Electronic pathway length manipulation and impact on conductivity networks in lithium-ion battery electrodes

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Next Generation Electrodes (NEXTRODE)

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- **WP3:** Yige Sun (1st Nov. 14:50)

- **WP5:** Geanina Apachitei (2nd Nov. 15:35)
**Electrode Electronic Conductivity**

**Particle design**

- Active material (AM) particle engineering
  - Particle surface coating
  - Core-shell structured particles
  - Hybrid composite particles (coating, doping)

- Carbon binder domain (CBD) engineering
  - Carbon coating on AM particles
  - Graphite/carbon nanotubes
  - Intensive dry mixing for homogenous carbon coverage

**Electrode design**

- High power and energy density requires thicker electrodes
- Efficient electron transport networks with decreasing proportions of conductive additives (CA)
- Incorporation of CA has secondary implications
  - Electrode porosity and tortuosity
  - Compressibility and mechanical properties
  - AM-binder interactions
  - Electrolyte reservoirs and wettability
  - SEI formation
  - Electrode thermal conductivity

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LONG- AND SHORT-RANGE ELECTRONIC CONTACTS

What we know

• Importance of long- and short-range electrical networks
• Destructive and constructive impacts of heterogeneity impacts rate capability\(^1\)
• Processing techniques affects CBD formation and electronic and ionic networks\(^2\)\(^3\)
• Targeted distribution of CA with binder in clusters localized next to contact areas with other AM particles\(^4\)

No fundamental understanding

• Optimal quantity and location/ distribution of CA in an electrode
• Optimal combination of long- and short-range contacts
• Advance characterization of contact structure
• Simulation of traditional composite or structured electrodes

\(^1\) Yari et al., ACS Appl. Energy Mater. 2020 3, 11820-11829
\(^2\) Saraka et al., ACS Appl. Energy Mater. 2020 3, 11681-11689
\(^3\) Dreger et al., Journal of Elec Mater. 2015 44, 4434-4443
\(^4\) Bauer et al., Journal of Power Sources. 2015 288, 359-367
MECHANOFUSION PROCESS

Use of mechanofusion to control degree of carbon black de-agglomeration as a measure of short-range contacts

Nobilta mixer

(Hosokawa Micron Corp.)
• Constant solids to AM (NMC622 BASF) : binder (PVDF 5130 Solvay)
• Conductive additives – Imerys C65 and KS6 graphite
• AM:B ratio at 98:2wt%
• NMC coated over a range of wt% CB to develop variation in local percolation curve
• Percolation threshold – critical conductive additive concentration

• Short to moderate mixing times
  • CB agglomerates broken down and NMC progressively coated
  • Improvements in electronic conduction
• Long mixing times
  • Compaction resulting in a thin and dense coating
  • Dense layer may impede ionic conduction
LONG- AND SHORT-RANGE CONTACTS

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Nobilta Mixed (AM:CA wt %)</th>
<th>Slurry Mixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>96:2:2 NMC:C65:PVDF (wt%)</td>
<td>-</td>
<td>96:2:2wt% (all slurry mixed)</td>
</tr>
<tr>
<td>Baseline (control)</td>
<td>Unknown</td>
<td></td>
</tr>
<tr>
<td>2% C65 Nobilta</td>
<td>96:2</td>
<td>2wt% – Binder</td>
</tr>
<tr>
<td>1% C65 Nobilta +1% C65 in slurry</td>
<td>96:1</td>
<td>1wt% – C65 2wt% – Binder</td>
</tr>
<tr>
<td>1% C65 Nobilta +1% Graphite in slurry</td>
<td>96:1</td>
<td>1wt% – Graphite (KS6) 2wt% – Binder</td>
</tr>
</tbody>
</table>

- Studying C65 and graphite and their ability to provide long range contacts
- Graphite used as an alternative LRC
- Comparing this to other formulations with lower carbon amounts (1wt%)
- Potential additional conductive additives e.g. carbon fibers, nanotubes have not been investigated

Spahr et al., Journal of Power Sources. 2011 196, 3404-3413
MECHANOFUSION EXPERIMENTS

Investigated 1-10 wt% coating of C65 on NMC
- Inspected with SEM at mixing times from 0 to 60 min
- Powder conductivity measured at time intervals
CONDUCTIVITY AND ELECTROCHEMISTRY

- (2%) Nobilta Coated (100% Short-Range Contacts)
- (1%) Nobilta Coated + 1% C-65 (50:50 Short:Long-Range)
- (1%) Nobilta Coated + 1% KS6 Graphite (50:50 Short:Long-Range)
- Baseline 2wt% C-65 Slurry mixed

Graph showing:
- Resistance of 1g Material under 2000N of force (Ohm)
- Capacity (mAh/g) vs. Cycle Number

Graph legend:
- C-65 (50:50 Short:Long-Range)
- Nobilta (100% Short-Range)
- Baseline
- KS6 Graphite (50:50 Short:Long-Range)
**Conclusions**

- Demonstrated mechanofusion as rapid and effective deagglomeration technique
- Manipulation of carbon black controls electronic conductivity
- Complex relationship between CBD processing and morphology on cell performance
- Binder location may differ in SR and mixed range structures
- Unknown impact of coating on calendering mechanics

**Future Work**

- Investigate mechanofusion mechanisms
- Further determination of control in long- and short-range electrical contacts
- Why does slurry casting perform so well?
- Best conductive additive for long-range contacts
- Better characterisation techniques to quantify pathways
- **Use our understanding and methods to produce designed conductive pathways and 3D architectures.**
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Thank you

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SHORT RANGE CONTACTS

Conventional slurry electrode NMC particle

Mechanofusion coated NMC particle
ELECTROCHEMICAL RESULTS

- Complex relationship between cell performance and CBD morphology
- Further work to investigate electrode pore properties, electrolyte reservoirs, EIS response etc.
- How does coating for short-range contacts change calendering mechanics