Engineering Routes Towards Synthesis and Performance of Layered Oxide Cathode Materials for Sodium-ion Batteries

OE Peer Review

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ORNL is managed by UT-Battelle, LLC for the US Department of Energy
ORNL Is Addressing Three Major Problems:

1. Advanced batteries are not being manufactured in the U.S.
2. Advanced batteries have insufficient energy density.
3. Advanced batteries still have high cost and insufficient long-term performance.

- **Cost**
  - Raw materials
  - Electrode processing
  - Cell manufacturing
  - Formation cycling
  - Module packaging

- **Performance**
  - Power limitations at low temperature
  - Low capacity at high discharge rates
  - Capacity fading

- **Safety**
  - Short circuiting
  - Overcharge
  - Over-discharge
  - Crush
  - Thermal runaway

- **Life**
  - Calendar life
Objective – Li-ion vs. Na-ion Batteries: Why Sodium?

<table>
<thead>
<tr>
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<th>Abundance in earth crust (ppm)</th>
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<tbody>
<tr>
<td>Lithium</td>
<td>20 (ranked 32\textsuperscript{nd})</td>
</tr>
<tr>
<td>Sodium</td>
<td>27500 (ranked 6\textsuperscript{th})</td>
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For cost analysis (53 kWh battery pack)
- Li-ion Batteries (LIBs):
  - NMC622 vs. graphite
- Na-ion Batteries (SIBs):
  - $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ vs. hard carbon

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Approach – Eutectic Synthesis Method Developed at ORNL

• Sodium-ion Battery current TRL is 3-4.

• Layered transition metal oxides have always been great candidates as cathodes for SIBs. However, the synthesis is usually energy-intensive, and often leads to impurities due to inhomogeneous mixing, further resulting in nonideal electrochemical performance.

Eutectic Synthesis (TRL 2)

• Mechanism: eutectic formation + liquid mixing.
• Advantages: uniform liquid-based mixing down to atomic level; higher crystallinity; homogeneous morphology; fast process.
• Accomplishments: provisional patent filed; first manuscript on P2-type Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$ published.
Shifting Towards Cathodes with Higher Voltage

• For potential high-energy applications, SIB cathodes with higher voltage and higher capacity are preferred.


P2/O3-Na_{x}Ni_{0.5}Mn_{0.5}O_{2}
Eutectic Synthesis of Na$_x$Ni$_{0.5}$Mn$_{0.5}$O$_2$ (Target $x=0.67$)

• 900 °C 2$^{\text{nd}}$-step annealing resulted into P2-phase (confirmed by XRD).

• Resulted $x$ value in the final product is roughly between 0.48 to 0.53 (due to Na leaching during high-temperature annealing).
P2-\( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) (\( x<0.67 \)) Delivered \(~200\) mAh/g Capacity

- Slurry: 80 wt\% active, 10 wt\% Super C60, 10 wt\% 5130PVDF.
- Half cells against Na metal vs. Full cells against pre-sodiated hard carbon.

- Initial capacity of 196 mAh/g can be achieved for P2-\( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) half cell, average voltage is \(~3.25\) V.
Increasing Na Content Above 0.78 Resulted in Phase Change (P2→O3)

- To compensate the Na loss during annealing, x=1 synthesis attempt was performed for \( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \).

- 900 °C 2\textsuperscript{nd}-step annealing resulted into O3-phase (confirmed by XRD).

- Resulted x value in the final product is roughly between 0.78 to 0.80 (not reaching x=1 yet but phase was already changed to O3).
O3-$\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($x<1$) Delivered 210 mAh/g Capacity

- Half cells against Na metal vs. Full cells against pre-sodiated hard carbon.

- Initial capacity of 230 mAh/g can be achieved for O3-$\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ half cell (higher than P2-$\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$), average voltage is ~3.5 V.
Na Content Was Further Increased from 0.78 to 1 in O3-Na\textsubscript{x}Ni\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}  

- To further increase the Na content in the final material, x=1.2 synthesis attempt was performed for Na\textsubscript{x}Ni\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}. 

- 900 °C 2\textsuperscript{nd}-step annealing resulted into O3-phase again (confirmed by XRD).  

- Resulted x value in the final product is roughly between 1.01 to 1.10.
Reduced Capacity Observed in O3-Na$_x$Ni$_{0.5}$Mn$_{0.5}$O$_2$ (x<1.2)

- Half cells against Na metal vs. Full cells against pre-sodiated hard carbon.

- A large 1$^{st}$ cycle charge capacity was observed (279 mAh/g), but only 197 mAh/g 1$^{st}$ cycle discharge capacity was delivered (less reversible compared to Na$_x$Ni$_{0.5}$Mn$_{0.5}$O$_2$ with x=1).
 Despite higher initial capacity achieved in both O3-type cathodes, the cycling stability was lower than P2-type Na$_x$Ni$_{0.5}$Mn$_{0.5}$O$_2$ (and the first cycle irreversible capacity loss was higher as well).

It is important to better understand the initial high capacity fading within 5 cycles for P2/O3 materials and to engineer the particle and composition to stabilize the cycling performance.
P2-Structure Exhibited Superior Rate Performance
Progression of SIB Cathode Development

**Eutectic Mixing**
(Smaller Particles, Improved Homogeneity)

**Sol-Gel**
(Larger, More Non-Uniform Particles)

Comparison Focusing on Eutectic Mixing:

\[
\begin{align*}
\text{Na}_x\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2 \\
\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2
\end{align*}
\]

\[0.67 \leq x \leq 1.1\]
FY20 Achievements and FY21 Future Work

**FY2020 Accomplishments:**
- Study on novel eutectic synthesis of $\text{P}_2\text{-Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ as high-performance cathode for sodium-ion batteries (SIBs) and advanced cell design by pairing with a pre-sodiated hard carbon anode was published on *ACS Applied Materials & Interfaces*. (ACS Appl. Mater. Interfaces 2020, 12, 21, 23951–23958).
- Provisional patent was filed on 12/19/19 for this improved synthesis method: D.L. Wood, III, J. Li, M. Li, and Y. Bai, U.S. Provisional Patent Application No. 62/946,525.
- Full pouch cells were made comparing the sol-gel and eutectic mixing method against hard carbon anodes.
- High-voltage cathode $\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was synthesized by the eutectic method for electrochemical studies.

**FY2021 Plan:**
- Investigate the initial fading mechanism for high-voltage cathode $\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (in-situ gas evolution analysis during 1st cycle, ex-situ XRD).
- Stabilize the cycling performances of P2/O3-type $\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by substitution.

- Down select the high-voltage cathode with the best electrochemical performance to scale up and produce 200 g batch of materials by eutectic mixing.
- R2R manufacturing of new cathodes for 1.5-Ah full pouch cell (multilayer) fabrication against hard carbon anodes.
ORNL – Michael Starke and Thomas King, Jr.

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