Sintered Cathodes for All-Solid-State Structural Lithium-Ion Batteries
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Objective
- Characterize processing-structure-property relationships in cathode materials for optimized sintering conditions, structural and chemical stability, and microstructural development for all-solid-state structural lithium-ion batteries.
- Evaluate mechanical and electrical performance through ring-on-ring mechanical testing and impedance spectroscopy.

Motivation
- Achieve systems level weight savings in aerospace applications by providing multifunctional load bearing energy storage for all-electric or hybrid-electric propulsion systems.
- Improve upon the safety and reliability of energy storage systems by transitioning from liquid electrolytes to inherently safe all-solid-state battery configurations.

Background
- Secondary (rechargeable) all-solid-state lithium-ion batteries store electrical energy as chemical potential energy.
- Anode – receives Li+ during charging, releases Li+ during discharge.
- Electrolyte – allows facile diffusion of Li+ between composite electrodes, negligible electronic conductivity prevents leakage.
- Cathode – receives Li+ during charging, releases Li+ during discharge.
- Typical composite electrodes are composed of active material, electrolyte, and a electronically conductive additive phase.
- Multifunctional structural batteries provide energy storage and load-bearing performance to achieve overall weight reduction.

Materials
- Commercially available cathode active material Li[Ni0.33Mn0.33Co0.33]O2 (NMC).
- As-received agglomerates ball milled to liberate particles, reduce and homogenize particle size distribution.

Structural and Chemical Stability

Table 1: ICP for various processing states and sintering conditions. AR – as received, M – milled.

<table>
<thead>
<tr>
<th></th>
<th>1000°C-1Hr</th>
<th>1050°C-1Hr</th>
<th>1100°C-1Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>Ni</td>
<td>20.7</td>
<td>21.4</td>
<td>20.8</td>
</tr>
<tr>
<td>Mn</td>
<td>19.0</td>
<td>19.5</td>
<td>19.0</td>
</tr>
<tr>
<td>Co</td>
<td>19.9</td>
<td>20.5</td>
<td>20.0</td>
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</tbody>
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- Li, Ni, Mn, & Co composition controlled with use of sacrificial powder bed.
- ICP indicates 3% lithium volatilization at highest sintering temperature and is within instrument uncertainty.
- XRD patterns of rhombohedral layered structure remain unchanged across processing temperature range from 1000°C to 1100°C.

Densification and Coarsening

Figure 1: All-solid-state lithium-ion battery

*1 http://smang.ucsd.edu/supercapacitors/  H. Wei, S. Kei, “Multifunctional composite materials for energy storage in structural load paths.”

Figure 2: Schematic plot for system design to achieve overall weight savings.

- Mechanical fracture stress correlates with densities greater than 83% of theoretical density. Weibull analysis indicates reliability increases with reduction in porosity.

Conclusions:
- Microstructural development of Li[Ni0.33Mn0.33Co0.33]O2 has been studied in relation to its mechanical and electrical properties.
- Greater than 90% density can be achieved when sintering at and above 1075°C.
- Fracture stress correlates with sample density and is maximized near 45MPa. Mechanical performance requires composite infiltration to overcome brittle fracture failure before structural application may be realized.
- At 1100°C, grain coarsening leads to higher electrical resistivity, indicating conduction dominated by grain boundaries.

Mechanical Performance

Figure 7: Above, sintered microstructures for samples processed with increasing sintering temperature. Average grain size is tabulated beneath each micrograph.

Figure 8: Significant grain growth occurs at sintering temperatures above 1075°C.

Electrical Performance

Figure 11: Left: Characteristic complex Nyquist plot for sintered cathode samples and equivalent circuit model used in impedance spectroscopy curve fitting.

Figure 12: Right: electronic conductivity as a function of inverse temperature. Activation energies were calculated from linear fit Arrhenius slopes.

Figure 13: Below: plot demonstrating direct correlation between grain volume and electrical resistance.

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