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

Malcolm Stein IV
Andreas Wiegmann and Partha P. Mukherjee

1Department of Mechanical Engineering, Texas A&M University, College Station, TX
2Math2Market GmbH, Kaiserslautern, Germany

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Overview

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

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

\[
\text{LiFePO}_4
\]


LiFePO_4

With carbon coating

\[
\text{LiFePO}_4
\]
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

<table>
<thead>
<tr>
<th>AM Particle</th>
<th>Length</th>
<th>Diameter</th>
<th>Volume</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>--</td>
<td>9.0 µm</td>
<td>3.82 E-16 m³</td>
<td>2.55 E-10 m²</td>
</tr>
<tr>
<td>Cylinder</td>
<td>12.48 µm</td>
<td>6.24 µm</td>
<td>3.82 E-16 m³</td>
<td>3.06 E-10 m²</td>
</tr>
<tr>
<td>Platelet</td>
<td>7.25 µm</td>
<td>--</td>
<td>3.82 E-16 m³</td>
<td>3.16 E-10 m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Material</td>
<td>.01 S/m</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1 S/m</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.0 × 10^4 S/m</td>
</tr>
<tr>
<td>PVDF</td>
<td>1.0 × 10^-13 S/m</td>
</tr>
</tbody>
</table>
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
Methodology – Conductivity

- Effective conductivity determined via the 3D stationary conduction equation

\[ \nabla (\sigma \nabla V) = \dot{j} \text{ in } \Phi \]

where \( V \) is the potential, \( \sigma \) is the local electrical conductivity, \( \dot{j} \) is a source term, and \( \Phi \) is the domain under consideration.

- Only conduction through the domain is considered so \( \dot{j} \to 0 \).

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

- Solution is implemented in simulation package GeoDict™

\*GeoDict™ is a trademark of Math2Market GmbH, Kaiserslautern Germany.*
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™

<table>
<thead>
<tr>
<th></th>
<th>Conductive Paths</th>
<th>Conductivity (S/m)</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35%</td>
<td>11</td>
<td>17.4</td>
<td>1.89</td>
</tr>
<tr>
<td>30%</td>
<td>39</td>
<td>28.2</td>
<td>1.54</td>
</tr>
<tr>
<td>25%</td>
<td>52</td>
<td>55.3</td>
<td>1.38</td>
</tr>
<tr>
<td>20%</td>
<td>97</td>
<td>81.8</td>
<td>1.42</td>
</tr>
<tr>
<td>Cylinder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35%</td>
<td>2</td>
<td>8.52</td>
<td>1.54</td>
</tr>
<tr>
<td>30%</td>
<td>10</td>
<td>23.1</td>
<td>1.51</td>
</tr>
<tr>
<td>25%</td>
<td>59</td>
<td>61.6</td>
<td>1.48</td>
</tr>
<tr>
<td>20%</td>
<td>84</td>
<td>70.7</td>
<td>1.42</td>
</tr>
<tr>
<td>Platelet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35%</td>
<td>1</td>
<td>4.95</td>
<td>1.61</td>
</tr>
<tr>
<td>30%</td>
<td>11</td>
<td>29.0</td>
<td>1.39</td>
</tr>
<tr>
<td>25%</td>
<td>46</td>
<td>46.1</td>
<td>1.51</td>
</tr>
<tr>
<td>20%</td>
<td>92</td>
<td>78.6</td>
<td>1.41</td>
</tr>
</tbody>
</table>
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,
  \[ \sigma_{\text{eff-sphere}} \approx \sigma_{\text{eff-cylinder}} \approx \sigma_{\text{eff-cube}} \]
- At 25%-35% AM,
  \[ \sigma_{\text{eff-sphere}} \approx \sigma_{\text{eff-cube}} \]
- 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 ($S_{\text{sphere}} < S_{\text{cylinder}} < S_{\text{cube}}$)
  
  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 \( \sigma \) is the standard deviation and \( \mu \) is the arithmetic mean

- Evaluation of coefficient of variation reveals acceptable level of homogeneity
Results – Model Validation

- 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


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!