Analysis of Long-range Interactions in Lithium-ion Battery Electrodes

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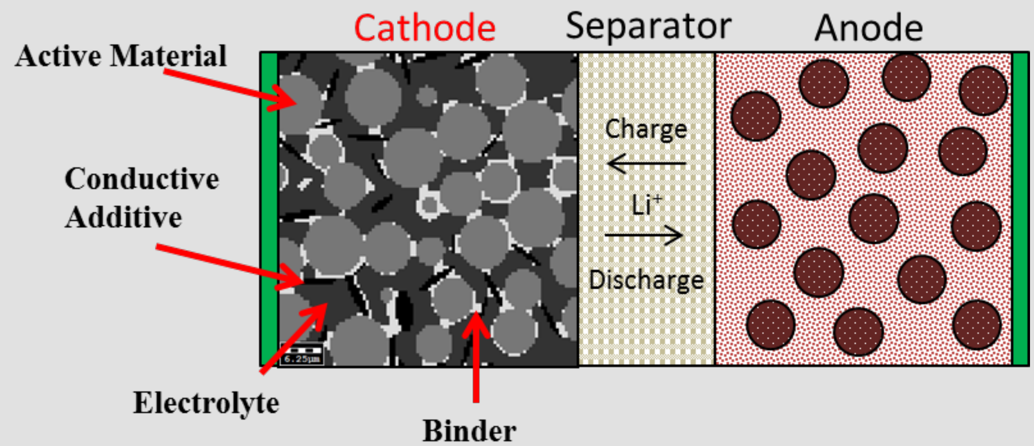
Overview

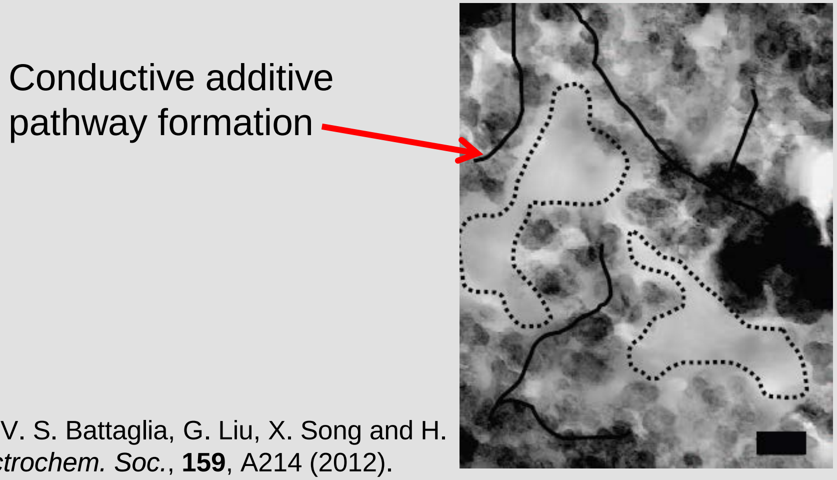
- ❖ Background/Motivation
- ❖ Objective
- ❖ Methodology
- ❖ Results
- ❖ Conclusions
- ❖ Outlook

Background/Motivation

- Battery composition: anode, cathode, porous separator, and current collectors
- Cathode composition: active material, conductive additives, binder, and an electrolyte.



- Low component electrical conductivity necessitates use of conductive additive
- Improvement in conductivity is dependent on percolation, or pathway formation



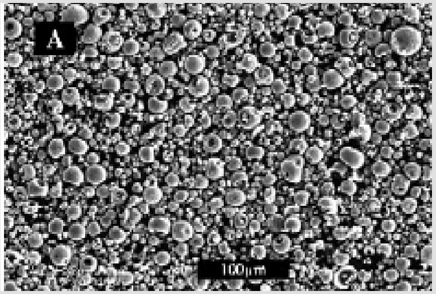
Adapted from V. S. Battaglia, G. Liu, X. Song and H. Zheng, *J. Electrochem. Soc.*, **159**, A214 (2012).

Background/Motivation

- ❖ Additive type and material content have been shown to affect pathway formation and thus electrical conductivity
    - ➢ Pathway formation is dependent on particle interaction within electrode
- ❖ Active material particle shape can be altered or can vary based on chemistry

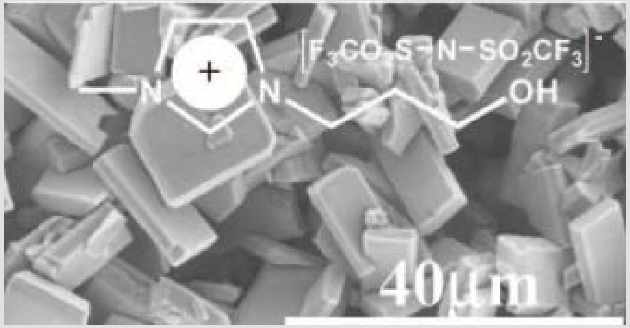
$LiFePO_4$

With carbon coating



Adapted from J. Liu, J. Wang, X. Yan, X. Zhang, G. Yang, A.F. Jalbout and R. Wang, Electrochim. Acta, **54**, 5656 (2009).

$LiFePO_4$



Adapted from N. Recham, L. Dupont, M. Courty, K. Djellab, D. Larcher, M. Armand and J.M. Tarascon, *Chem. Mater.*, **21**, 1096 (2009).

- ➢ Variation in AM shape could alter the effectiveness of conductive additives

Objective

❖ Objective

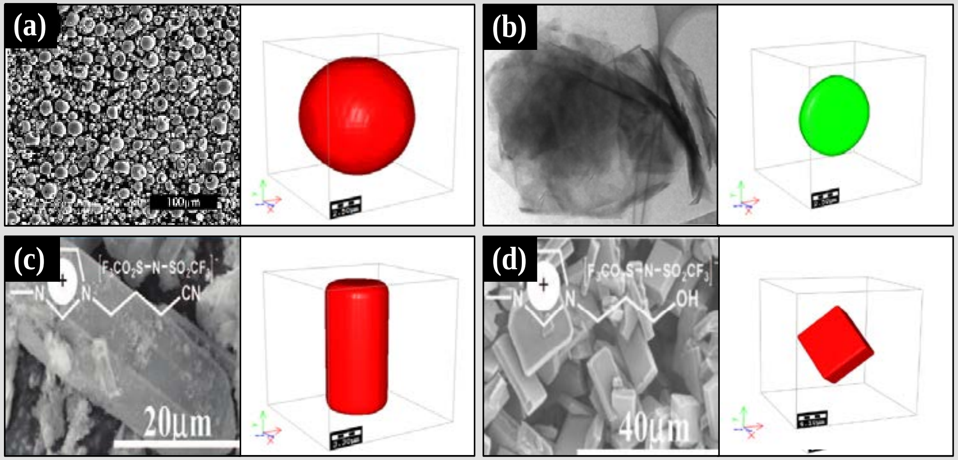
- Determine the effect of active material morphology and electrode composition on the effective conductivity of LIBs.

❖ Tasks

- Stochastically generate 3D electrodes (**GeoDict**)
- Evaluate effective electrical conductivity (**GeoDict**)
- Characterize results and draw conclusions

Methodology – Particle Modeling

- Finite-volume based modeling approach
- AM particles modeled as pseudo-spherical, pseudo-cylindrical, and platelet particles
- Graphite modeled as thin, ellipsoidal disks
- Volume set constant, with standard deviations set for equivalent volume change
- Conductivity of additive is much higher than remaining components

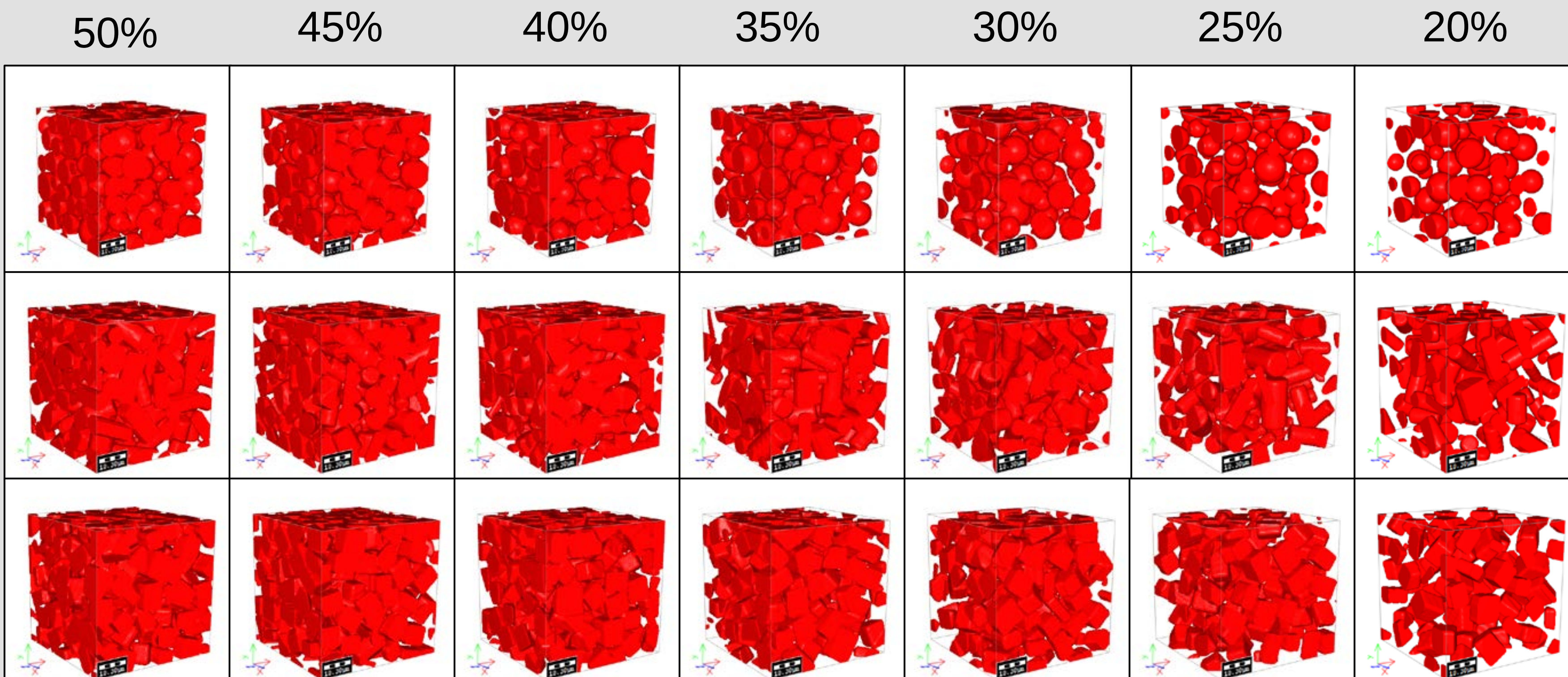


AM Particle	Length	Diameter	Volume	Surface Area
Sphere	--	9.0 μm	3.82 E-16 m^3	2.55 E-10 m^2
Cylinder	12.48 μm	6.24 μm	3.82 E-16 m^3	3.06 E-10 m^2
Platelet	7.25 μm	--	3.82 E-16 m^3	3.16 E-10 m^2

Material	Electrical Conductivity
Active Material	.01 S/m
Electrolyte	1 S/m
Graphite	1.0×10^4 S/m
PVDF	1.0×10^{-13} S/m

Methodology – Model Generation

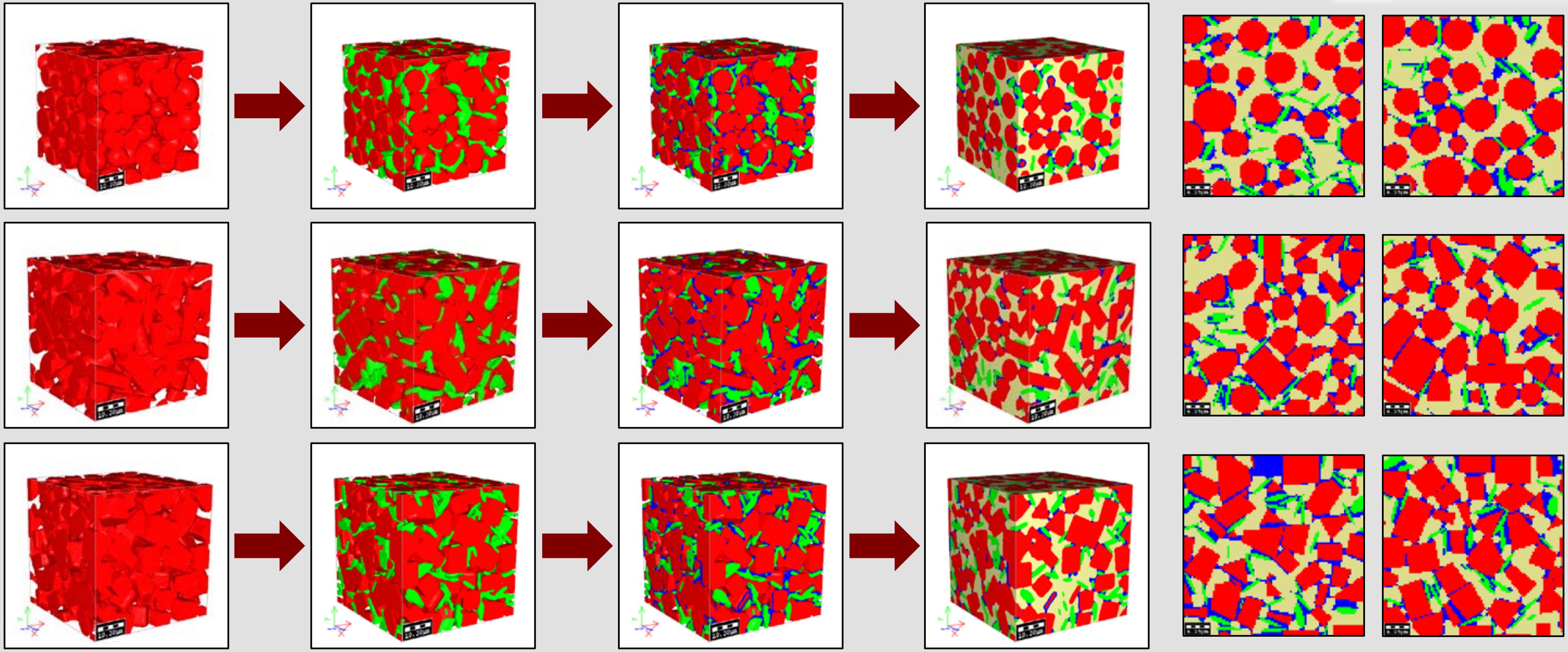
- Three groups of seven cells were generated in **GeoDict** using spheres, cylinders, and cubes of equal volume
- Volume percent of each cell was varied from 20 to 50 percent in constant intervals
- Later, conductive additive and binder are added also with **GeoDict**



Methodology – Model Generation

- Ratio of conductive additive to binder kept constant at 0.8:1.0
- Porosity maintained at 35%
- Decrease in AM correspond to increase in additive and binder

Red	Active Material
Green	Conductive Additive
Blue	Binder
Cream	Electrolyte



Methodology – Conductivity

❖Effective conductivity determined via the 3D stationary conduction equation

$$\nabla(\sigma\nabla V) = \dot{J} \; in \; \varphi$$

where V is the potential, σ is the local electrical conductivity, $\dot{J}$ is a source term, and Φ is the domain under consideration.

❖ Only conduction through the domain is considered so $\dot{J} \rightarrow 0$.

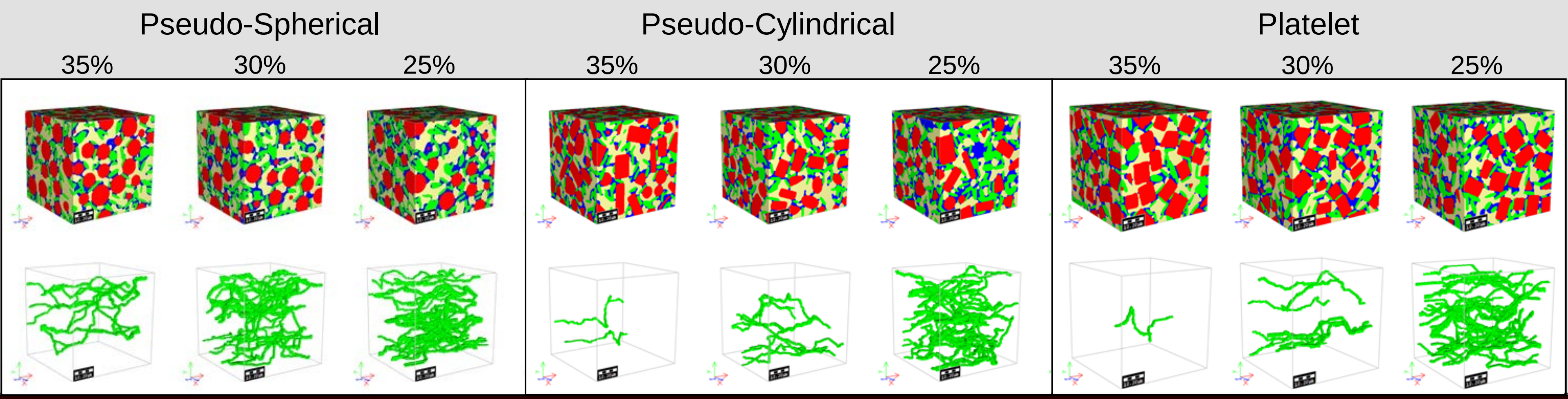
❖ Potential is the same for two objects on opposite sides of an interface

❖ Solution is implemented in simulation package **GeoDict**™

Results – Percolation

- Higher degree of percolation occurs with lower volume % AM
- Effective conductivity increases with path number and decreasing overall path tortuosity
- Percolation, effective conductivity and tortuosity are available in GeoDict™

	Conductive Paths	Conductivity (S/m)	Tortuosity
Sphere			
35%	11	17.4	1.89
30%	39	28.2	1.54
25%	52	55.3	1.38
20%	97	81.8	1.42
Cylinder			
35%	2	8.52	1.54
30%	10	23.1	1.51
25%	59	61.6	1.48
20%	84	70.7	1.42
Platelet			
35%	1	4.95	1.61
30%	11	29.0	1.39
25%	46	46.1	1.51
20%	92	78.6	1.41



Results – Effective Conductivity

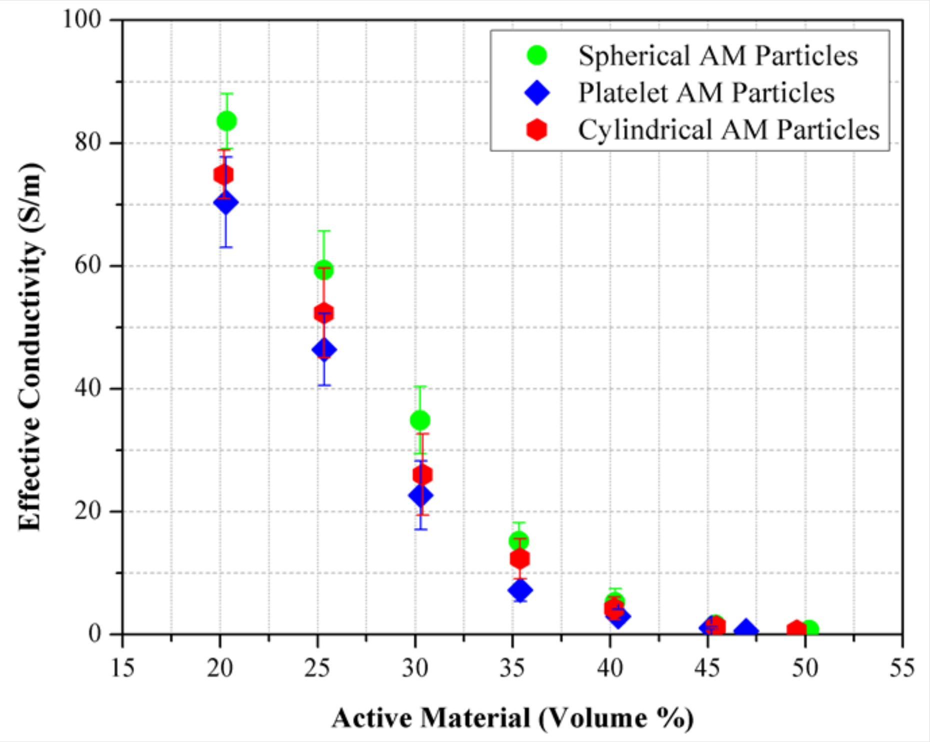
- Simulation results for the effective electrical conductivities for each set of electrodes are shown to the right.
- Averaged data were plotted in the figure, with error bars of ±σ.
- At > 35% AM,

  $\sigma_{\text{eff-sphere}} \square \sigma_{\text{eff-cylinder}} \square \sigma_{\text{eff-cube}}$
- At 25%-35% AM,

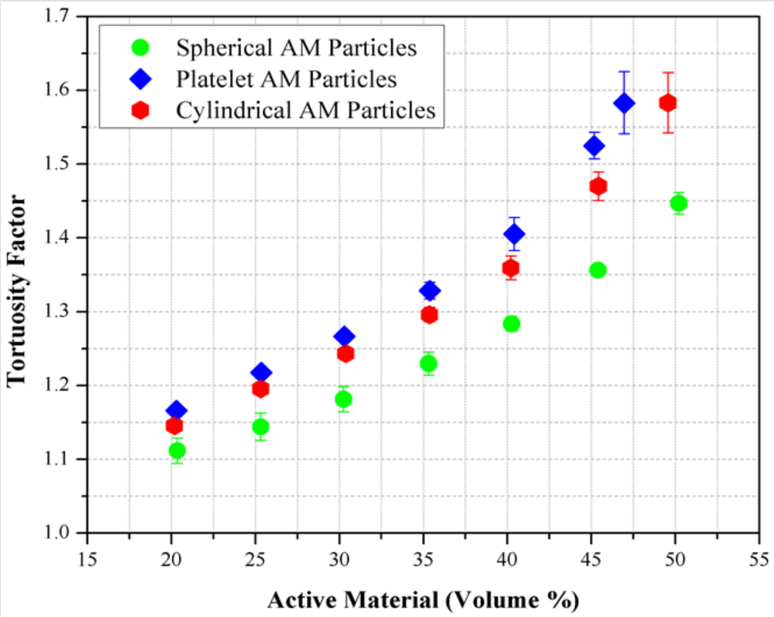
  $\sigma_{\text{eff-sphere}} \square \sigma_{\text{eff-cube}}$
- At 20%,

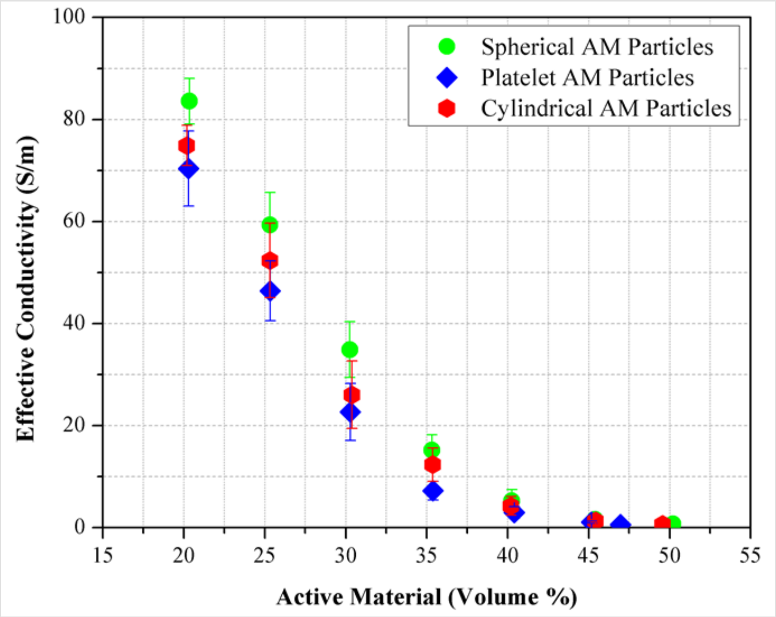
  $\sigma_{\text{eff-sphere}} > \sigma_{\text{eff-cylinder}} \approx \sigma_{\text{eff-cube}}$
- Distribution of AM affects pathway formation

  → quantified in terms of tortuosity



Results – Tortuosity Factor

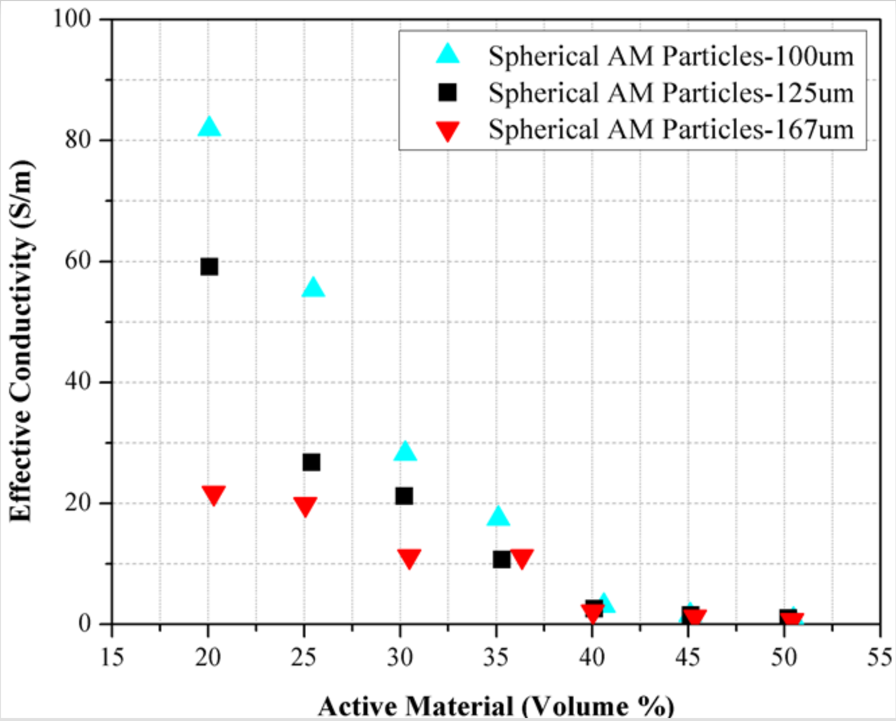




- Tortuosities ↑ with ↑ in active material particle surface area (Sa_{sphere}<$Sa_{cylinder}$<Sa_{cube})

  where Sa is the surface area for each active material shape
- Above a certain tortuosity threshold, the formation of pathways is very difficult
- General trend can be seen in terms of average effective conductivity and tortuosity factor
- Random nature of pathway formation obscures this

Results – Resolution



- Electrodes consisting of spherical active material particles at varying resolution created
- Trends expected to be similar for all AM shapes
- General increase in conductivity with voxel size
- Lowest resolution utilized for speed; experimental validation required

Results – Domain Size

❖ Domain must be large enough to obtain consistent results

❖ Domain length/Particle diameter ratio chosen as >5

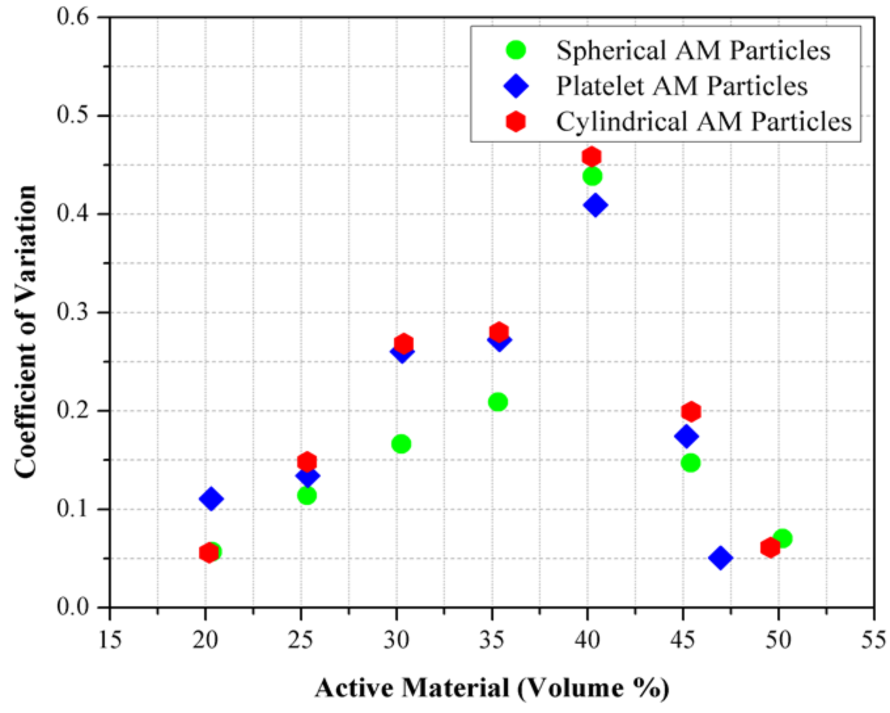
❖ To ensure that the generated models were free from variation of size effect, the coefficient of variation was evaluated for the final conductivity data.

$$CV = \frac{\sigma}{\mu}$$

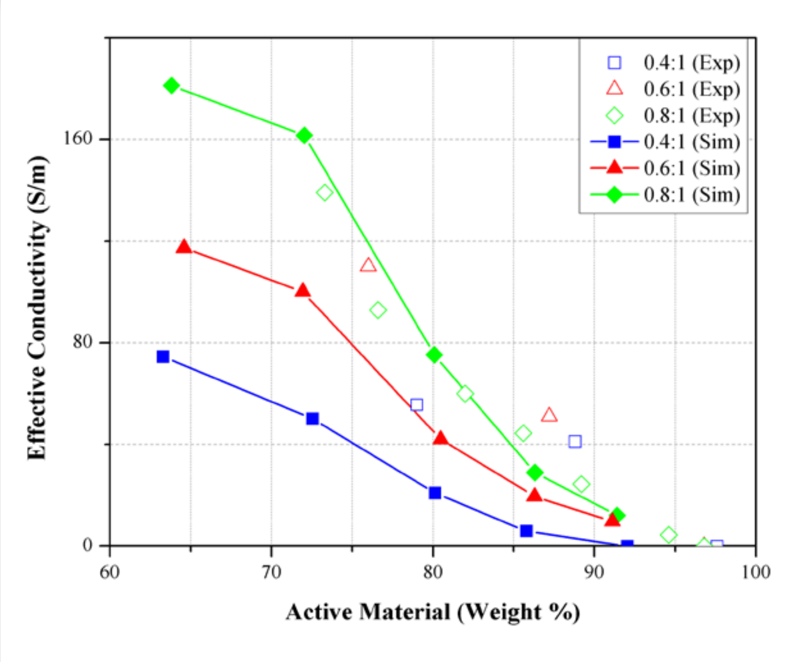
0.0<CV<0.5 homogenous
0.5<CV<1.0 heterogeneous
1.0<CV very heterogeneous

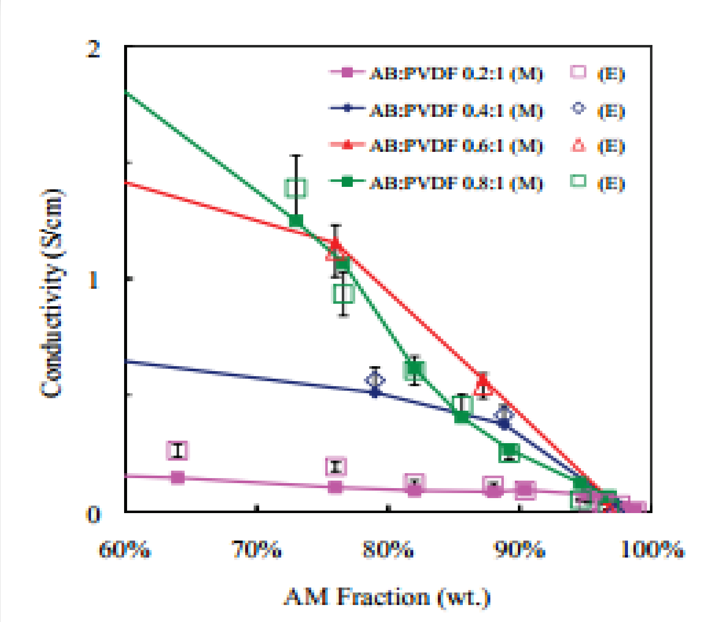
where σ is the standard deviation and μ is the arithmetic mean

❖Evaluation of coefficient of variation reveals acceptable level of homogeneity



Results – Model Validation





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- Separate set of models made to correlate with results of Liu et. al.
- Percolation achieved at 4% acetylene black by weight for both sets
- A decrease in AM results in an increase in effective conductivity for both sets of data
- Simulations deviate from experimental data in terms of expected trends based on CA/B ratio

Stein, Wiegmann, Mukherjee, *in preparation* (2013).

Conclusions

- At loadings greater than 35% the active material shape does not have a significant bearing on the effective conductivity.

- For loadings less than 35%, spherical active material particles will likely yield the greatest return for effective conductivity – although this effect could be obscured.

Outlook/Future Work

- Experimentally validate results and assumptions
- The modeling technique utilized can be extended to more complex geometries for property analysis
- 3D structures generated via this method can be coupled with external programs for electrochemical analysis

Acknowledgements

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Thank you!