Sodium Battery Research at ORNL

Oct. 12th, 2022

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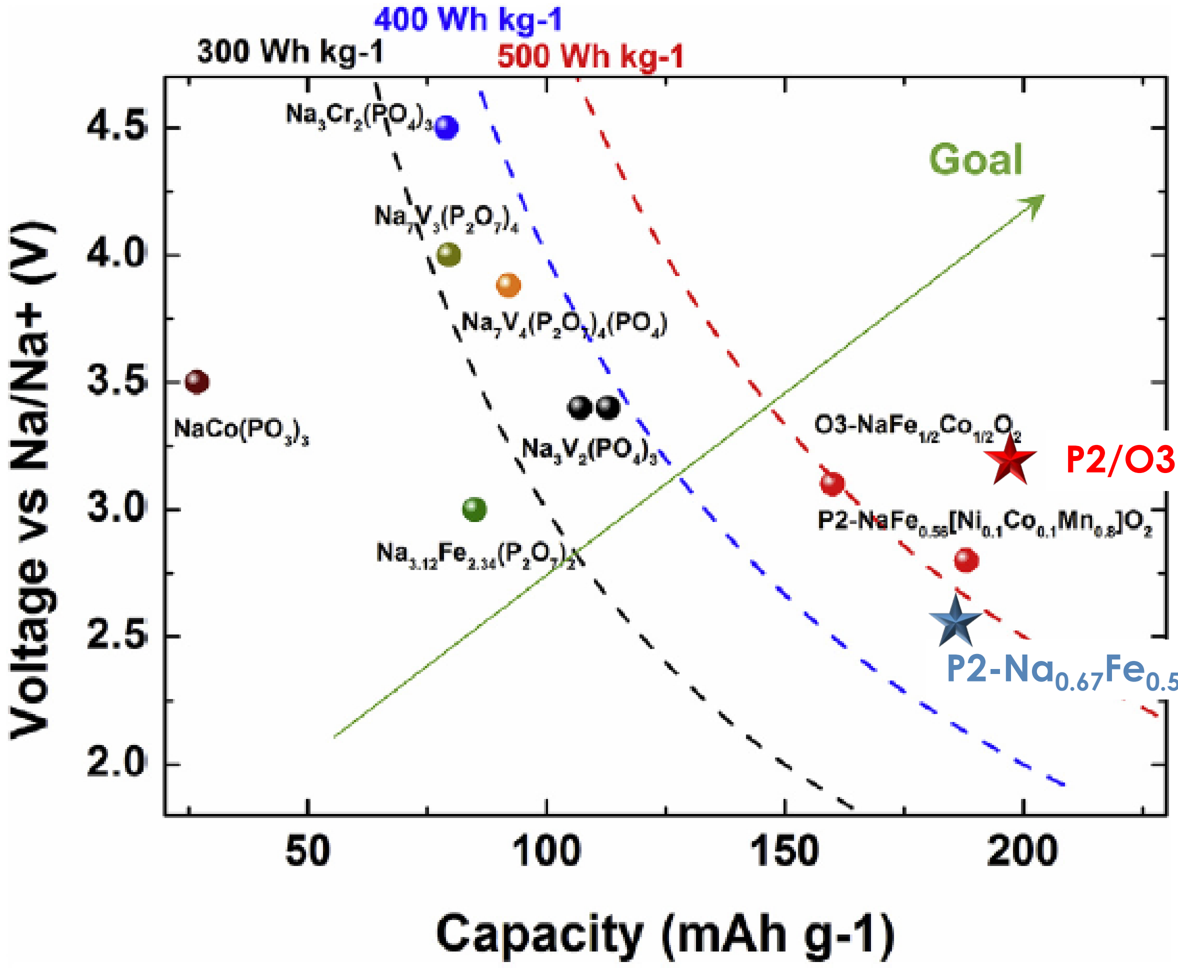
Oak Ridge National Laboratory

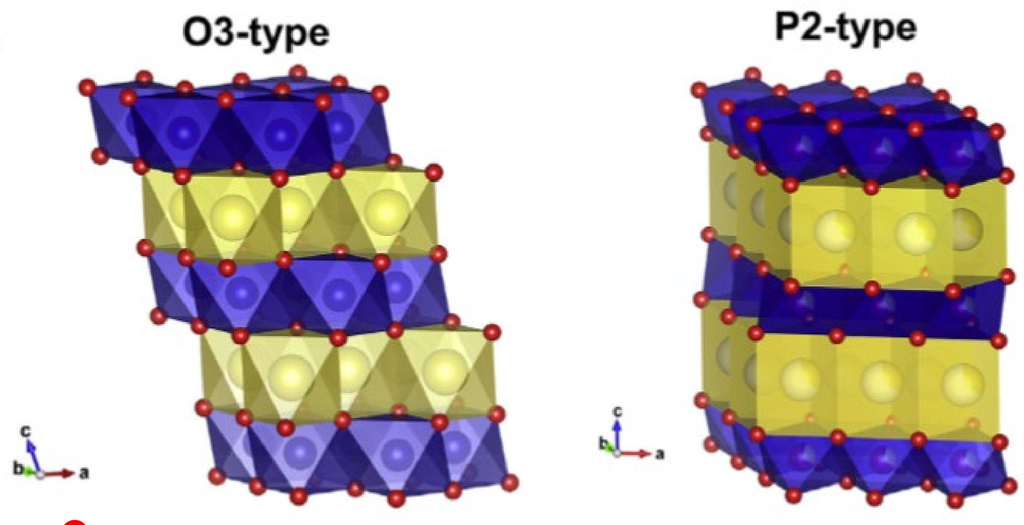
Presentation ID: 405

ORNL's Initial Focus on Low-cost Na Layered Transition-Metal Oxide Cathodes



P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$

P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$



Li et al., ***Energy Storage Materials*** 25 (2020) 520–536.

Li et al, ***Adv Energy and Sustainability Research*** (2022): 2200027.

Li et al., ***ACS Applied Materials & Interfaces*** 12 (2020), 23951-23958.

	O3	P2
C-spacing	large	small
Stability upon charge/discharge	low	high
Voltage	high	low

Objectives: Develop **low-cost** and **high capacity/voltage** sodium ion batteries.

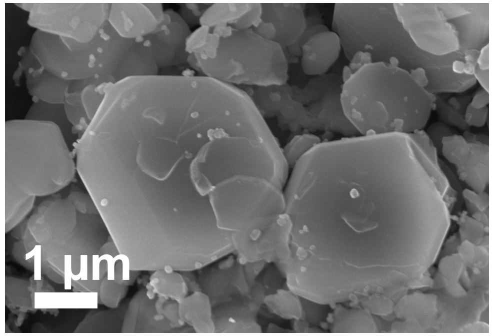
Novel Eutectic Synthesis Method Developed for Na-ion Cathodes here at ORNL.

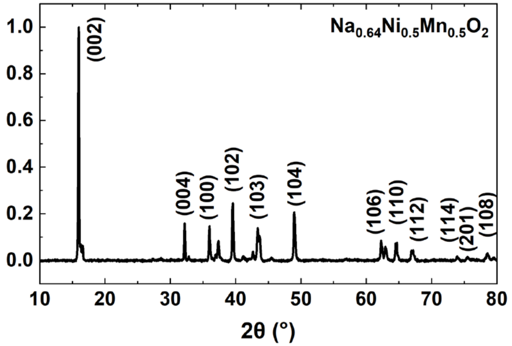
Deep Dive into the Oxygen Anion Redox in $Na_xNi_{0.5}Mn_{0.5}O_2$

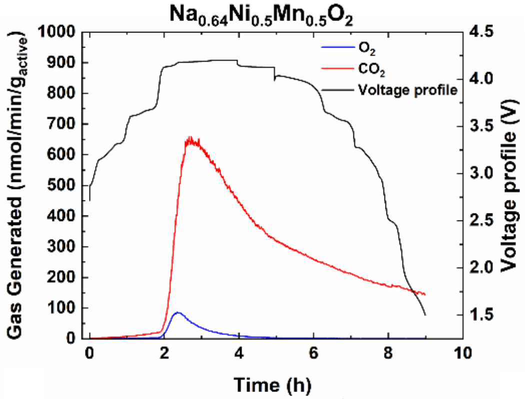
Li et al, ***Adv Energy and Sustainability Research*** (2022): 2200027.

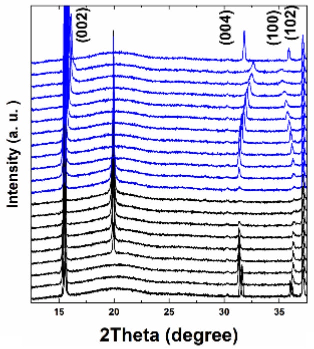
P2 - Less volume change. More reversible phase transition.

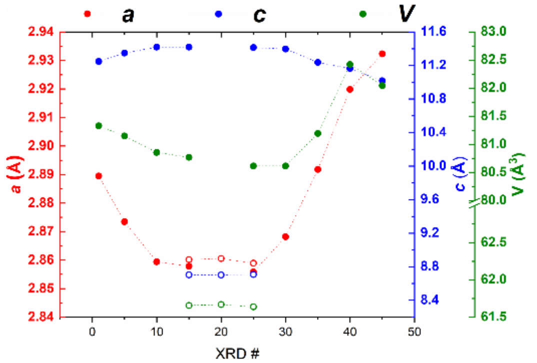
$Na_{0.64}Ni_{0.5}Mn_{0.5}O_2$



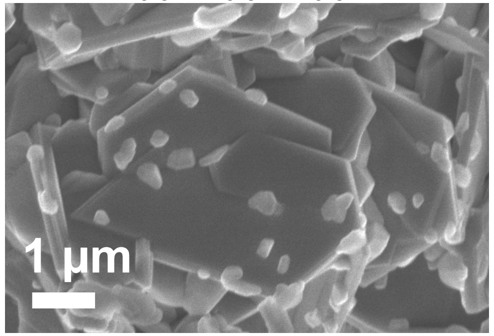


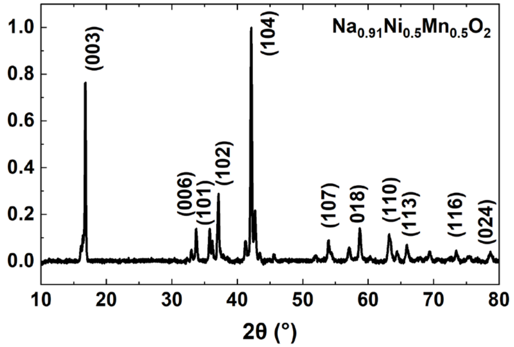


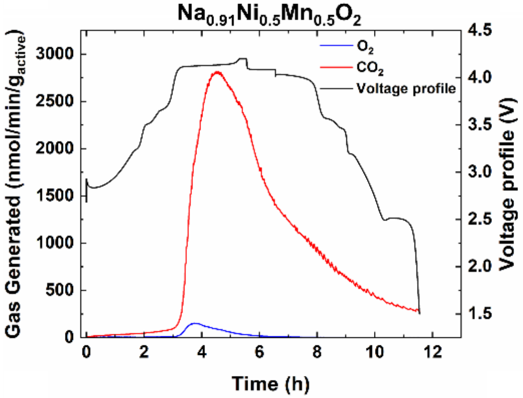


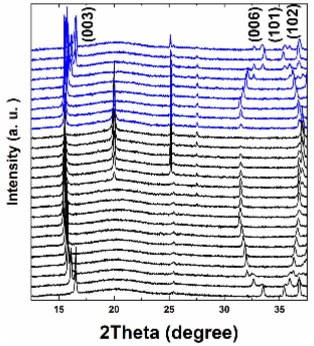


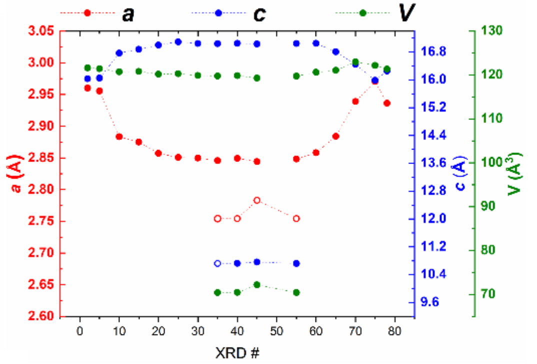
$Na_{0.91}Ni_{0.5}Mn_{0.5}O_2$



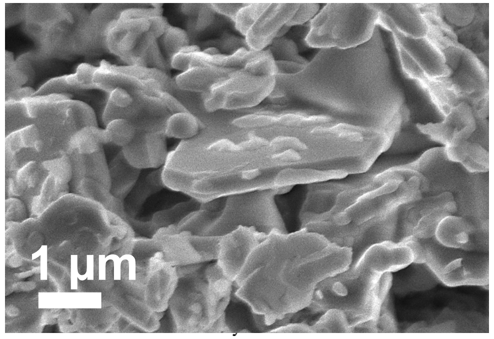


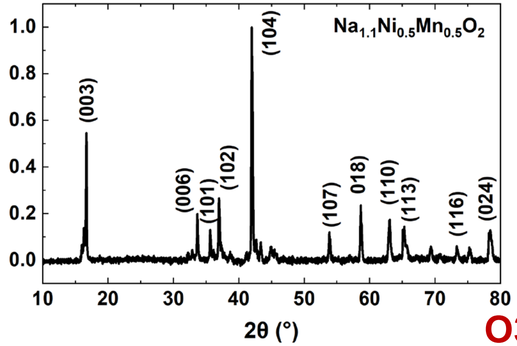


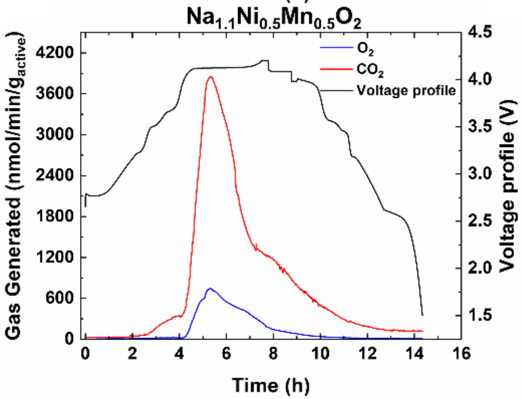


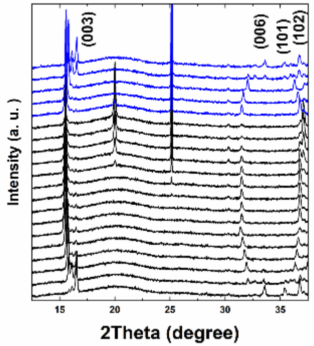


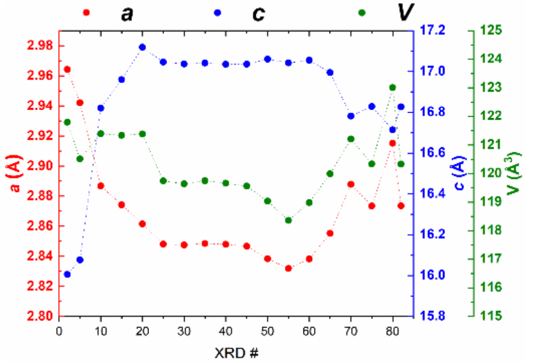
$Na_{1.1}Ni_{0.5}Mn_{0.5}O_2$





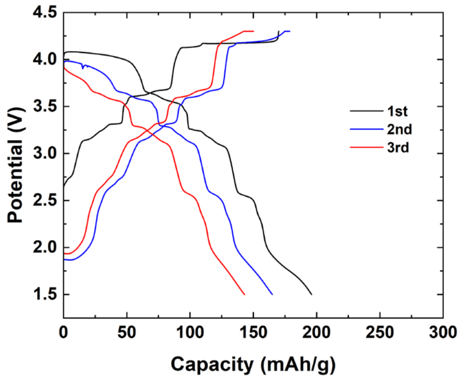




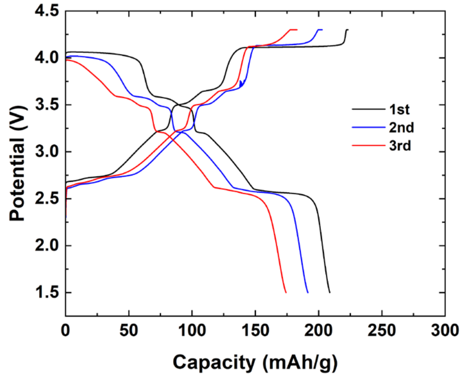


O3 - Severe volume change. Less reversible phase transition & new phase formation.

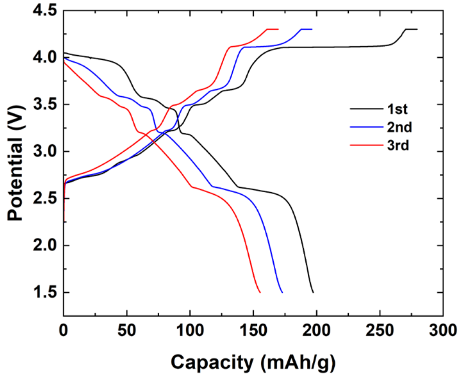
Neutron Scattering Results of P2/O3-$Na_xNi_{0.5}Mn_{0.5}O_2$ & Half Cell Data



P2-$Na_{0.64}Ni_{0.5}Mn_{0.5}O_2$

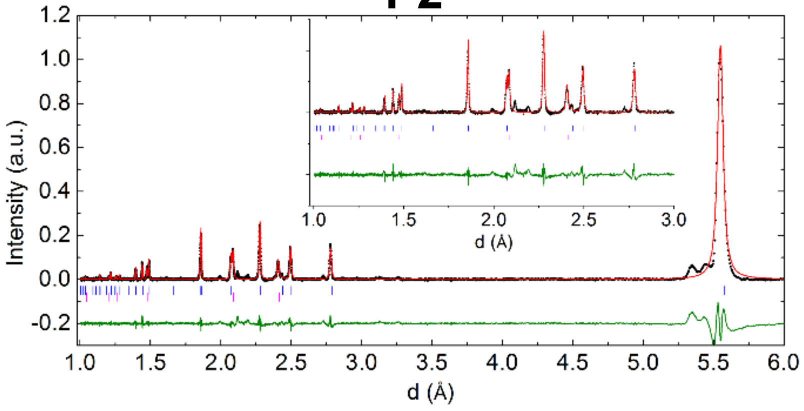


O3-$Na_{0.91}Ni_{0.5}Mn_{0.5}O_2$

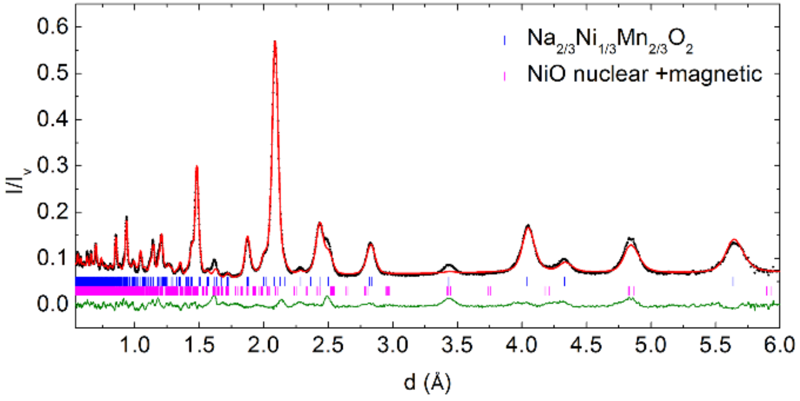


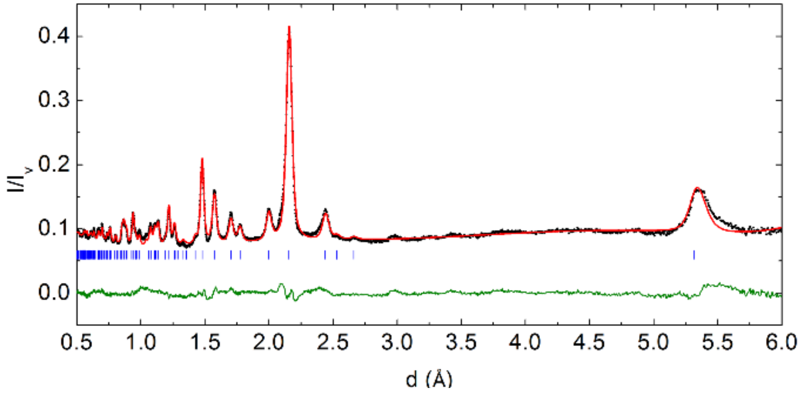
O3-$Na_{1.1}Ni_{0.5}Mn_{0.5}O_2$

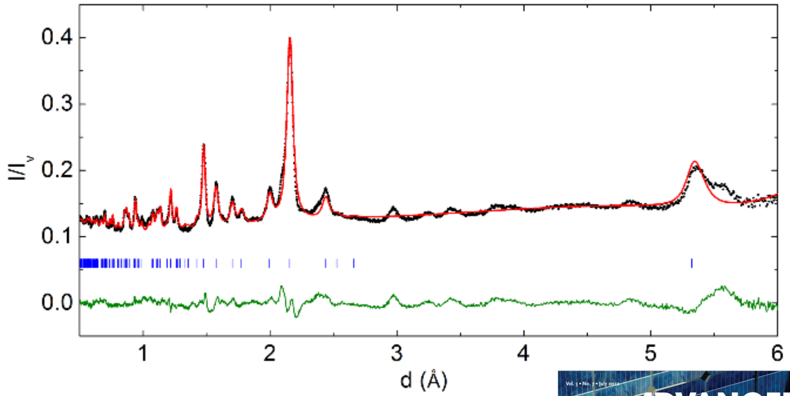
P2

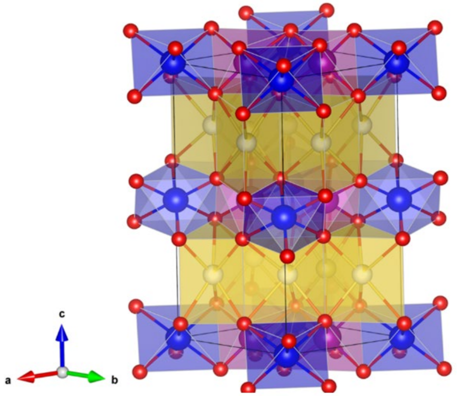


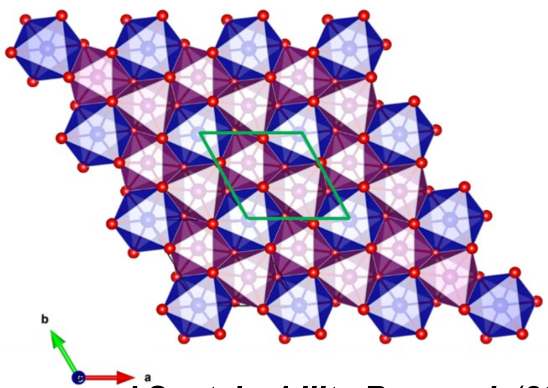
O3

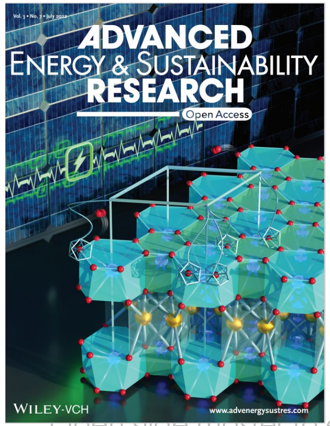






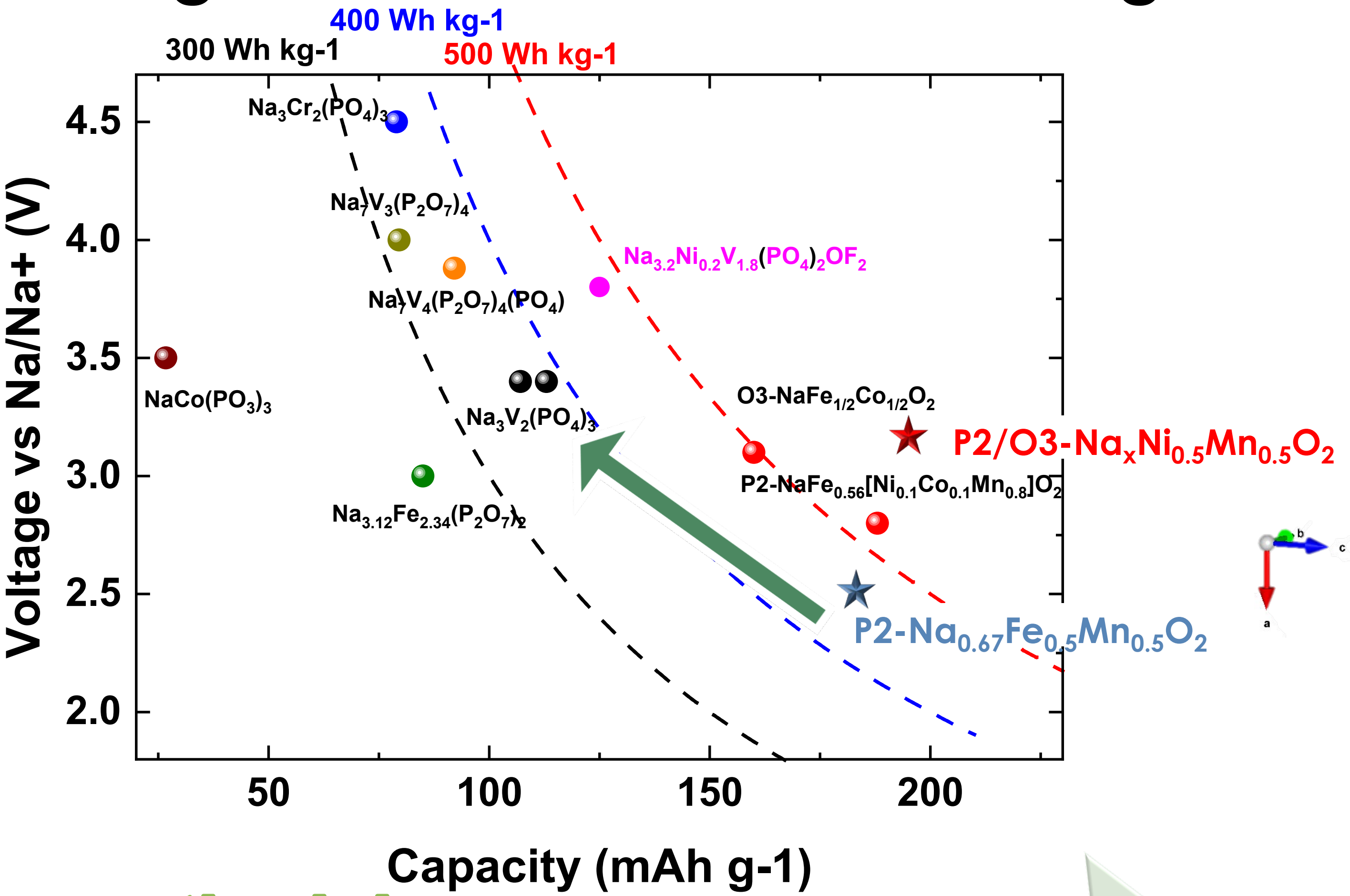


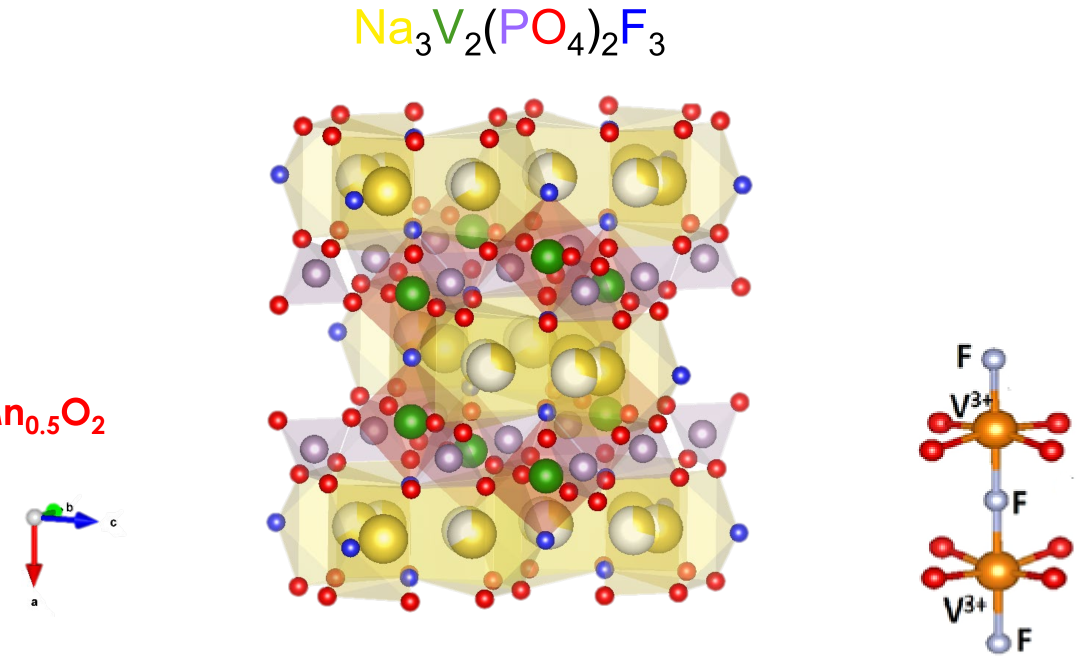


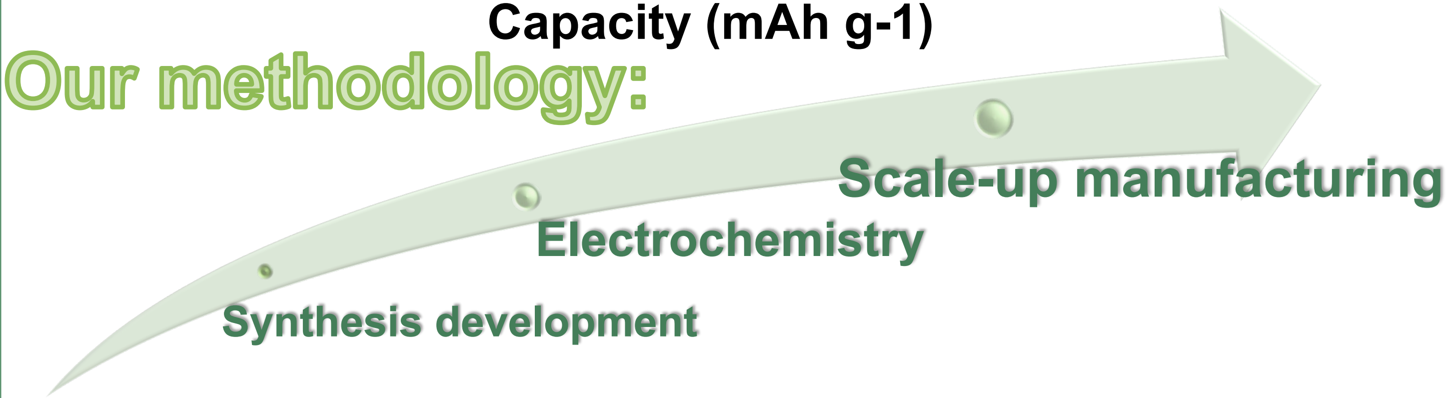


Li et al, ***Adv Energy and Sustainability Research*** (2022): 2200027.

Shifting Towards Cathodes with Higher Voltage







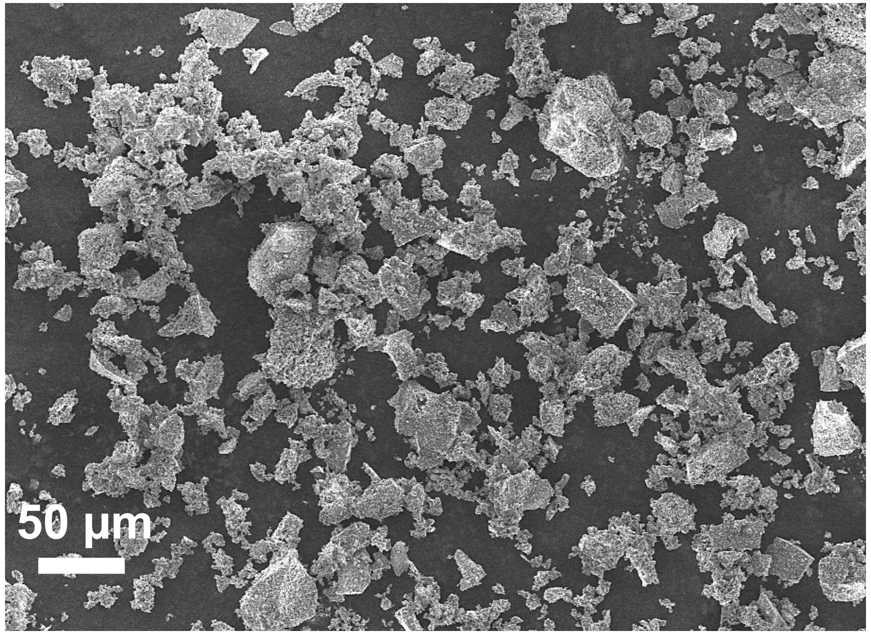
Primarily composed of bioctahedron $V_2O_8F_3$, PO_4 tetrahedra:

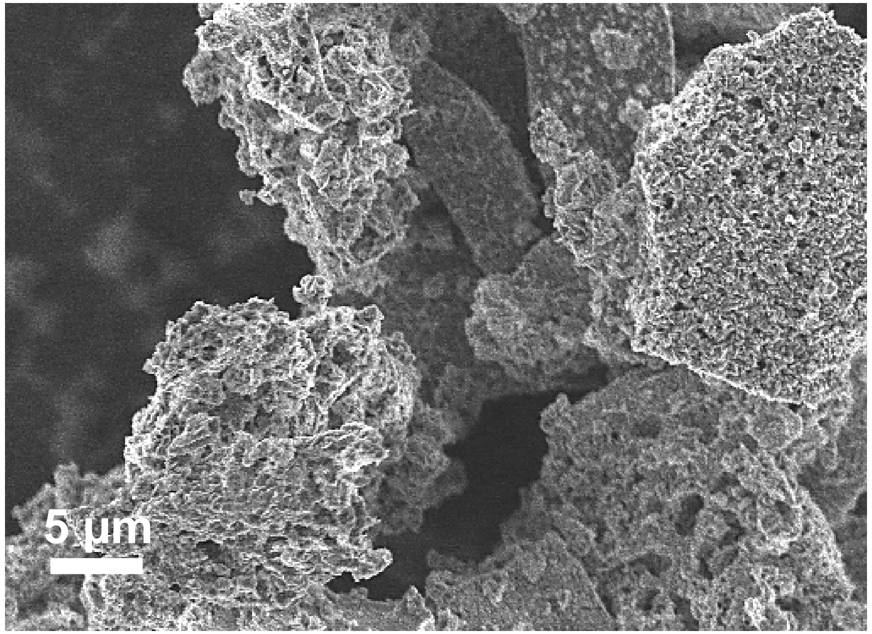
- High Voltage Cathode (**~3.7 V** operating voltage)
- Fast ion conducting channels
- Stable Cycling

Theoretical capacity: **128 mAh/g**

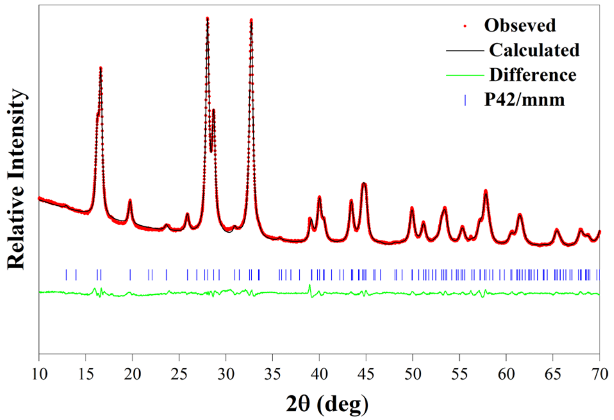
J. Phys. Chem. C 2020, 124, 43, 23511–23522.

Synthesis Development of $Na_3V_2(PO_4)_2F_3$ by Sol-Gel Method

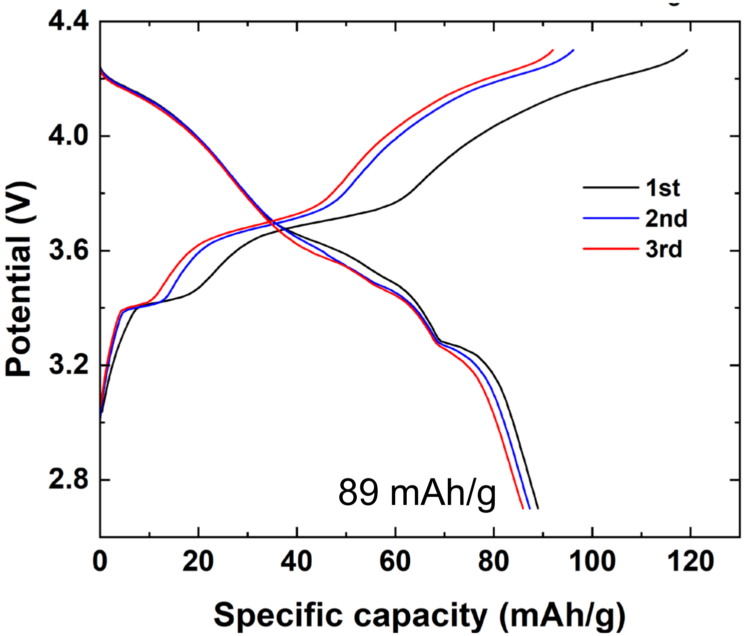


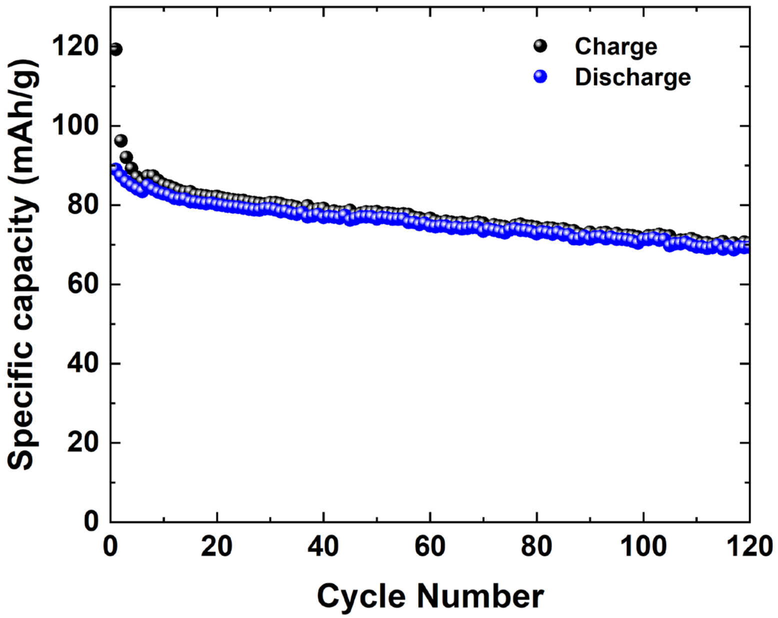


- Synthesis can be done at **10 grams** per batch with pure phase obtained.
- Morphology is not controlled, and aggregates can be seen.



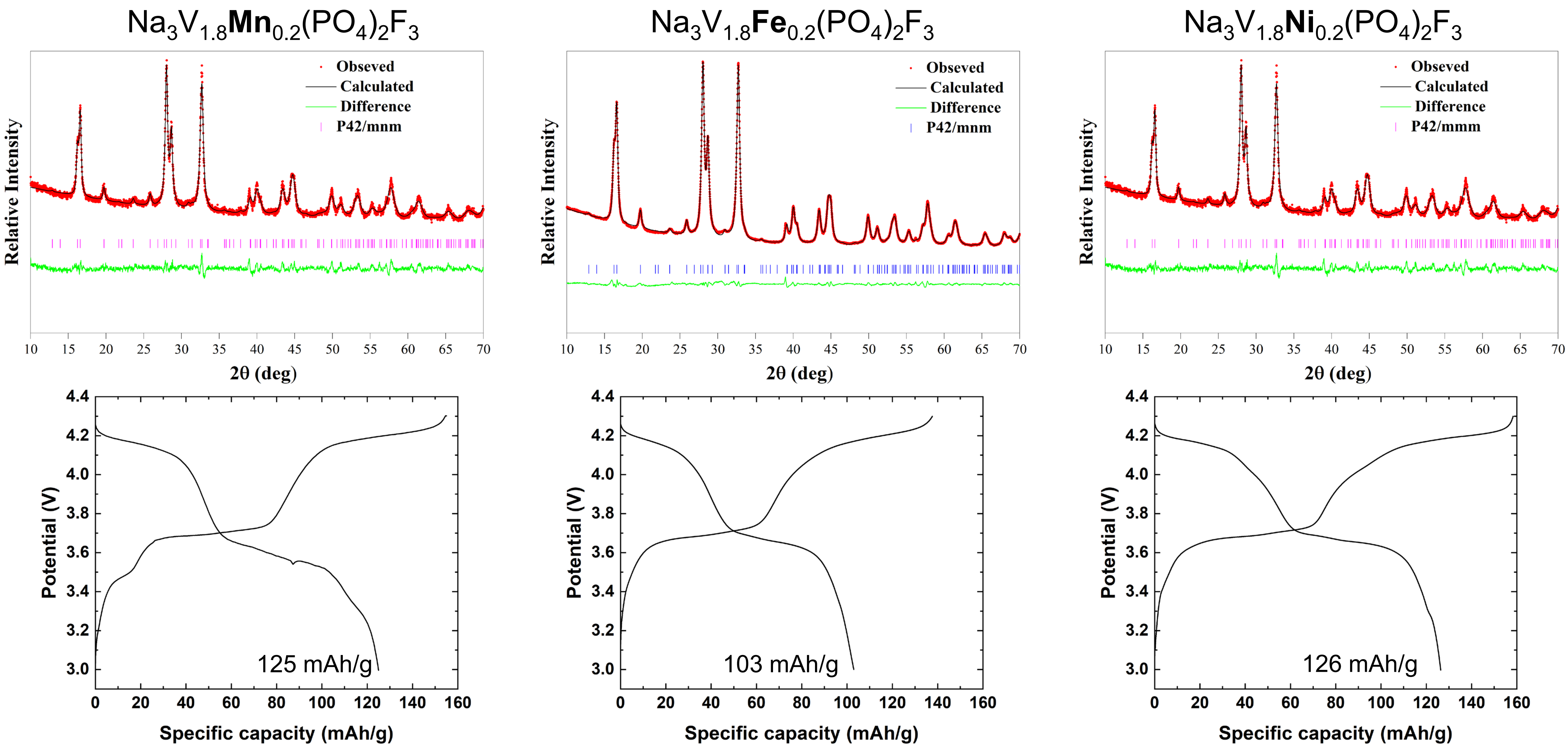
- Galvanostatic testing: 2.7-4.3 V @ 0.1 C (1 C=128 mAh/g)



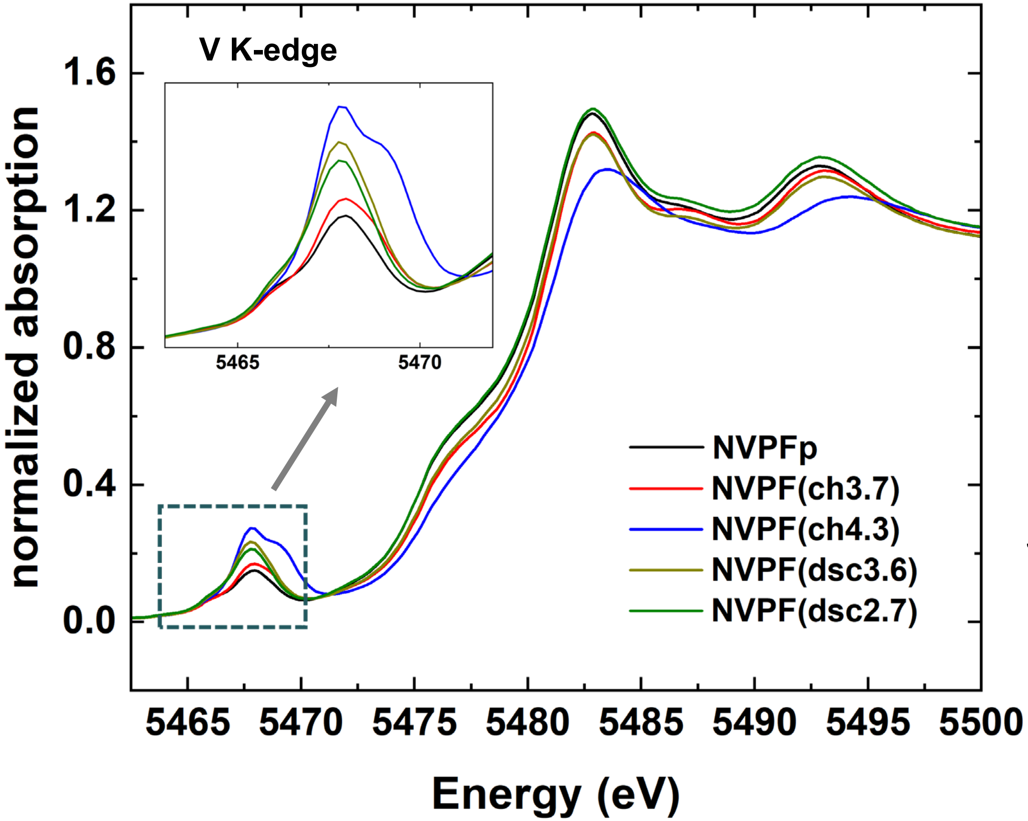


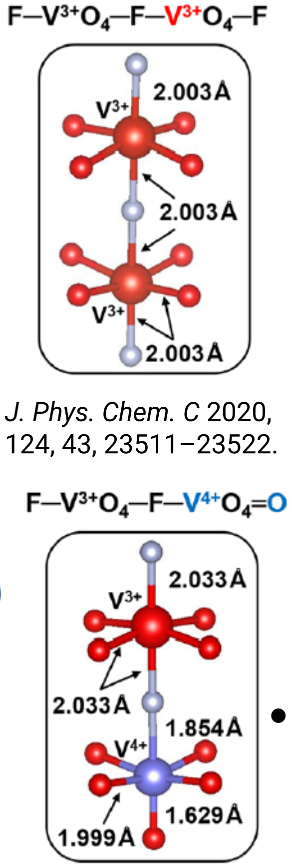
- **80%** capacity retention after 100 cycles with active material loading of **8.5 mg/cm²**.

$Na_3V_{1.8}TM_{0.2}(PO_4)_2F_3$ (TM=Mn, Fe, Ni) Synthesized by Sol-Gel Method

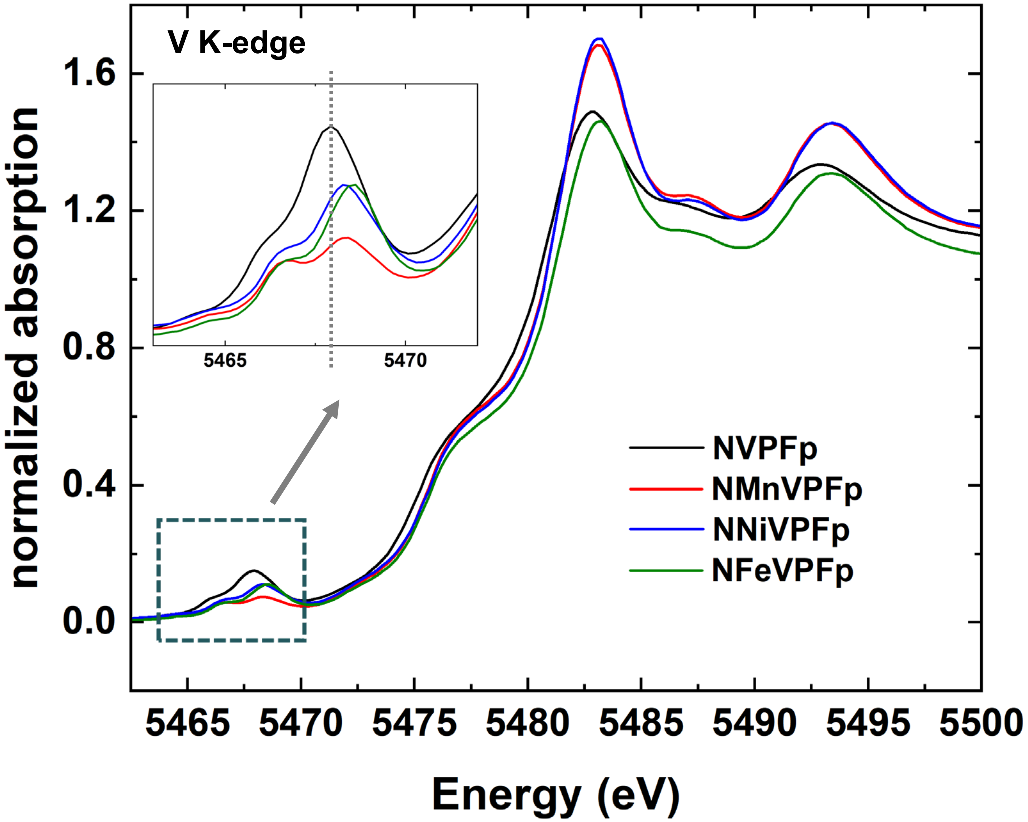


Change Compensation Mechanism of V in NVPF Characterized by Synchrotron X-Ray Absorption Near Edge Spectroscopy (XANES)





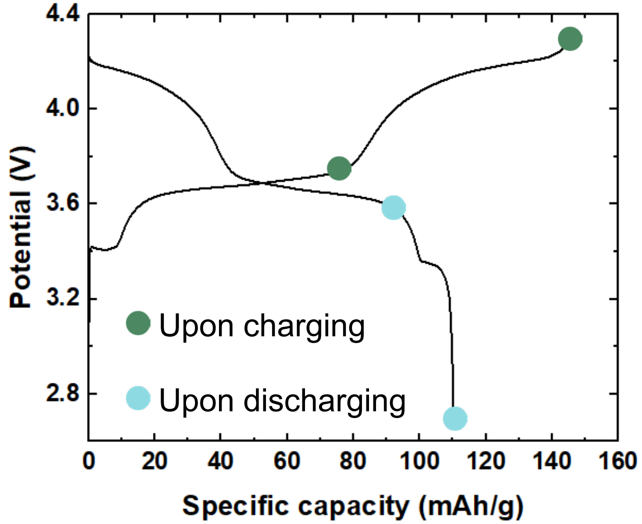
J. Phys. Chem. C 2020, 124, 43, 23511−23522.



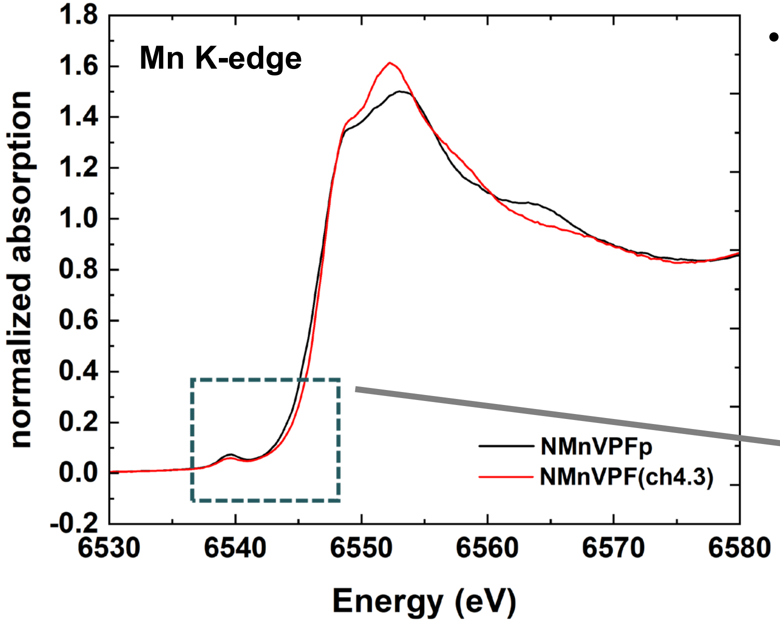
- Presence of V^{5+} at the fully charged state is observed.
- Clear indication of V^{3+} to V^{5+} transition upon charging.

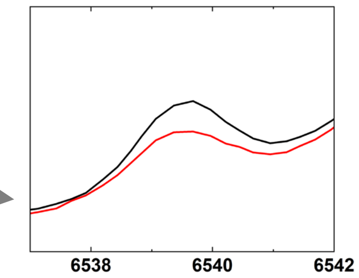
- The V in the $Na_3TM_xV_{2-x}(PO_4)_2F_3$ are primarily in the V^{3+} state. For F-O_4V^{3+}-F, 1s->3d transition in the pre-edge is forbidden.
- With TM doping, some of the F-O_4V^{3+}-F could be replaced by F-O_4V^{4+}=O, and thus increase the 1s->3d transition.

Oxidation States Evolutions Characterized by Synchrotron X-Ray Absorption Near Edge Spectroscopy (XANES)

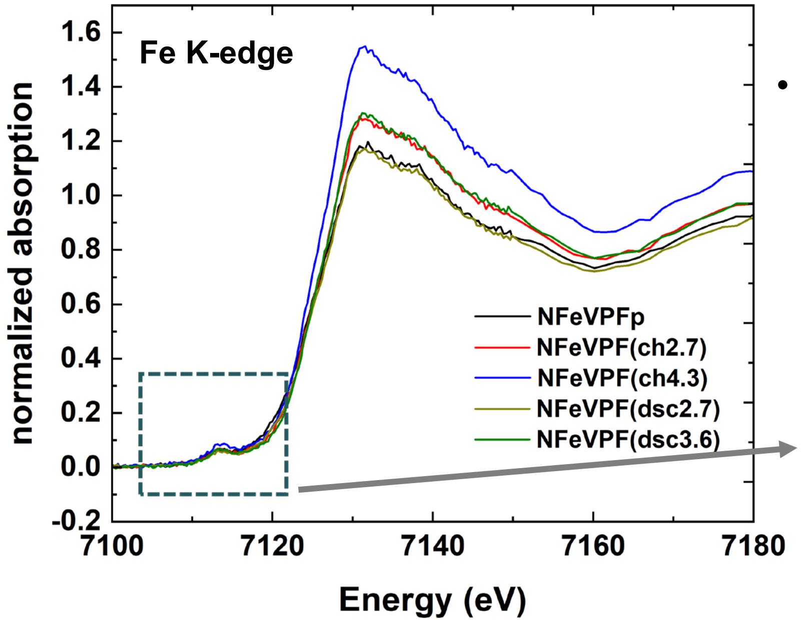


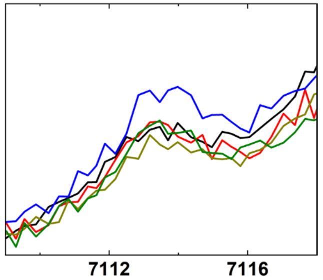
- Electrodes were taken out at different cut-off voltages for synchrotron characterization.
- Each cut-off voltage corresponds to 1 or 2 Na^+ extracted/intercalated.



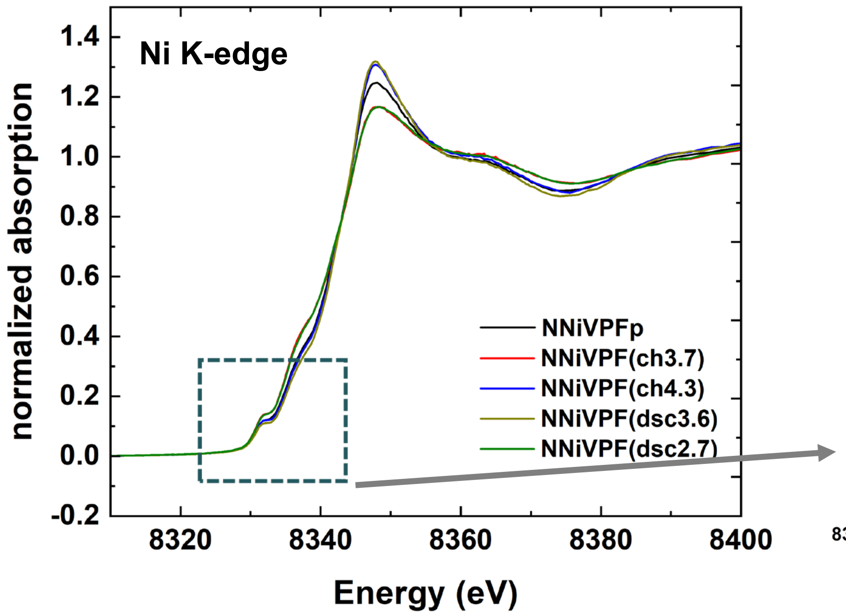


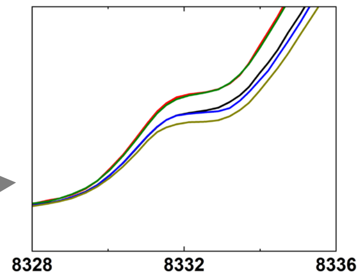
- Peak shifts at the edge indicated probable Mn^{3+} / Mn^{4+} transition in the Mn K-edge spectra.





- No obvious changes were observed in the Fe K-edge spectra.

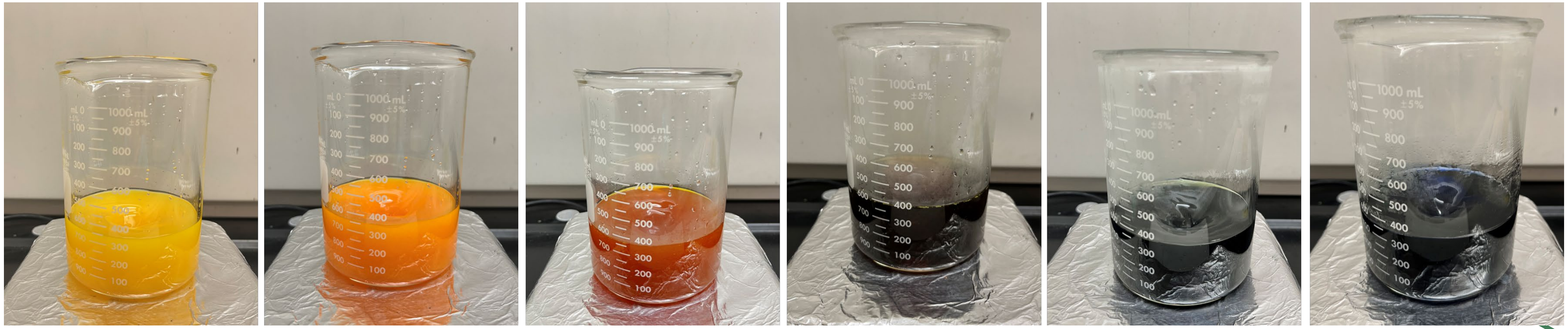




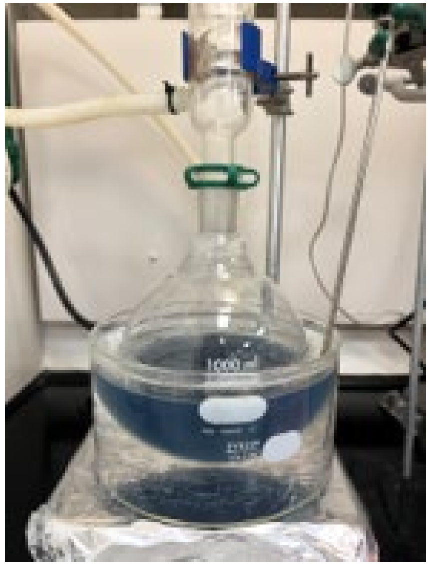
- The peak at 8347 eV does not shift upon charge/discharge, indicating no changes in the Ni oxidation state from the Ni K-edge spectra.

Improved Morphology Obtained after Synthesis with the Reflux System

- Reaction: $3NaF + 2NH_4VO_3 + 2NH_4H_2PO_4 \rightarrow Na_3V_2(PO_4)_2F_3$.

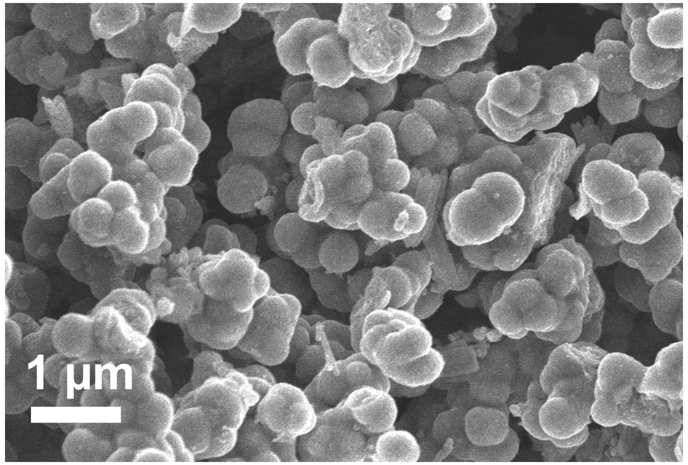


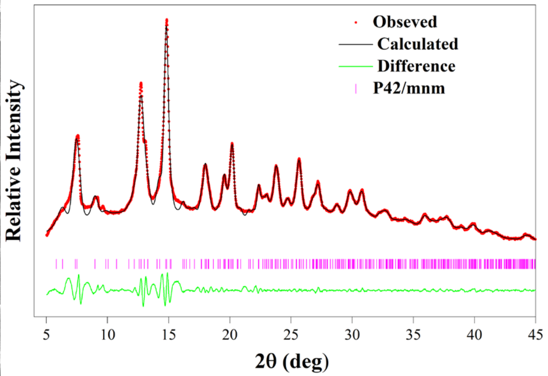
V^{5+} to V^{3+} and associated color changes



Maximum Yield:
20 g per batch.

$Na_3V_2(PO_4)_2F_3$

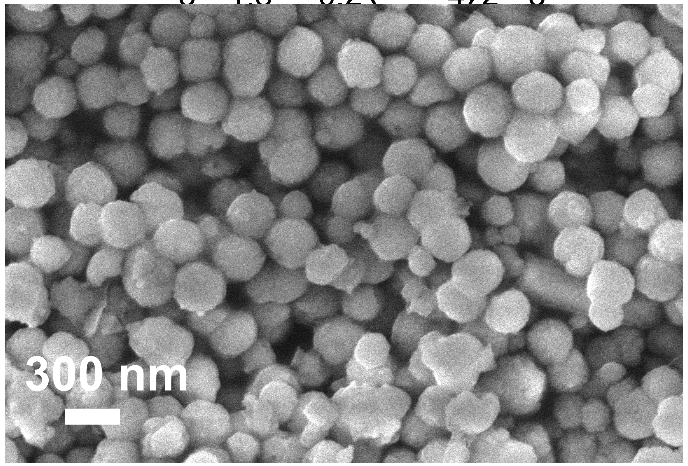


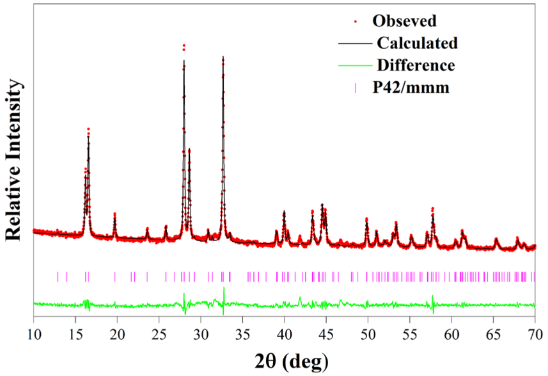


Precursor looks fine, however, some impurities observed after annealing.

Average particle size: ~400nm

$Na_3V_{1.8}Ni_{0.2}(PO_4)_2F_3$

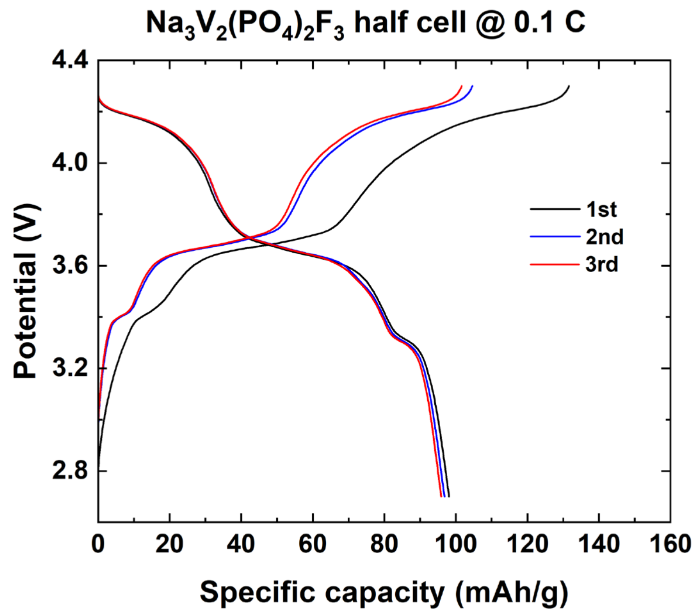


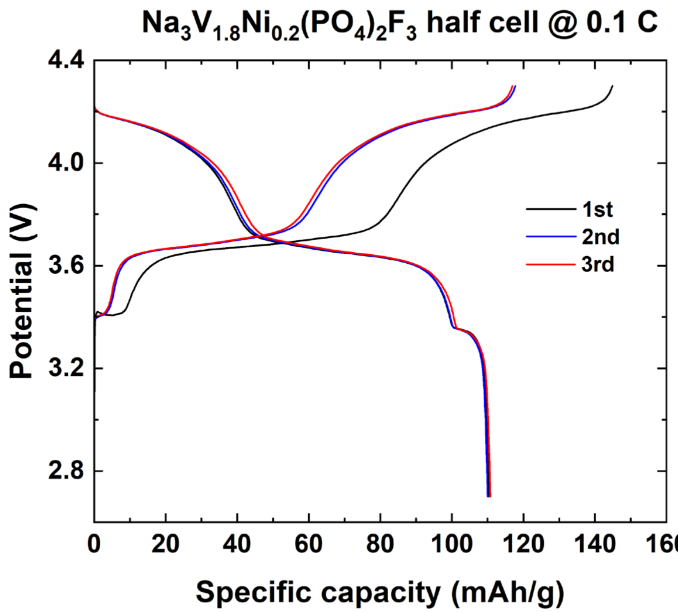


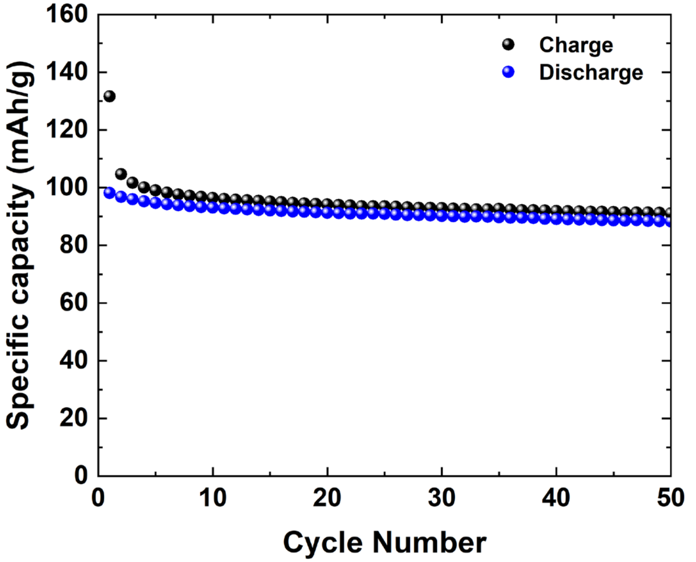
Able to obtain pure phase for $Na_3V_{1.8}Ni_{0.2}(PO_4)_2F_3$ with reflux system.

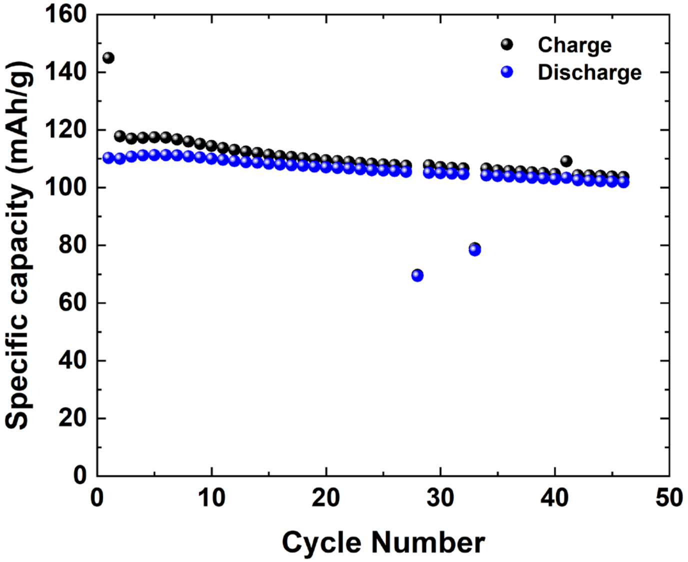
Average particle size: ~200nm

Electrochemical Performances of NVPF synthesized by Reflux system



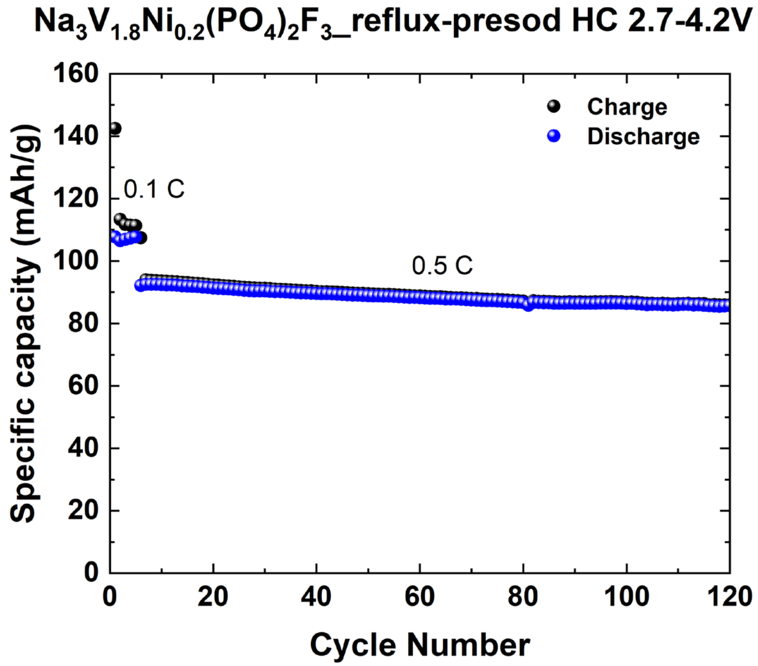






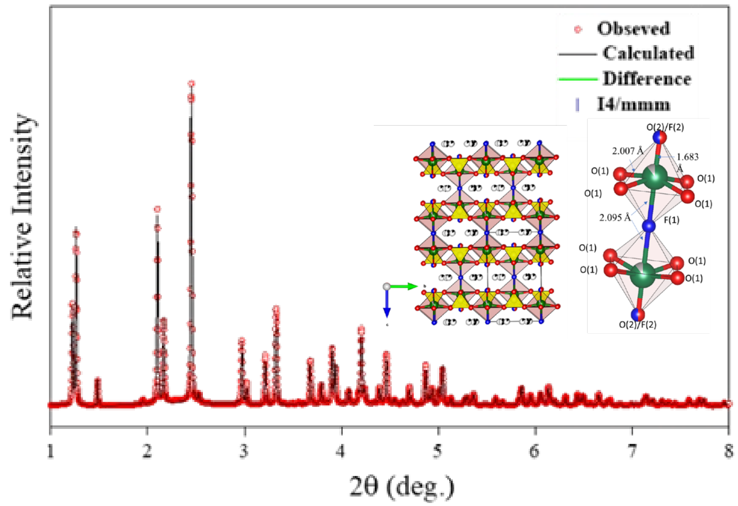
	$Na_3V_2(PO_4)F_3$	$Na_3V_{1.8}Ni_{0.2}(PO_4)F_3$
Initial reversible capacity (mAh/g)	98	110

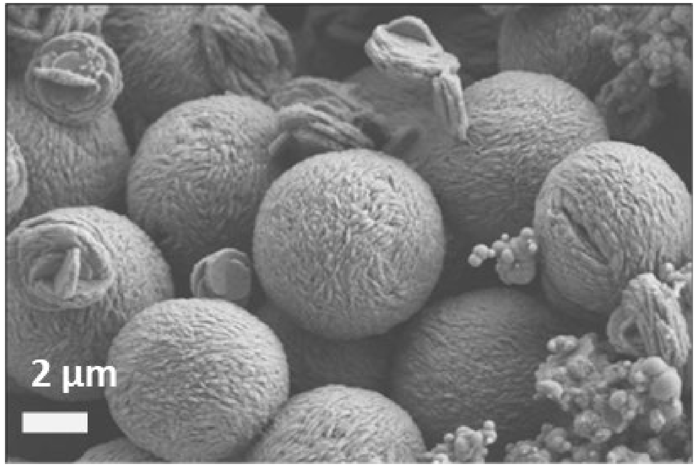
- We paired $Na_3V_{1.8}Ni_{0.2}(PO_4)F_3$ with presodiated hard carbon anode to make Na full cells.



93% capacity retention after 120 cycles @ 0.5C.

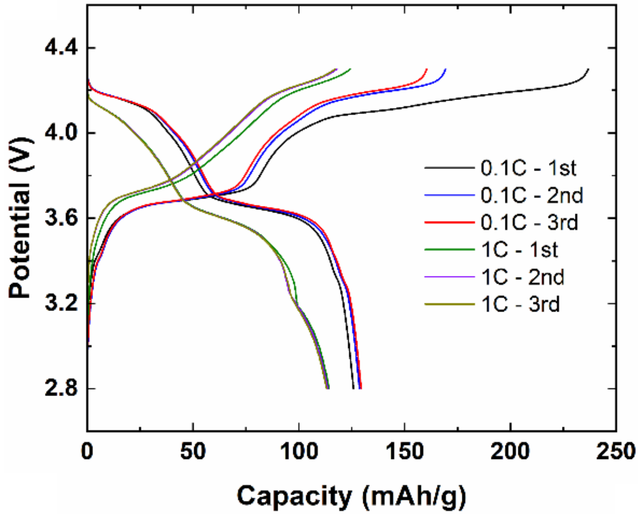
Performed Thorough Electrochemical Analysis on $Na_{3.2}Ni_{0.2}V_{1.8}(PO_4)_2F_2O$ Synthesized by Hydrothermal Reaction

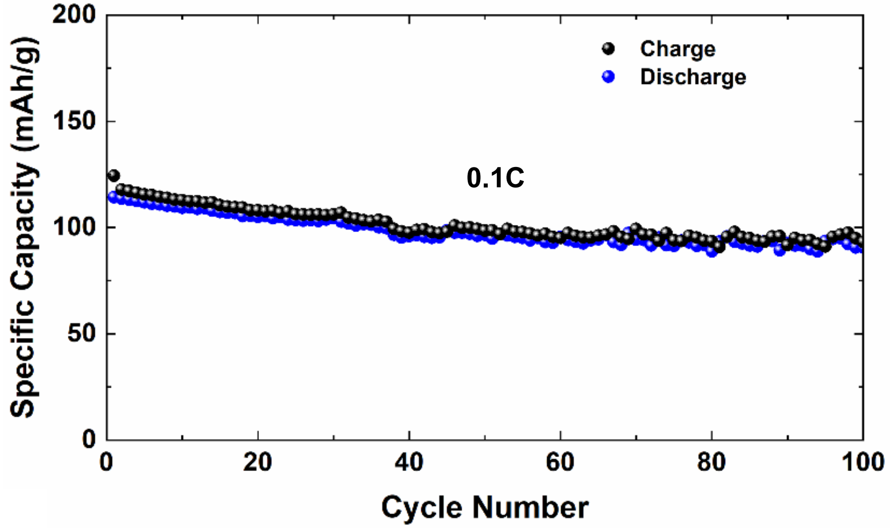


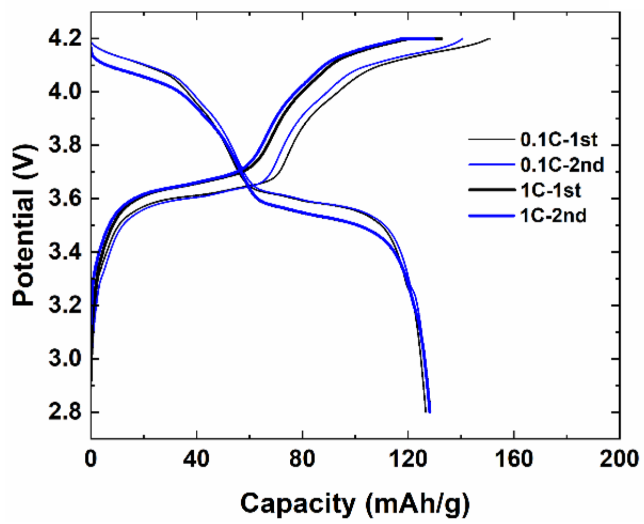


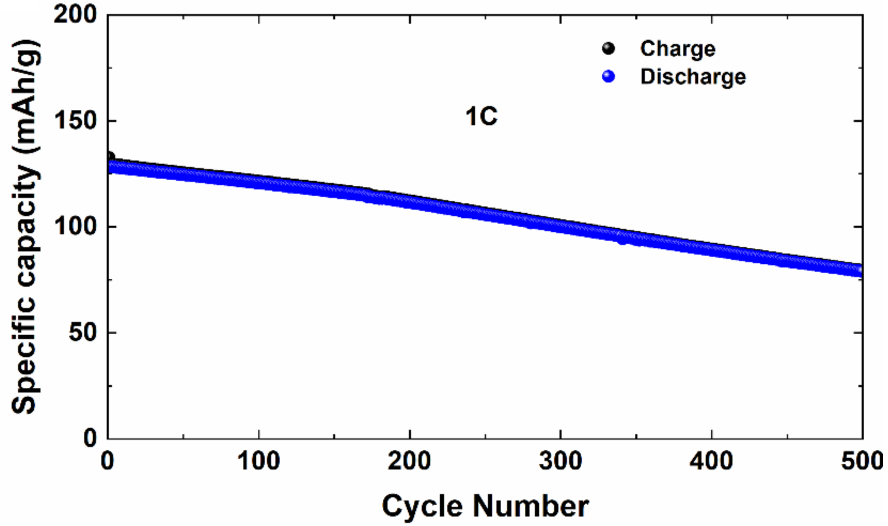
Essehli, Li, Belharouak et al., submitted.

Na half-cell data at 50°C









Na full-cell data against hard carbon at RT.

FY22 Achievements and FY23 Future Work

FY2022 Accomplishments:

- Deep-dive into the reaction mechanism and structural evolution upon electrochemical charge/discharge assisted by neutron characterizations with paper published and highlighted as journal front cover.
- Developed two methods of synthesizing $Na_3V_2(PO_4)_2F_3$ and $Na_3V_{1.8}TM_{0.2}(PO_4)_2F_3$ (TM=Mn, Fe, Ni) with both methods able to achieve 10 g per batch with pure phase.
- Performed advanced characterizations on the $Na_3V_{1.8}TM_{0.2}(PO_4)_2F_3$ (TM=Mn, Fe, Ni) for better understanding the charge compensation mechanism upon electrochemical charge/discharge.

FY2023 Plan:

- Perform roll-to-roll coating of the $Na_3V_2(PO_4)_2F_3$ cathode materials synthesized by reflux system and assemble baseline single-layer pouch cells.
- Perform roll-to-roll coating of the $Na_3V_{1.8}Ni_{0.2}(PO_4)_2F_3$ cathode materials synthesized by reflux system and prepare 1 Ah pouch cells against hard carbon anode and demonstrate cycling up to 1000 cycles at C/3.
- Finalize the data analysis of the advanced synchrotron characterization results for manuscript.

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