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

OE Peer Review

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Oak Ridge National Laboratory

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

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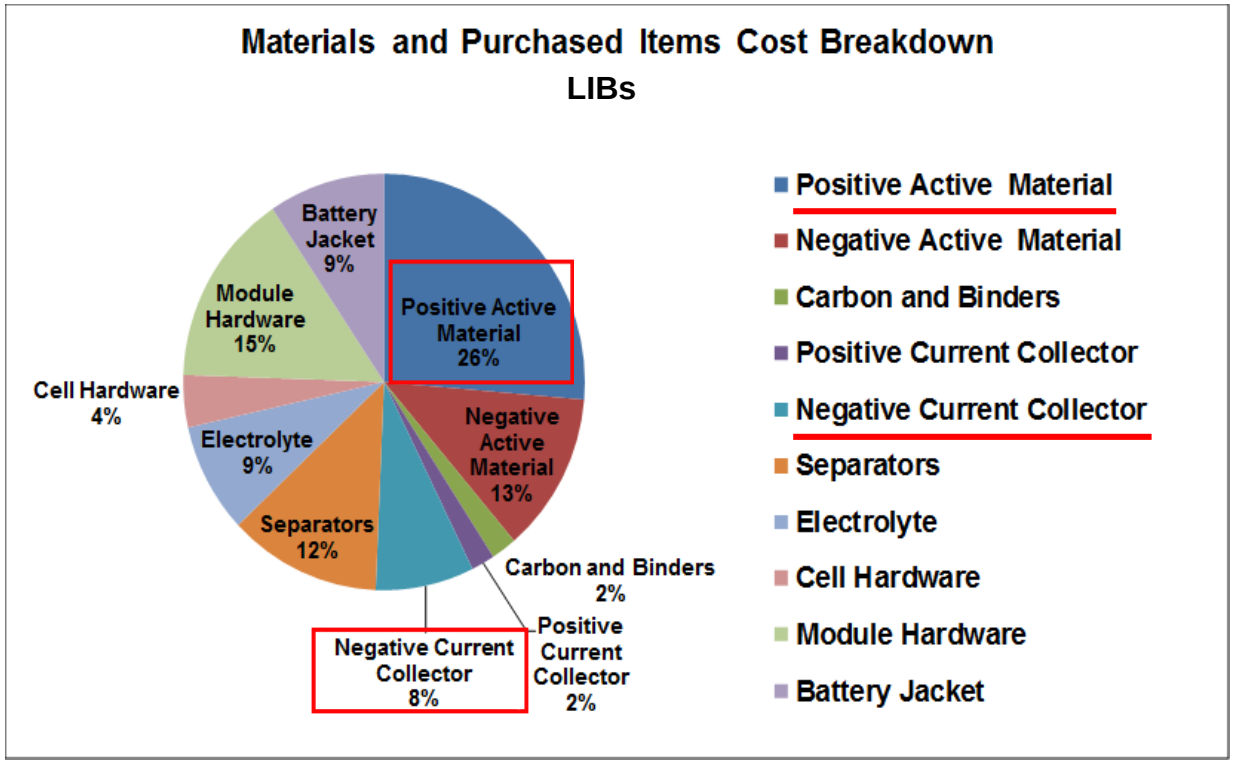
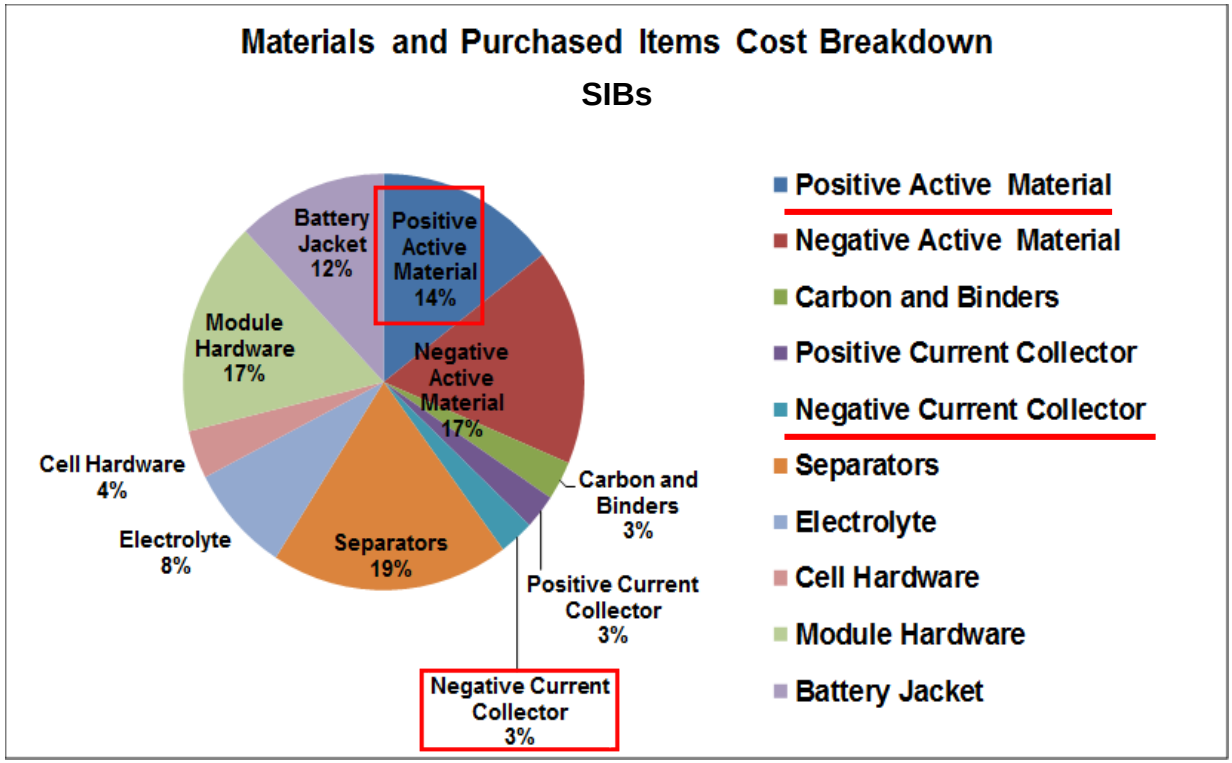
Objective – Li-ion vs. Na-ion Batteries: Why Sodium?

	Abundance in earth crust (ppm)
Lithium	20 (ranked 32nd)
Sodium	27500 (ranked 6th)

For cost analysis (53 kWh battery pack)

- Li-ion Batteries (LIBs):
  NMC622 vs. graphite
- Na-ion Batteries (SIBs):
  $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ vs. hard carbon





Energy Storage Materials 25 (2020) 520–536.

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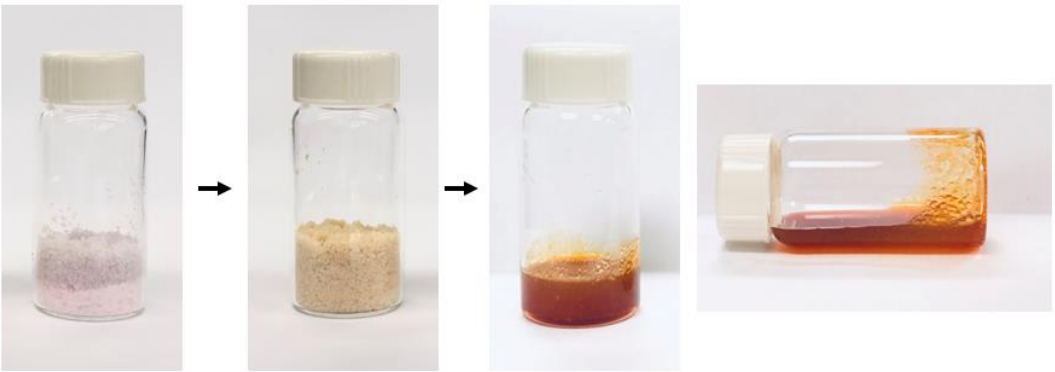
Approach – Eutectic Synthesis Method Developed at ORNL

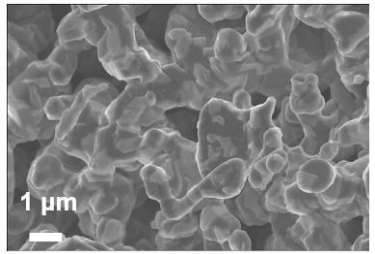
- Sodium-ion Battery current TRL is 3-4.
- Layered transition metal oxides have always been great candidates as cathodes for SIBs. However, the synthesis is usually energy-intensive, and often leads to impurities due to inhomogeneous mixing, further resulting in nonideal electrochemical performance.

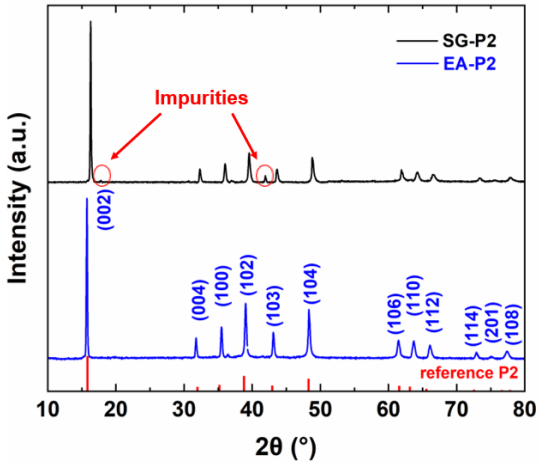


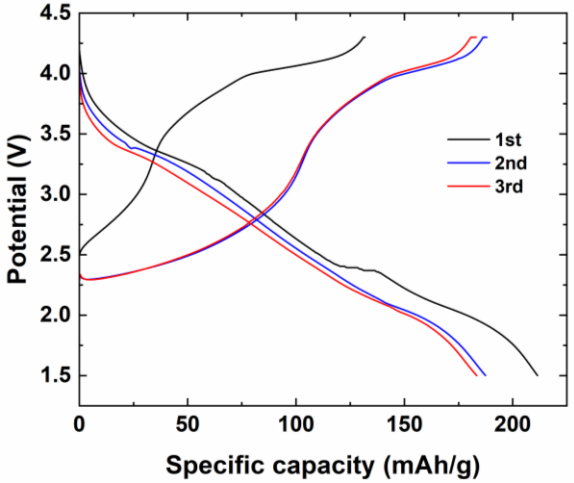
From metal nitrates precursors to liquid eutectic formation in 0.5 hr

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.







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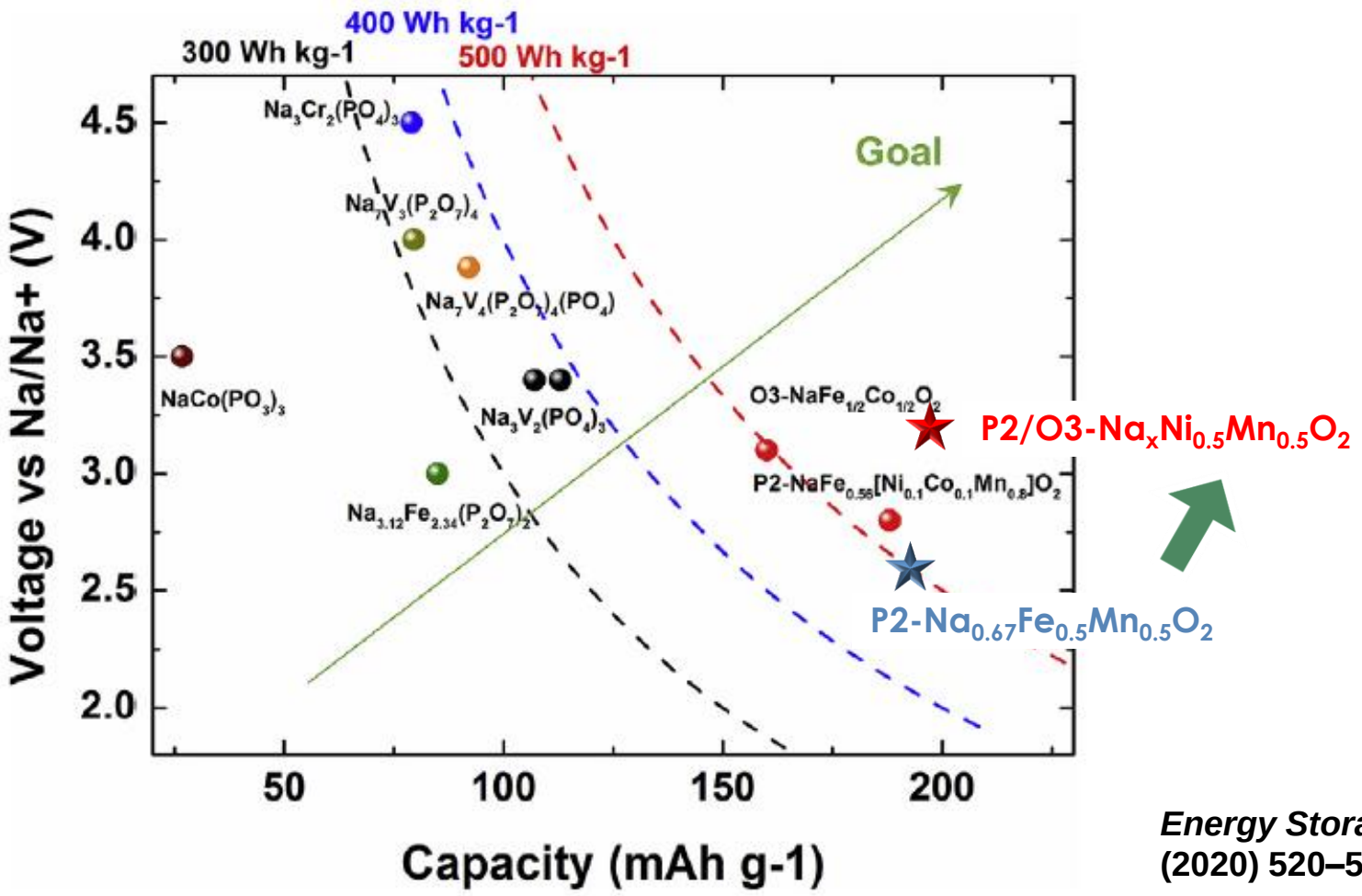
Shifting Towards Cathodes with Higher Voltage

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



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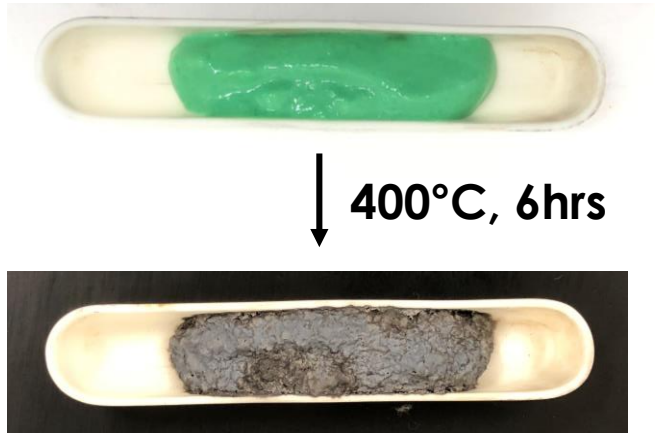
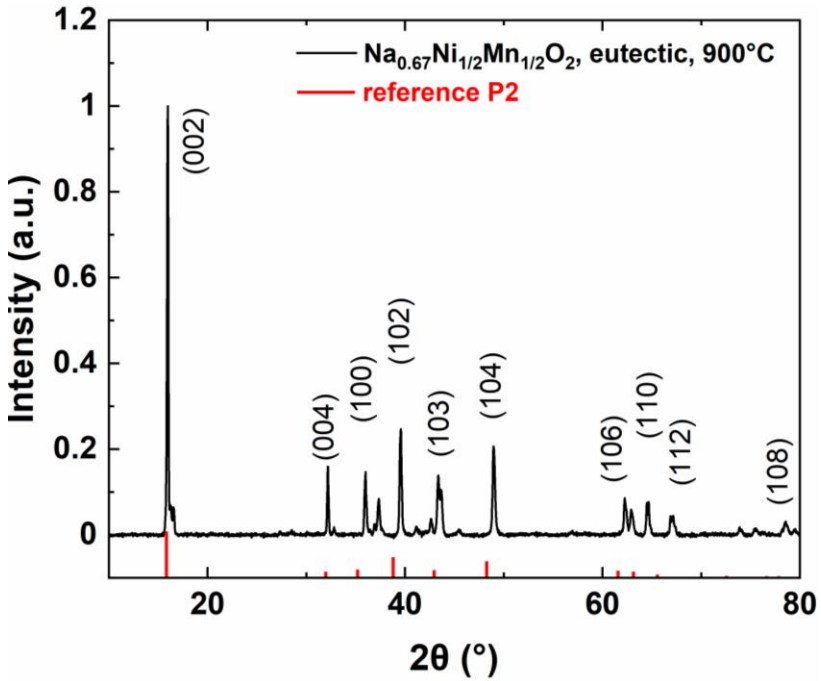
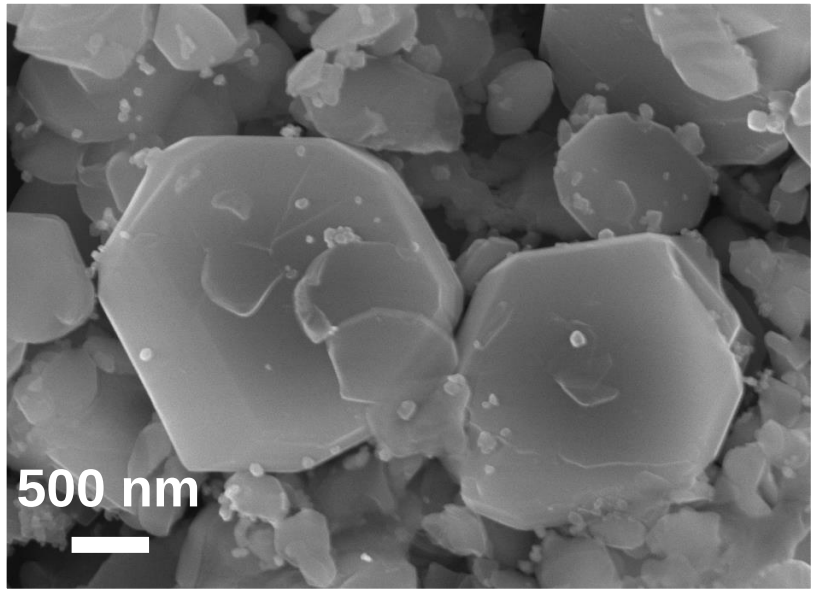
Eutectic Synthesis of $Na_xNi_{0.5}Mn_{0.5}O_2$ (Target x=0.67)







- 900 °C 2nd-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).

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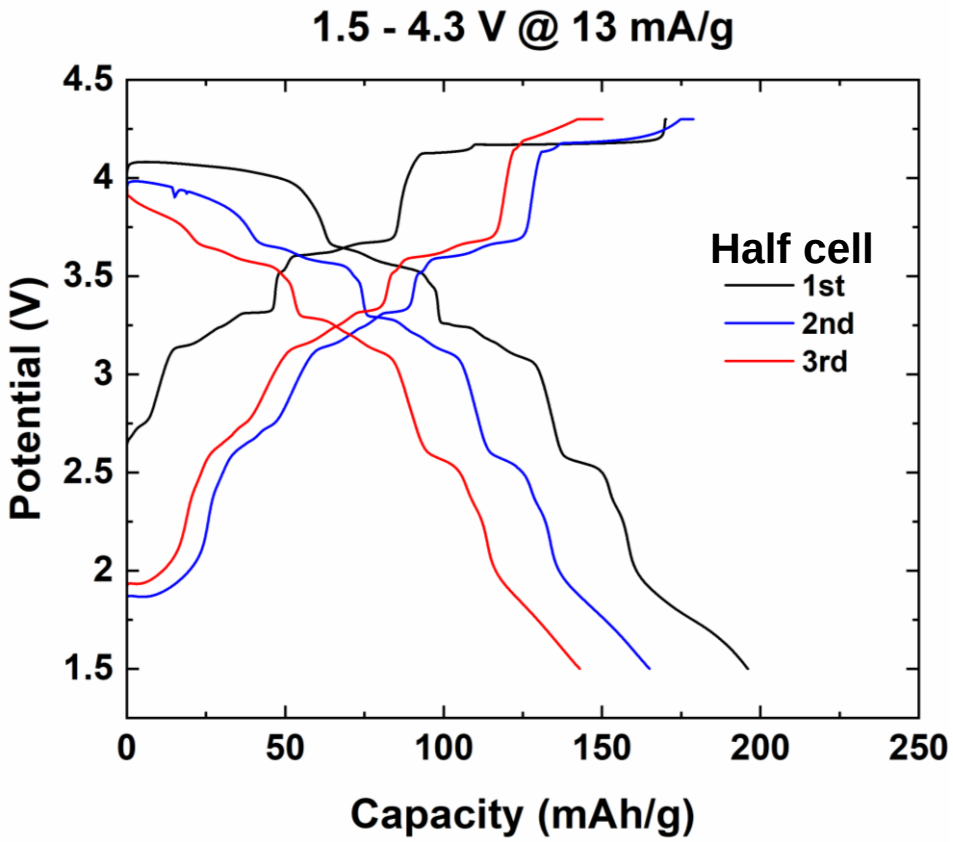
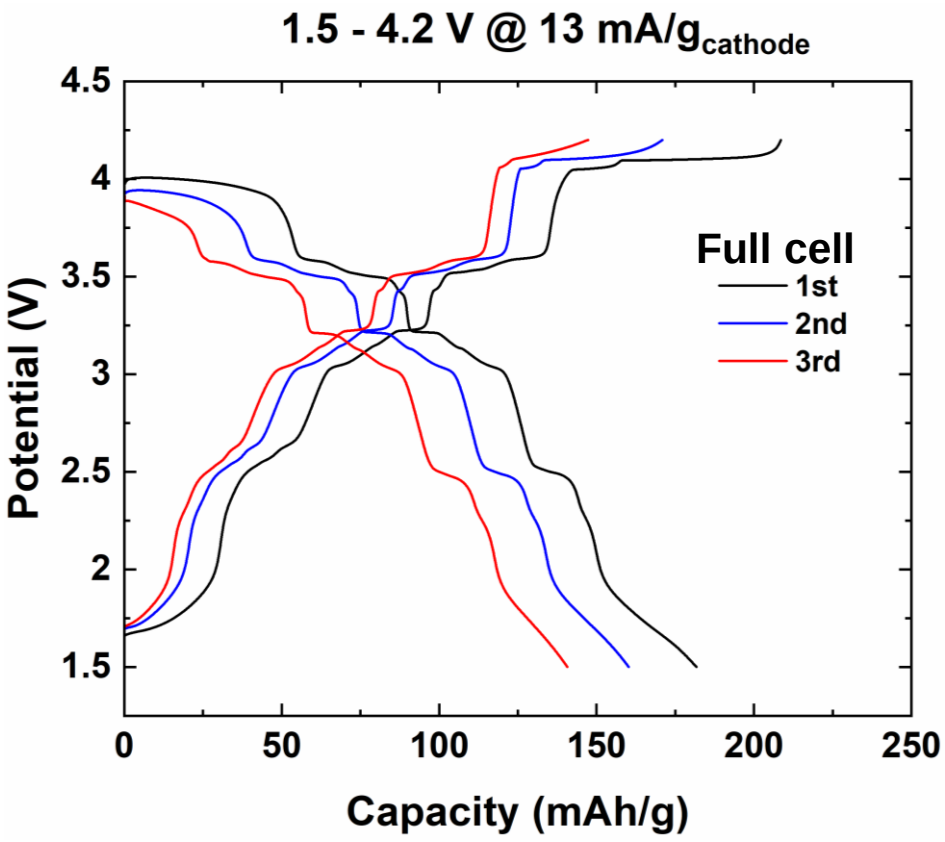
P2-$Na_xNi_{0.5}Mn_{0.5}O_2$ (x<0.67) Delivered ~200 mAh/g Capacity

- 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-$Na_xNi_{0.5}Mn_{0.5}O_2$ half cell, average voltage is ~3.25 V.

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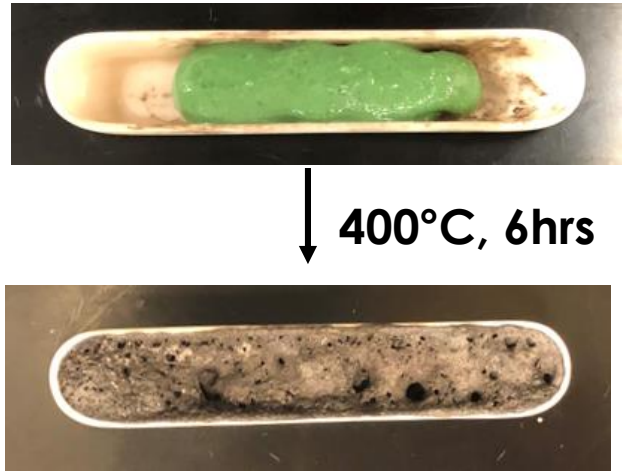
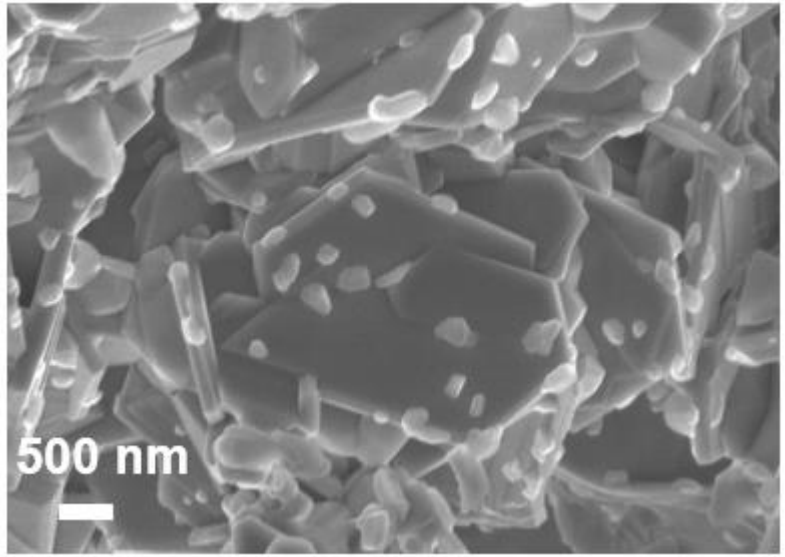
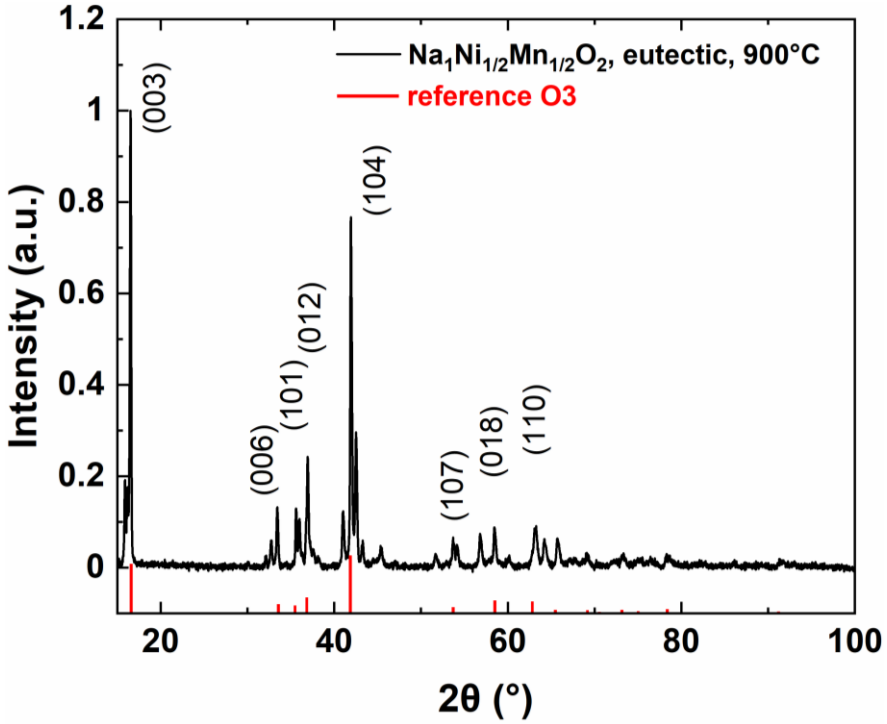
Increasing Na Content Above 0.78 Resulted in Phase Change (P2→O3)

- To compensate the Na loss during annealing, x=1 synthesis attempt was performed for $Na_xNi_{0.5}Mn_{0.5}O_2$.







- 900 °C 2nd-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).

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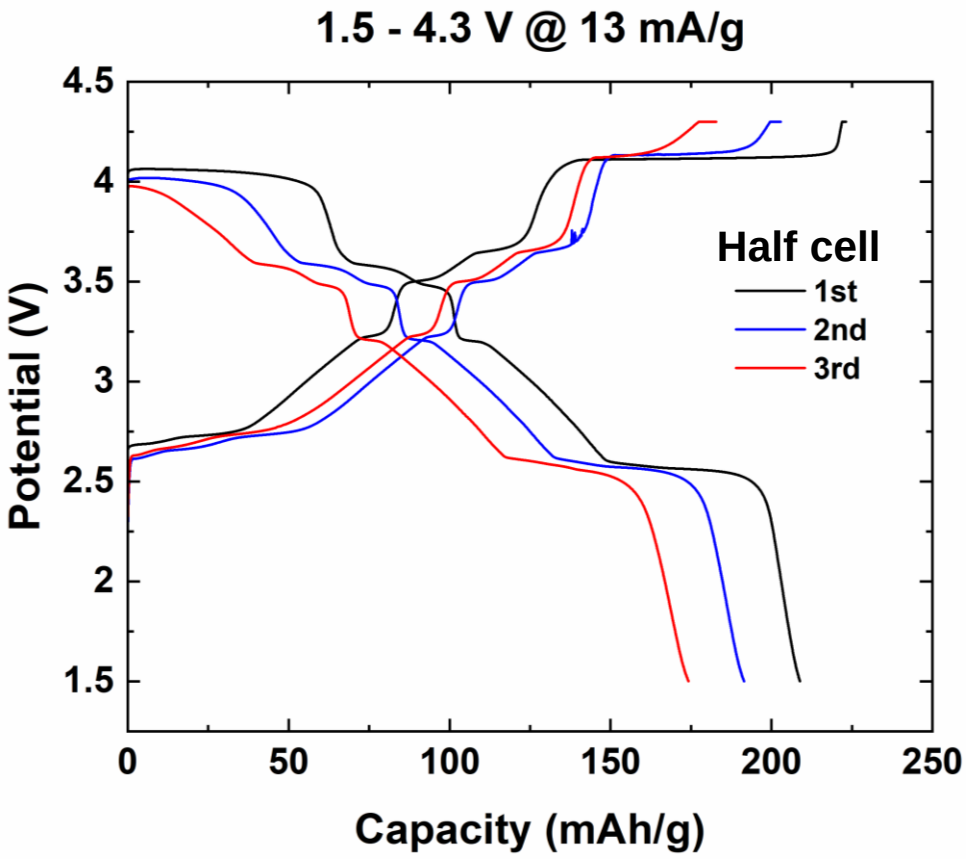
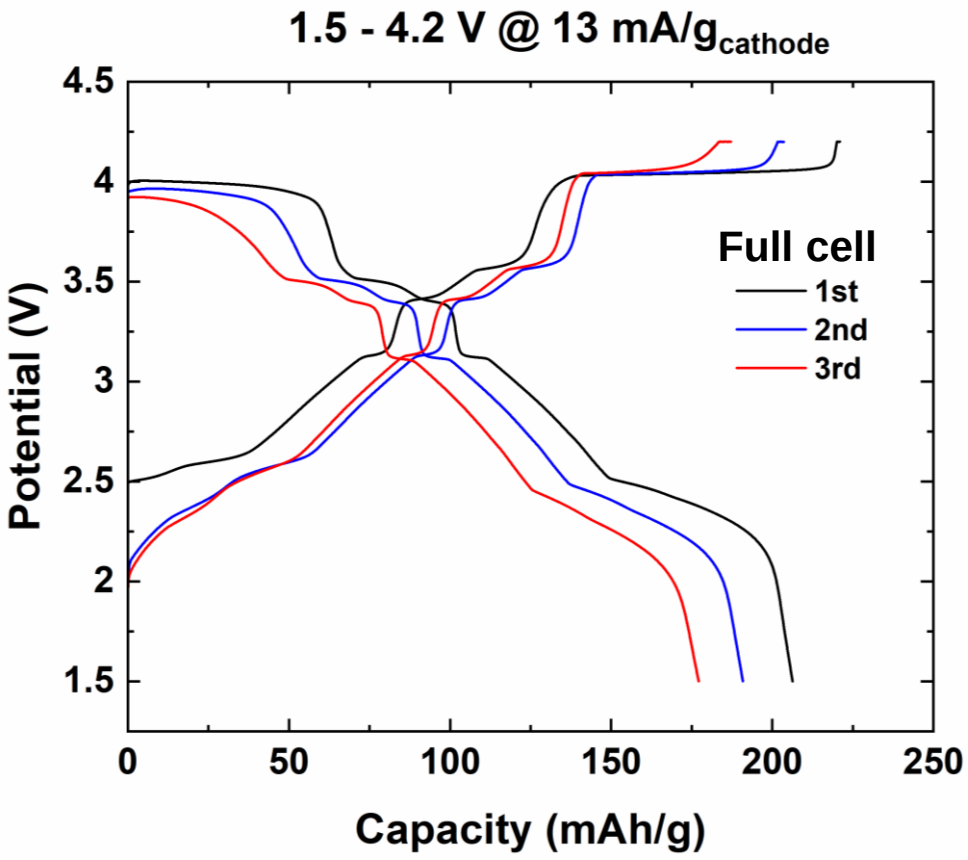
O3-$Na_xNi_{0.5}Mn_{0.5}O_2$ (x<1) Delivered 210 mAh/g Capacity

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





- Initial capacity of 230 mAh/g can be achieved for O3-$Na_xNi_{0.5}Mn_{0.5}O_2$ half cell (higher than P2-$Na_xNi_{0.5}Mn_{0.5}O_2$), average voltage is ~3.5 V.

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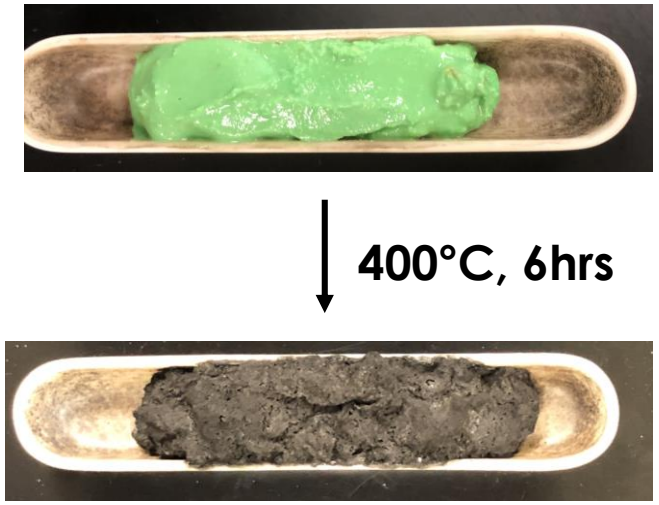
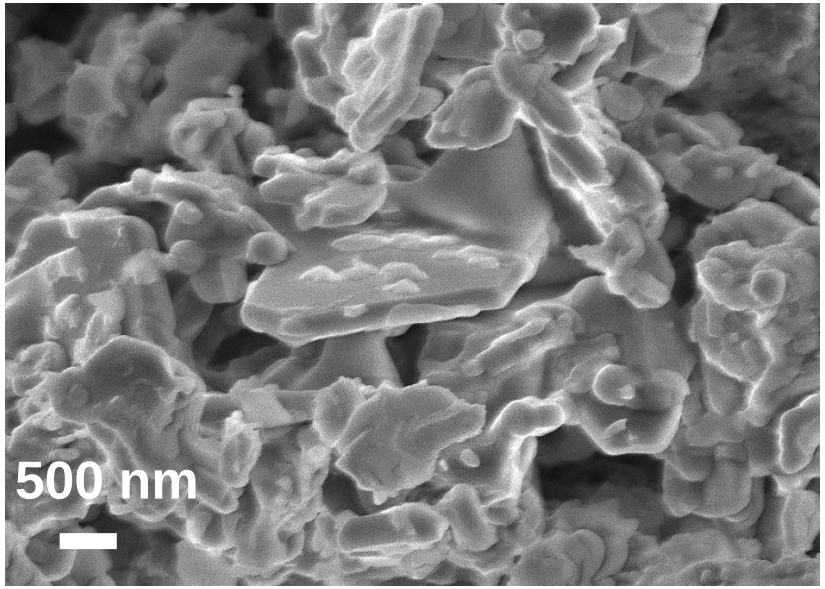
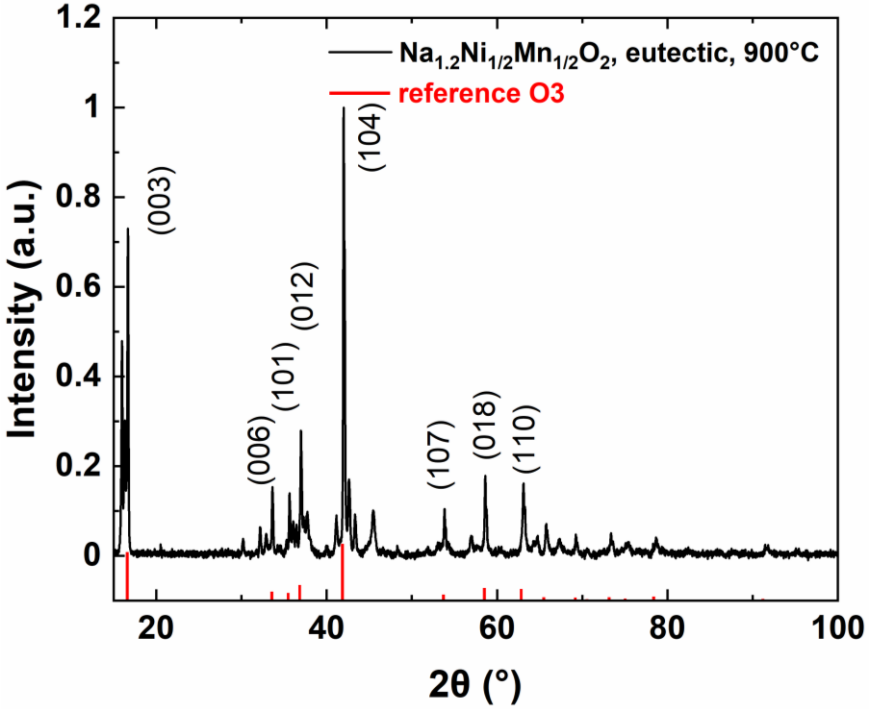
Na Content Was Further Increased from 0.78 to 1 in O3-$Na_xNi_{0.5}Mn_{0.5}O_2$

- To further increase the Na content in the final material, x=1.2 synthesis attempt was performed for $Na_xNi_{0.5}Mn_{0.5}O_2$.







- 900 °C 2nd-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.

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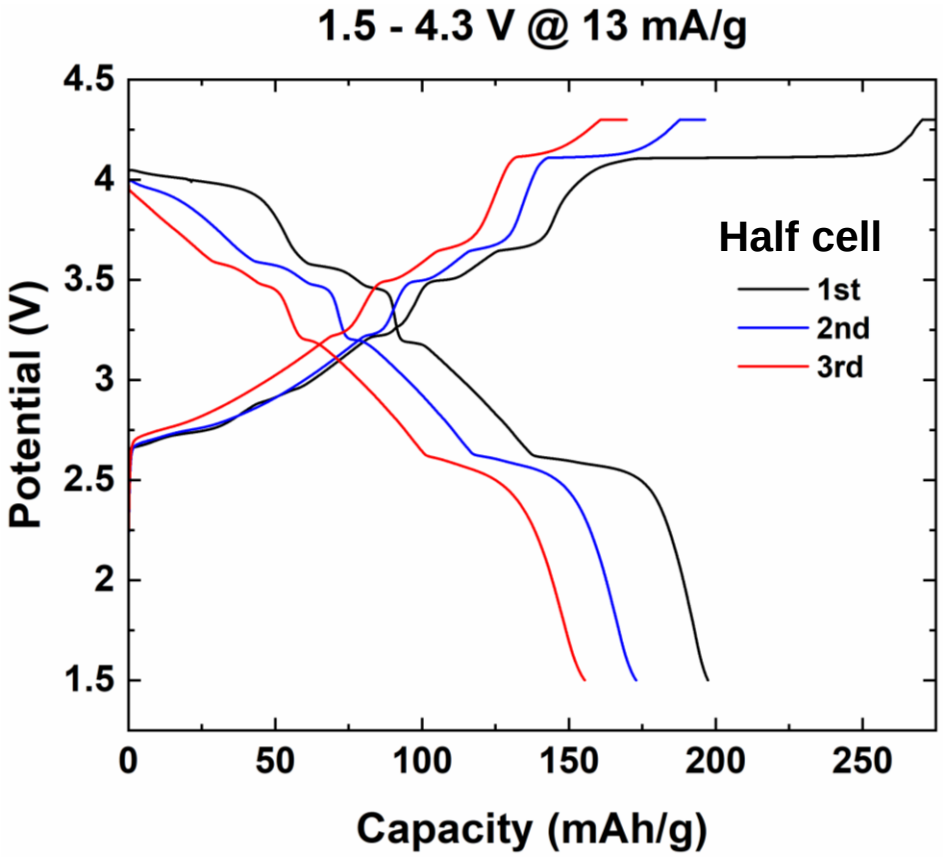
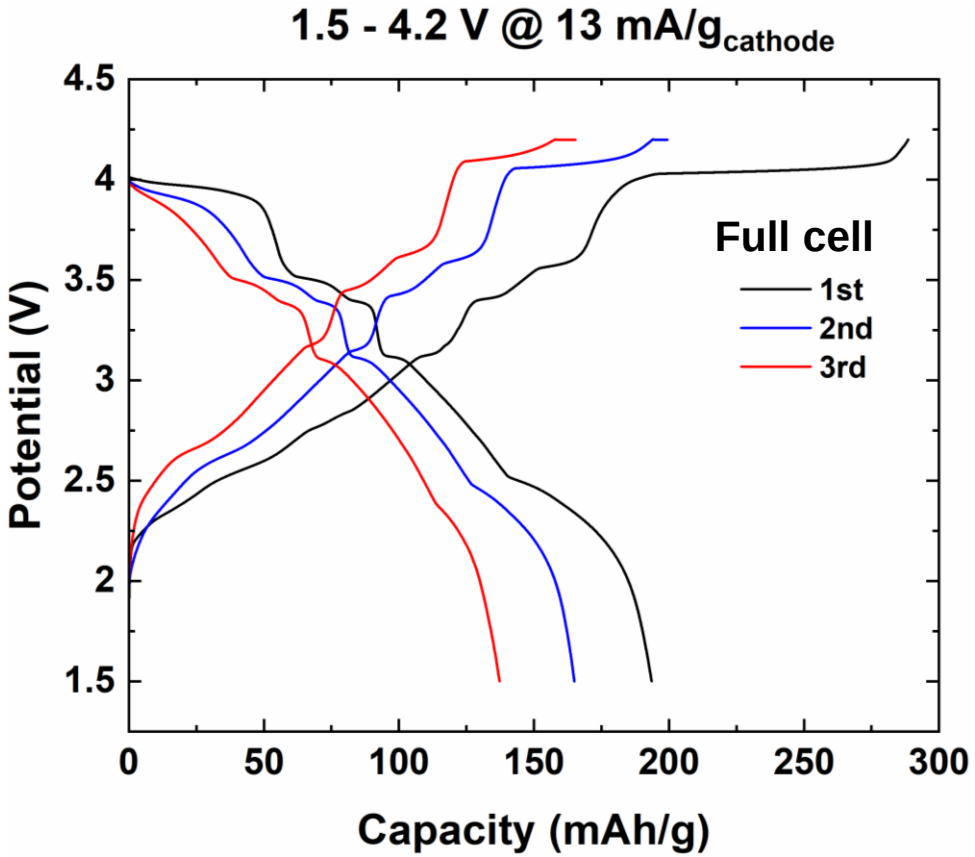
Reduced Capacity Observed in O3-$Na_xNi_{0.5}Mn_{0.5}O_2$ (x<1.2)

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





- A large 1st cycle charge capacity was observed (279 mAh/g), but only 197 mAh/g 1st cycle discharge capacity was delivered (less reversible compared to $Na_xNi_{0.5}Mn_{0.5}O_2$ with x=1).

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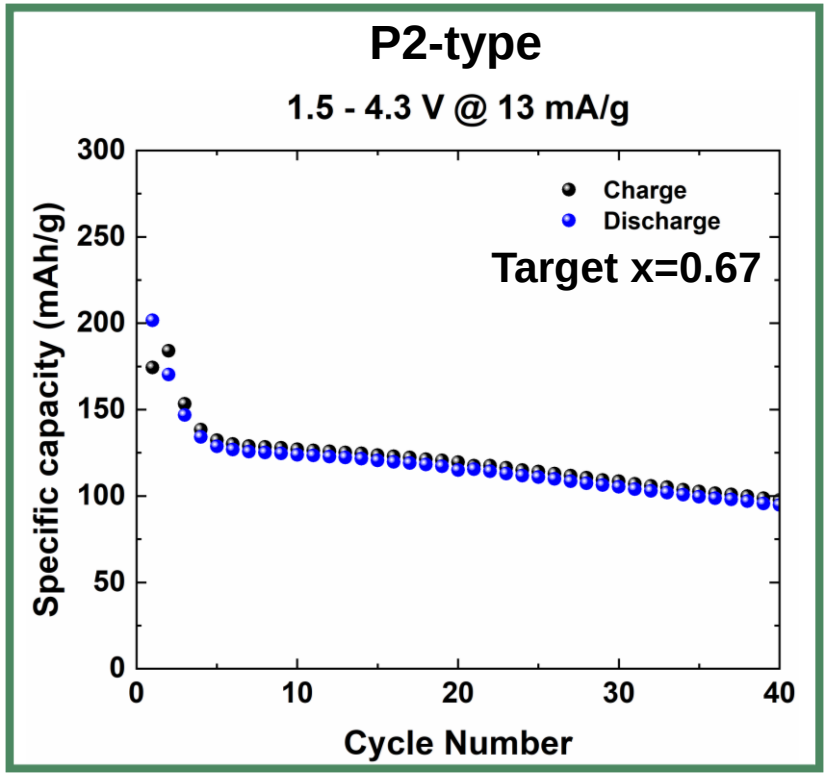
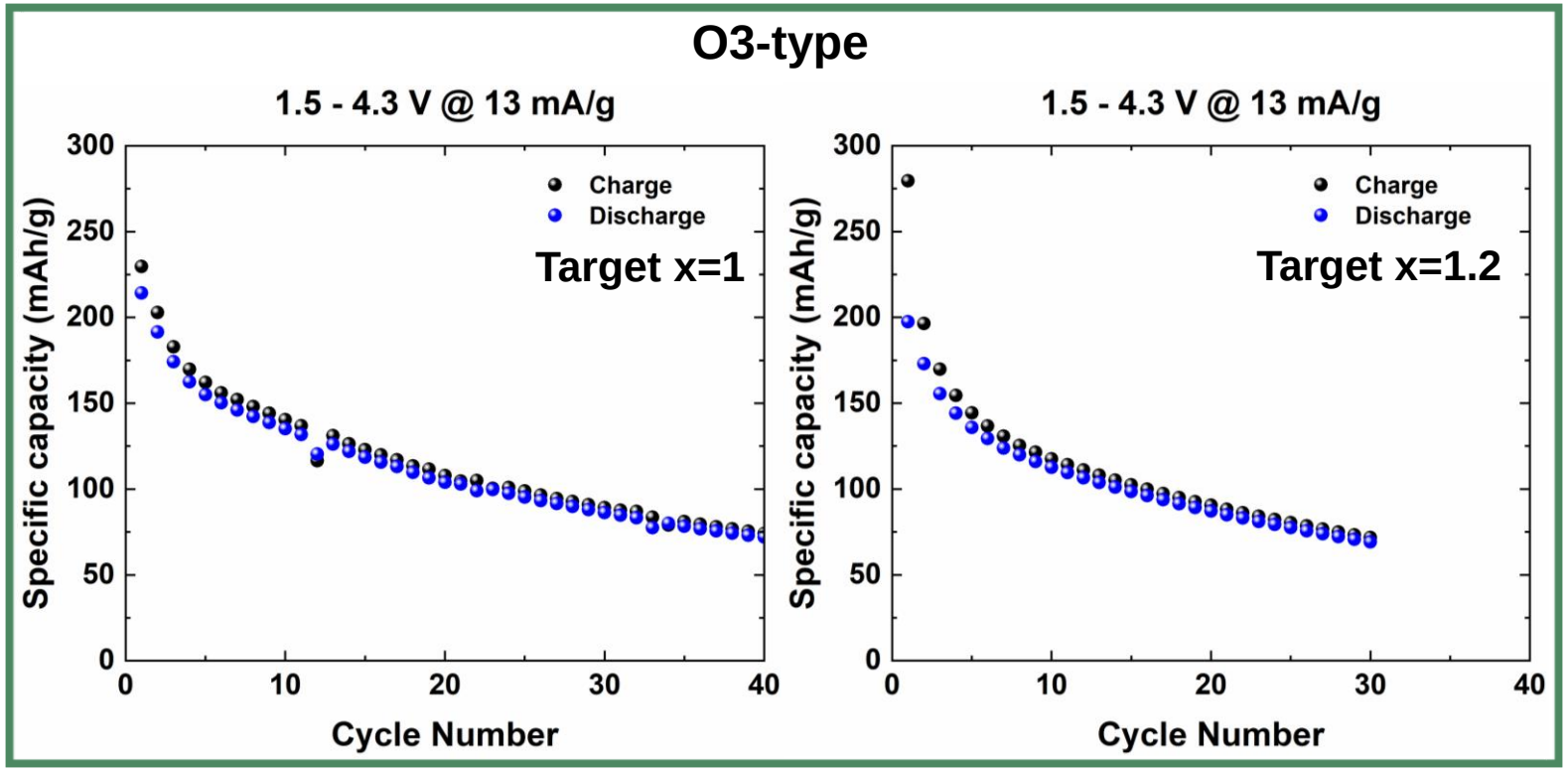
Half Cell Cycling Performances of P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$





- Despite higher initial capacity achieved in both O3-type cathodes, the cycling stability was lower than P2-type $Na_xNi_{0.5}Mn_{0.5}O_2$ (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.

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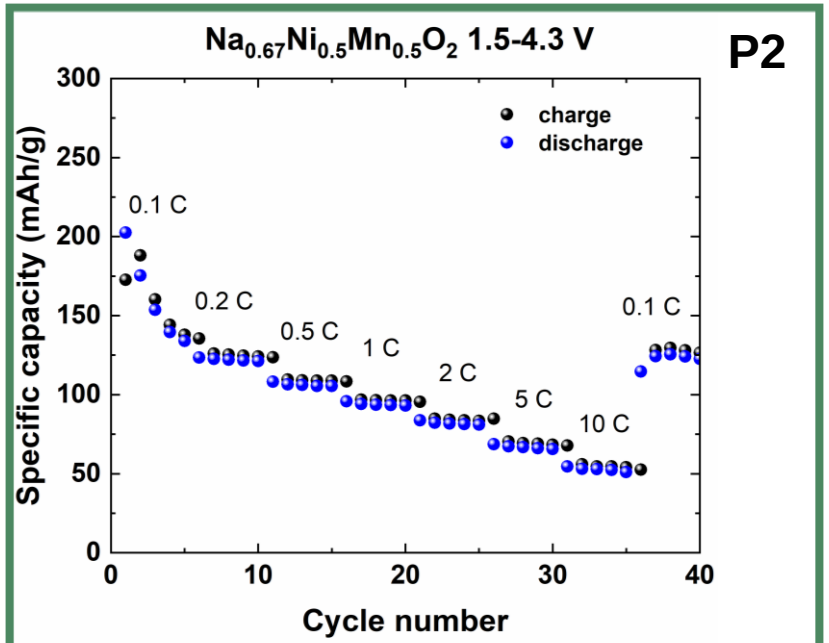
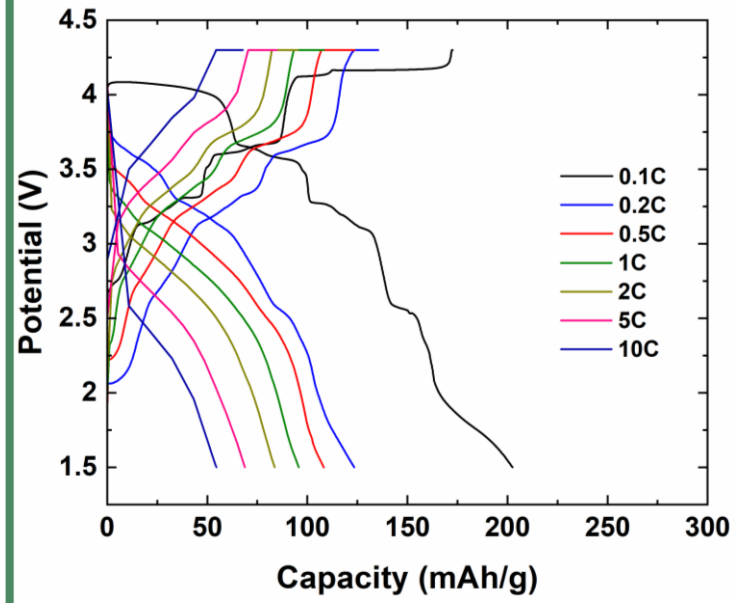
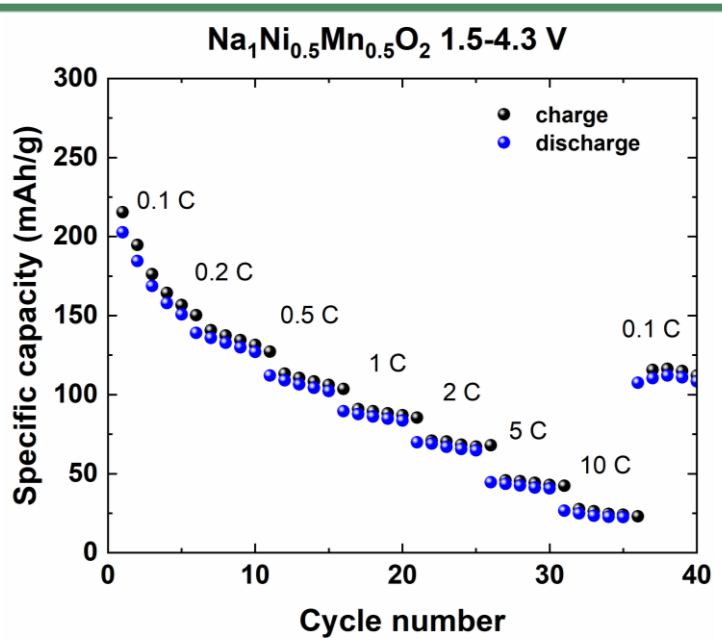
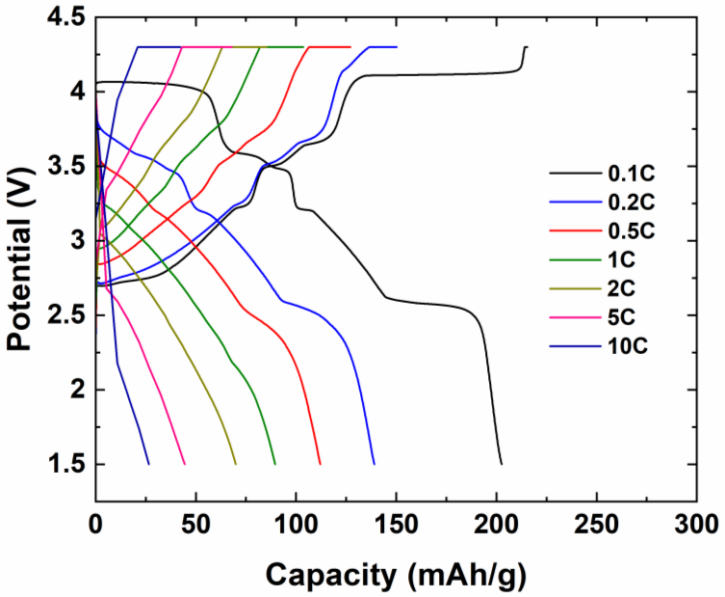
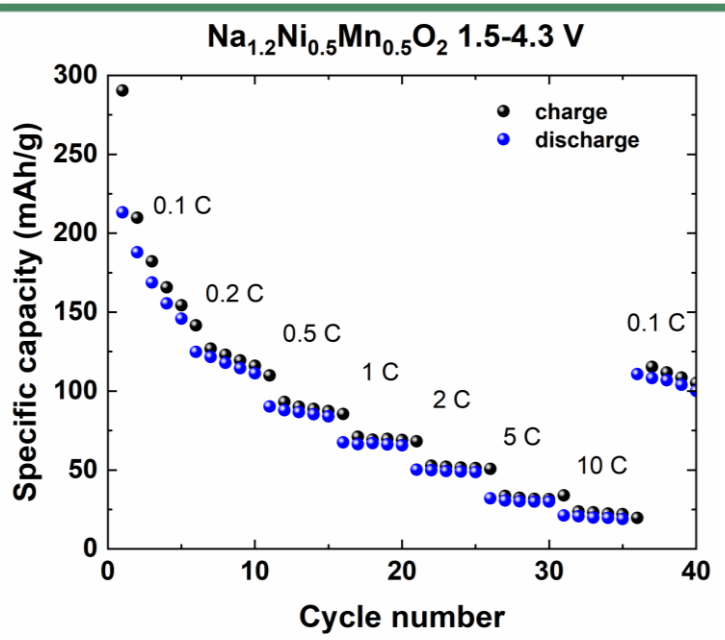
P2-Structure Exhibited Superior Rate Performance

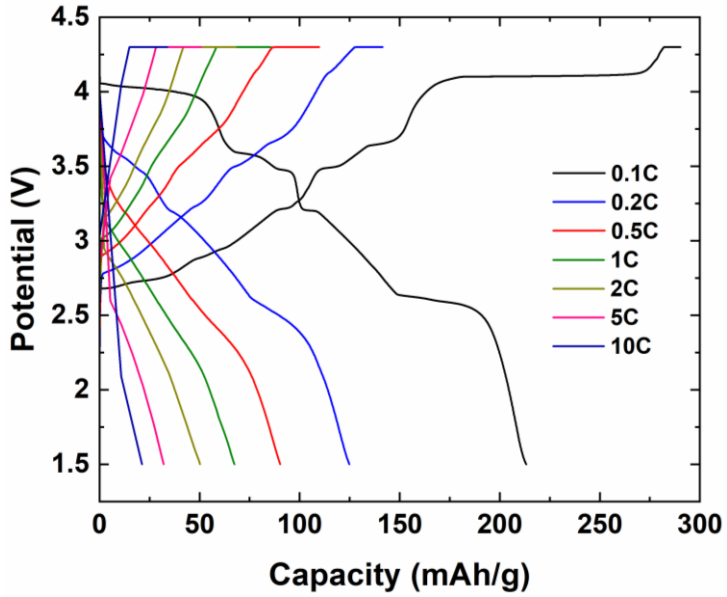












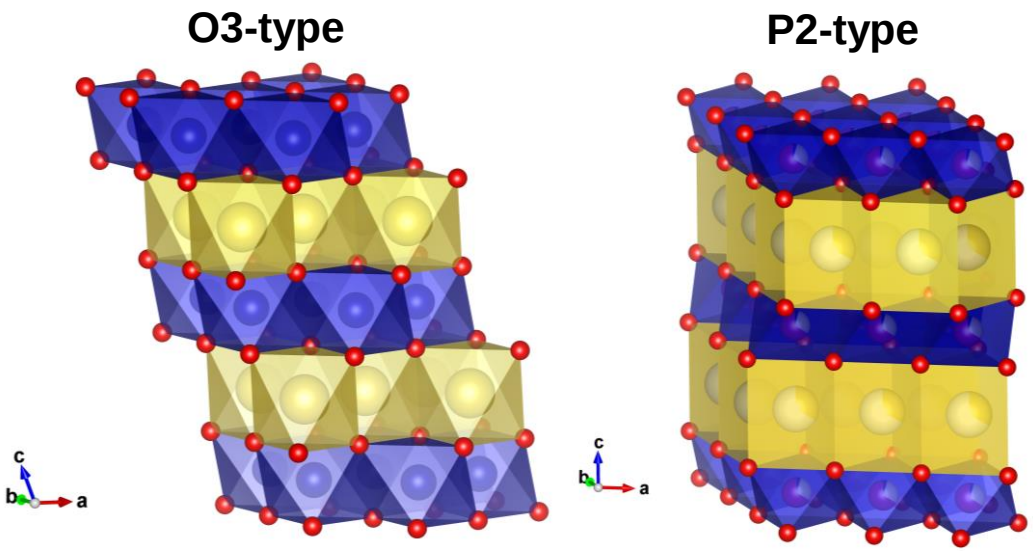
Progression of SIB Cathode Development

Eutectic Mixing
(Smaller Particles, Improved Homogeneity)

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

Comparison Focusing on Eutectic Mixing:

$Na_xFe_{0.5}Mn_{0.5}O_2$
$Na_xNi_{0.5}Mn_{0.5}O_2$
$0.67 \leq x \leq 1.1$



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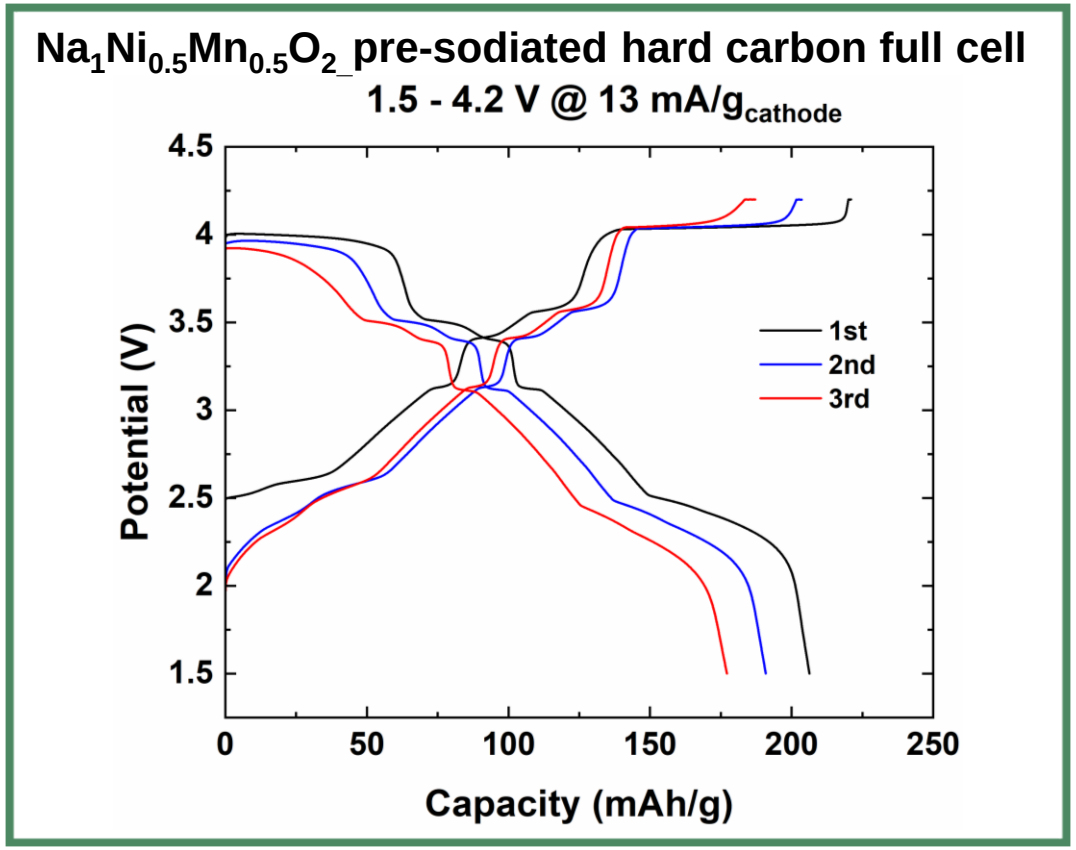
FY20 Achievements and FY21 Future Work

FY2020 Accomplishments:

- Study on novel eutectic synthesis of P2-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ 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 $Na_xNi_{0.5}Mn_{0.5}O_2$ was synthesized by the eutectic method for electrochemical studies.



FY2021 Plan:

- Investigate the initial fading mechanism for high-voltage cathode $Na_xNi_{0.5}Mn_{0.5}O_2$ (in-situ gas evolution analysis during 1st cycle, ex-situ XRD).
- Stabilize the cycling performances of P2/O3-type $Na_xNi_{0.5}Mn_{0.5}O_2$ 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.

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Acknowledgement

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