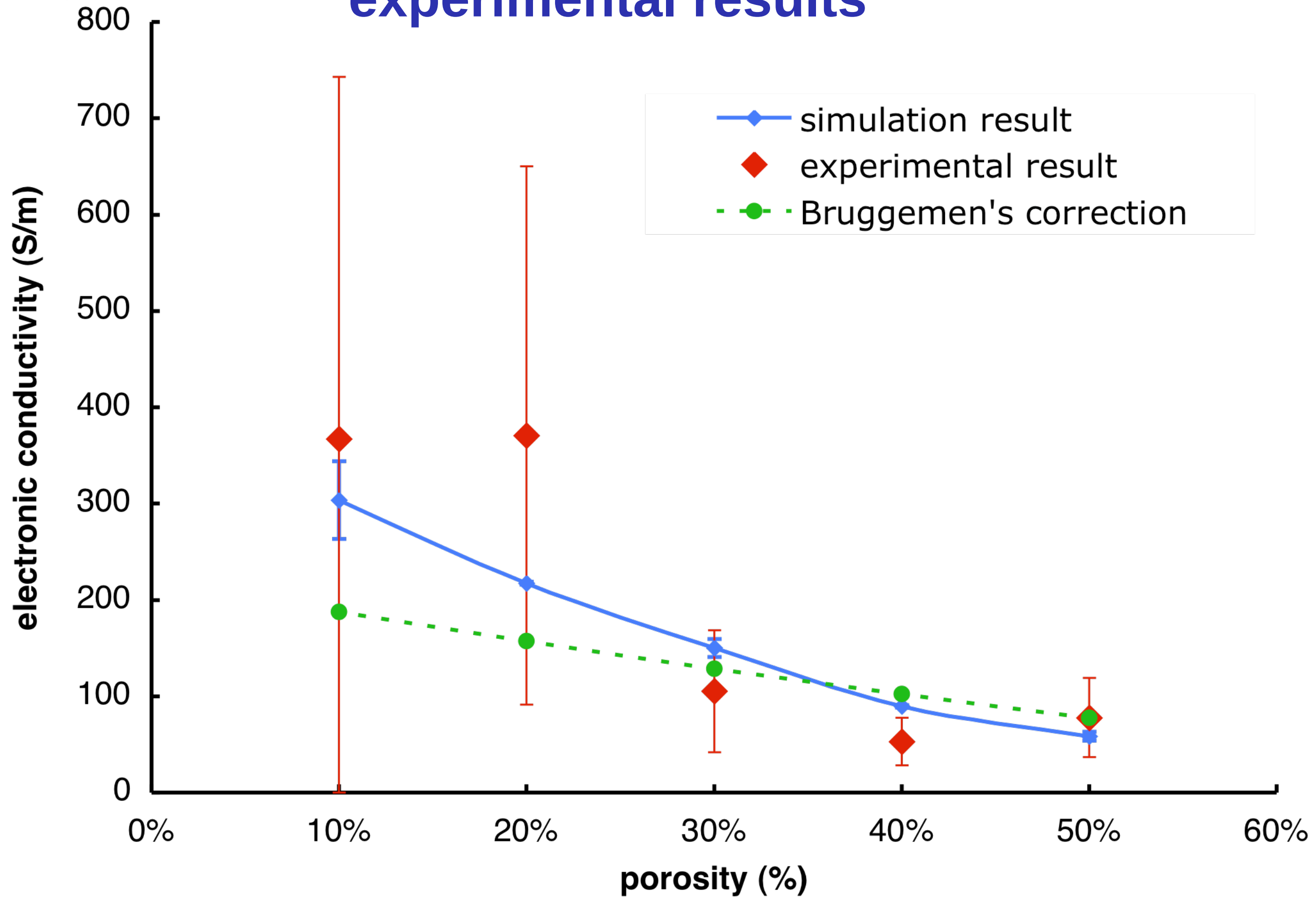
3] http://www.matweb.com (date: 01/20/2008).

4] M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, and J. –M. Tarascon, Comparison of modeling predictions with experimental data rom plastic lithium ion cells, *Journal of the Electrochemical Society*, **143** (6), 1890-1903 (1996).

electronic conductivity (packing):

FINDINGS:

comparison between simulation and experimental results

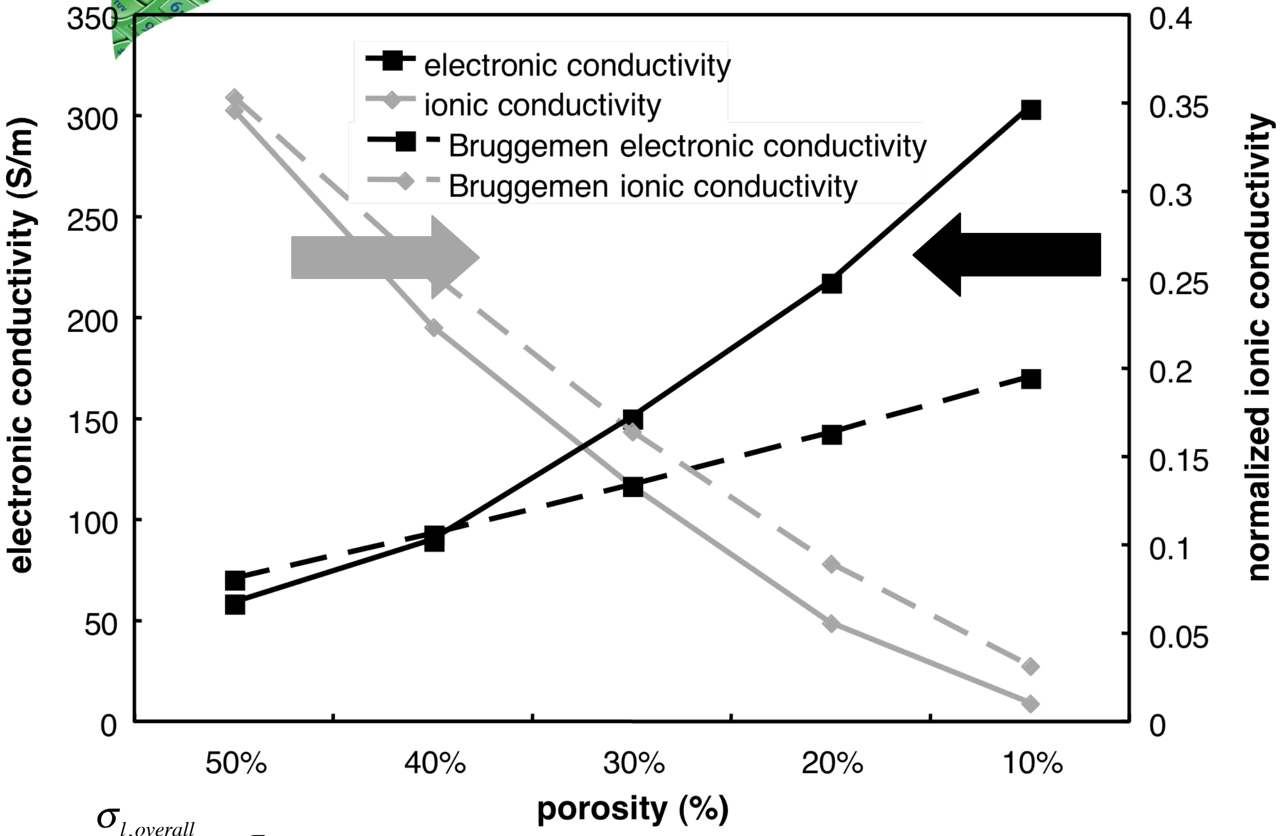


- $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ electrodes were obtai from (V. Battaglia, LB
- experimental results w measured by using ou four-point-probe meth
- Bruggemen's correctio ($\sigma_{effective}=\sigma_0\varepsilon^{1.5}$)

1. Wang, C.-W., Sastry, A.M., Striebel, K. A. and Zaghib, K., 2005, "Extraction of Layerwise Conductivities in Carbon-Enhanced, Multilayered LiFePO4 Cathodes," Electrochemical Society, v. 152 (5), pp.A1001-A1010.

simulation result (packing):

FINDINGS:



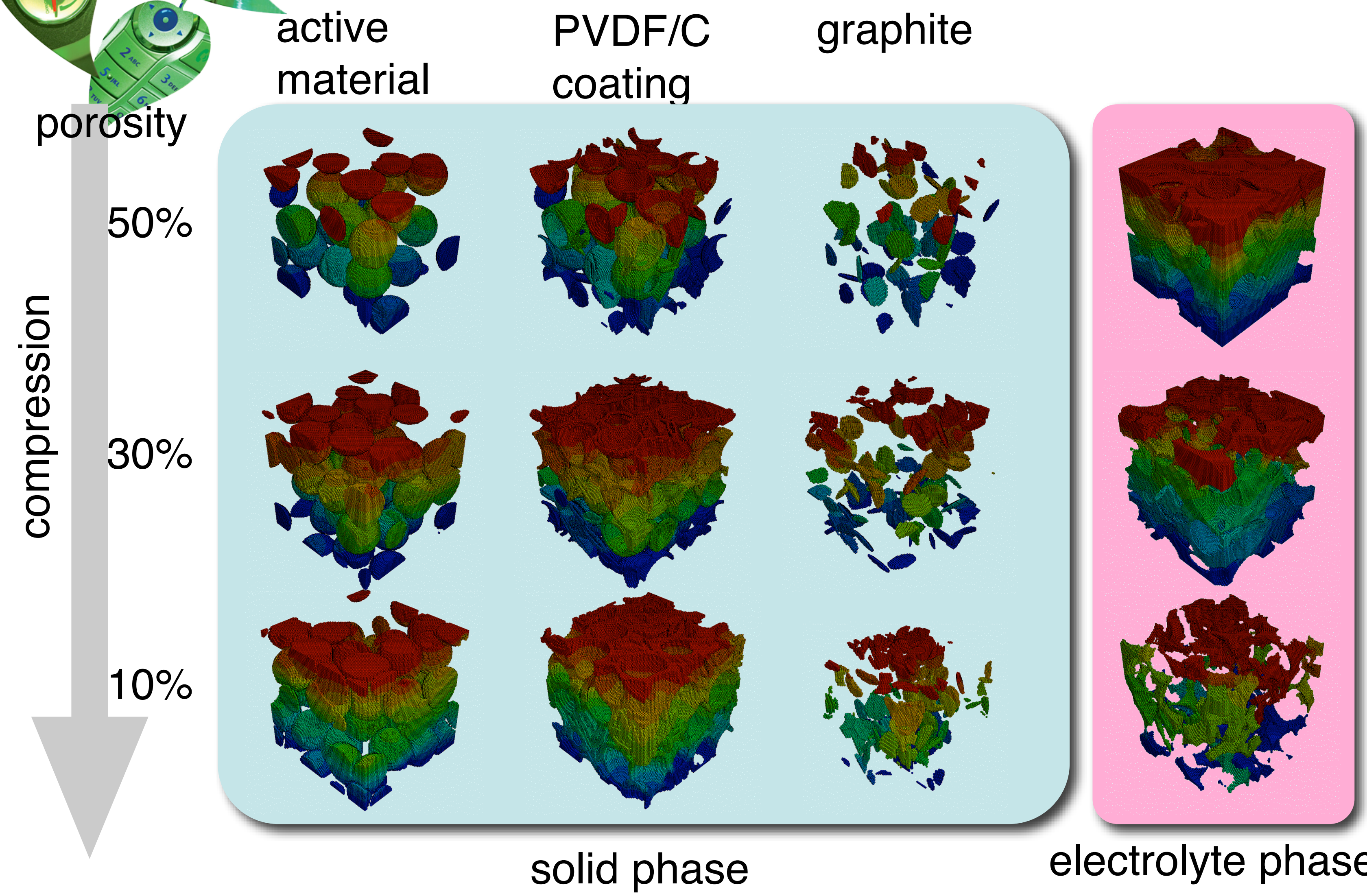
$$\frac{\sigma_{l,overall}}{\sigma_{l,bulk}} = \sigma_{e,ionic}$$

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

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

- σ_0 in Bruggemen predi ($\sigma_{effective}=\sigma_0\varepsilon^{1.5}$) is basec experimental results in porosity
- there is a trade-off betw the ionic conductivity of electrolyte phase and electronic conductivity c solid phase; therefore, i requires whole cell electrochemical perforn model to identify the prc porosity

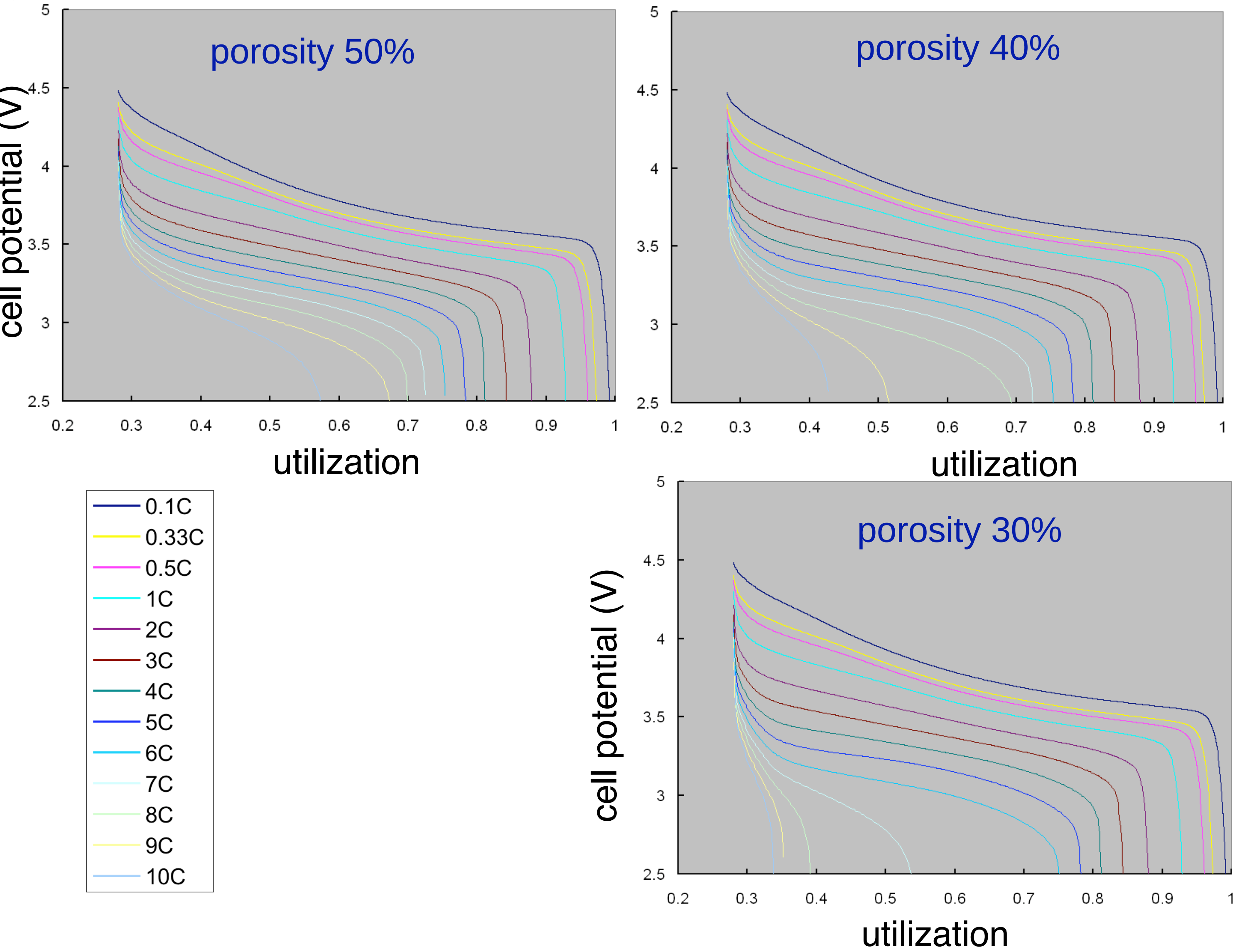
morphology change



FINDINGS

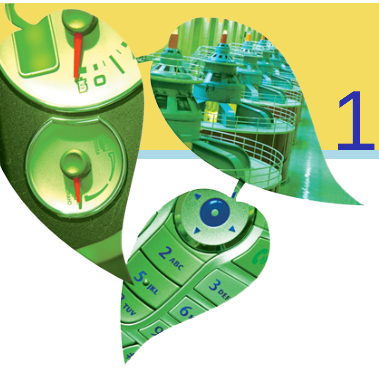
two phase
compleme
increasing
conductivi
one phase
reduces th
conductivi
other

1D simulation result



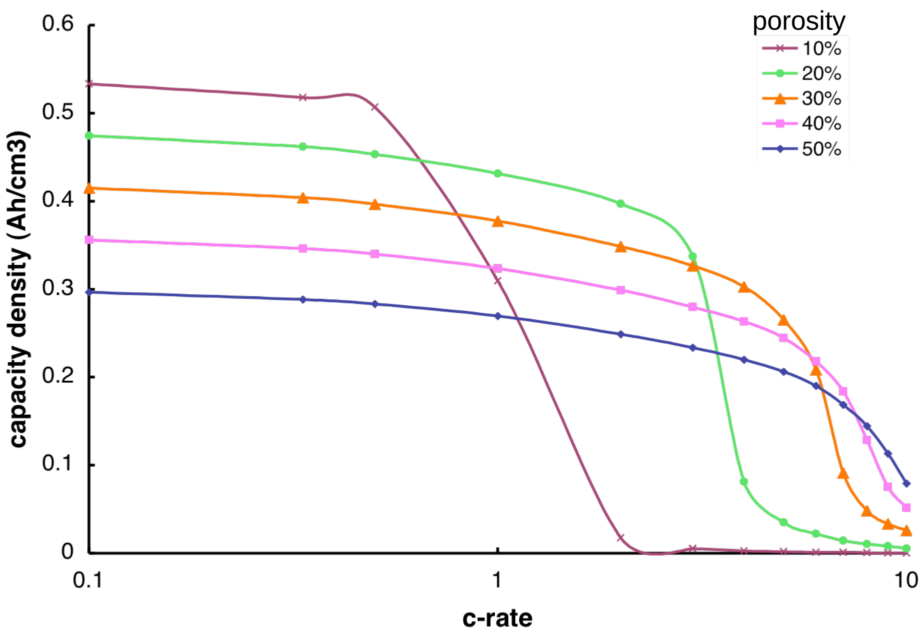
FINDINGS:

- cathode thickne 200μm
- at lower c-rate, utilization does change with po
- at higher c-rate, utilization decre as the porosity decreases



1D simulation result (continued)

FINDINGS:



simulation result

- cathode thickness: 200μm
- effective ionic and electronic conductiv from 3D FEM simulations were applie battery simulation
- simulations started from 30% state of (SOC)
- in 1/10C rate, the lower porosity showe better capacity density; the transport mechanism is not a limiting factor
- as the c-rate increases, the higher por electrode has higher capacity density.
- optimal porosity depends on

how the cell is used

accomplishments & status

- **a simulation scheme has been developed to determine the effectiv conductivity of composite electrode**
  - this scheme has been verified with experimental results
  - more work needs to be done to identify the source of estimation dev from experimental results at lower porosity region

- **a modified electrochemical performance simulation scheme has b used to determine the performance of the Li-ion cell, and verificati this approach is underway**
  - basic concept demonstrated
  - experimental work is needed to verify the accuracy of the estimation is underway

summary

- **Fundamental**: conductive coatings result in low contact resistance, which is key in creati conductive networks. **Practical:** using carbon black/pvdf composite coatings is more advantageous than addition of conductors (e.g. graphite) to composite cathodes, in impro conductivity, for all baseline materials investigated.

- **Fundamental:** particle morphology affects the generation of intercalation stress and heat **Practical:** smaller aspect ratio particle reduces the heat generation due to intercalation. However, induced stresses increases first, then decrease as the aspect ratio of the partic increases. Hence, care is required in selecting the aspect ratio which reduces both heat a induced stress.

- **Fundamental:** compressing the electrode to lower porosity can increase the overall elect capacity density. **Practical:** a low porosity electrode is not optimal for higher c-rates. Opti porosity depends on how the whole cell is used.

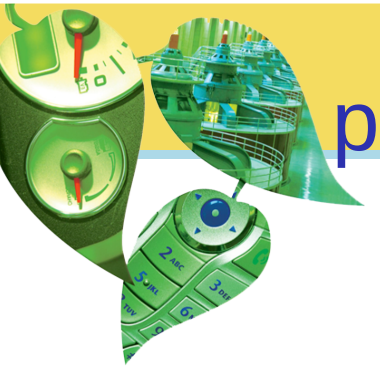
- **Fundamental:** compressing the electrode to smaller porosity can increased the overall electrode electrical conductivity. **Practical:** low porosity electrodes have hindered transpo ions in the electrolyte phase. Hence, there is a trade-off selecting the superior porosity fo electronic conductivity and ionic conductivity for the solid and electrolyte phases.

future work

- Damage is progressive, and the cumulative effect of intercalation stresses and generation will be studied as part of future work on lifetime modeling, including multiscale modeling (collaboration with Grey/Ceder).

- Particle size, orientation, and interface conditions impact kinetic performance o cell, especially the particle interface conditions with other particles or the curren collector. Fibers work well and will be studied (collaboration with Doeff).

- Cell operation affects models, baseline materials will be refined; optimal combinations will be continuously sought (collaboration with Battaglia).



publications

1. Zhang, X.-C., Shyy, W., and Sastry, A.M., 2007, "Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles," Journal the Electrochemical Society, v. 154 (10), pp. A910-A916.

2. Chen, Y.-H., Wang, C.-W., Liu, G., Song, X.-Y., Battaglia, V.S. and Sastry, A.M., 2007, "Selection of Conductive Additives in Li-ion Battery Cathodes: Numerical Study," Journal of the Electrochemical Society, v. 154 (10), pp. A978-A986.

3. Wang, C.-W. and Sastry, A.M., 2007, "Mesoscale Modeling of a Li-Ion Poly Cell," Journal of the Electrochemical Society, v. 154 (11), pp. A.1035-1047