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, receives Li+ during discharge.
• Typical composite electrodes are composed of active material, electrolyte, and an electronically conductive additive phase.
• Multifunctional structural batteries provide energy storage and load-bearing performance to achieve overall weight reduction.

Materials

• Commerically available cathode active material LiNi0.33Mn0.33Co0.33O2 (NMC).
• As-received agglomerates ball milled to librate particles, reduce and homogenize particle size distribution.

Structural and Chemical Stability

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

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>AR</th>
<th>1000°C - 1Hr</th>
<th>1050°C - 1Hr</th>
<th>1100°C - 1Hr</th>
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<tbody>
<tr>
<td>Li</td>
<td>7.3</td>
<td>7.1</td>
<td>7.1</td>
<td>7.0</td>
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<tr>
<td>Ni</td>
<td>20.9</td>
<td>20.7</td>
<td>21.4</td>
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<tr>
<td>Mn</td>
<td>19.0</td>
<td>18.8</td>
<td>19.5</td>
<td>19.0</td>
</tr>
<tr>
<td>Co</td>
<td>19.9</td>
<td>19.7</td>
<td>20.5</td>
<td>20.0</td>
</tr>
</tbody>
</table>

• Li, Ni, Mn, & Co composition controlled with use of sacrificial powder bed.
• ICP indicates 3% lithium volatilization at highest sintering temperature and within instrument uncertainty.
• XRD patterns of rhombohedral layered structure remain unchanged across processing temperature range from 1000°C to 1100°C.

Conclusions:

• Microstructural development of LiNi0.33Mn0.33Co0.33O2 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 450MPa. Mechanical performance requires composite infiltration to overcome brittle fracture failure before structural application may be realized.
• Significant grain growth occurs at 1075°C and above.


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

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

Figure 3: Layered structure displaying transition metal octahedrons and lithium layers.

Figure 4: Volume fraction particle size distribution of milled NMC from dynamic light scattering.

Figure 5: Top: NMC agglomerates. Bottom: NMC after 20hrs of ball milling.

Figure 6: Typical XRD pattern for layered R3m LiNi0.33Mn0.33Co0.33O2

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

Figure 8: Below, plot displaying average percentage of theoretical density and average grain size for samples for all sintering temperatures.

• >90% theoretical density reached at 1075°C and above.

Figure 9: Left: ring-on-ring mechanical fracture stress as a function of percent theoretical density.

Figure 10: Above: ring-on-ring mechanical testing and analysis performed according to ASTM C3499-15.

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

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.

• Grain growth correlates with increase in overall resistance, indicating grain boundary conduction as the dominant mechanism for electrical conductivity.