Novel Lithium-Iron and Aluminum Nickelate (NFA) as Advanced Cobalt-Free Cathode Materials

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Oak Ridge National Laboratory

2021 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 25, 2021 **Project ID: BAT412**

Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 80%

Budget

- FY19 Funding: $710,000
- FY20 Funding: $710,000
- FY21 Funding: $710,000

Barriers

- Cost: DOE's ultimate goal for EV batteries includes reducing production cost of a Battery-EV to $80/kWh.
- Energy density: High energy density ≥ 650-750 Wh/kg at the material level.
- Performance: 1000 deep charge/discharge cycles with less than 20% capacity fade.

Partners/Collaborators

- ORNL – Project Lead
- INL
- NISSAN Technical Center
- XALT Energy

Relevance

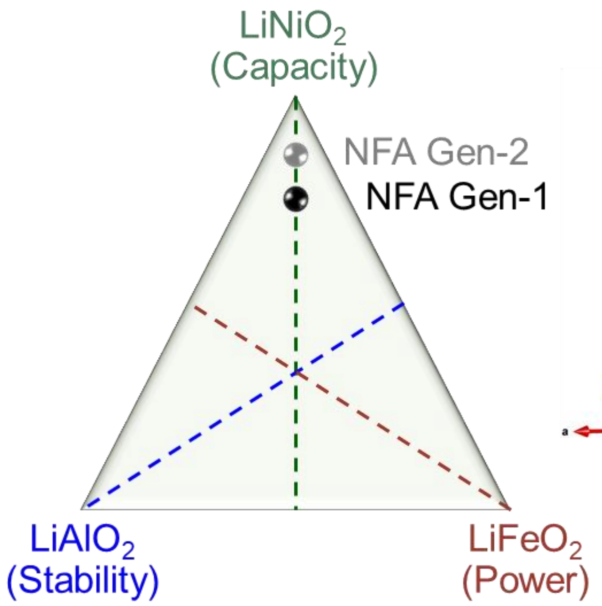
Cobalt is the key limiting factor in the production of next generation electric vehicles

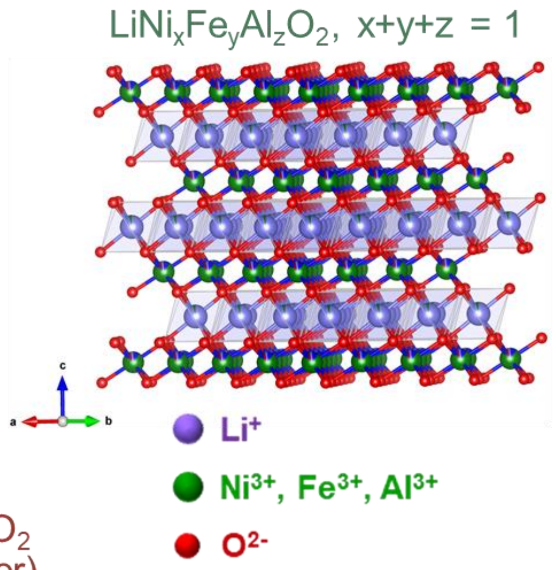
Project Objectives:

- Zero (0) cobalt loading as NFA cathodes only have nickel (80-90%), and the balance (10-20%) is a combination of iron and aluminum.
- 650-750 Wh/kg usable specific energy at C/3 rate at the material level at the beginning of life.
- Thousand (1000) deep charge and discharge cycles at the C/3 rate with less than 20% capacity fade in 2-Ah cells.
- Less than $100 per kWh at the cell level.

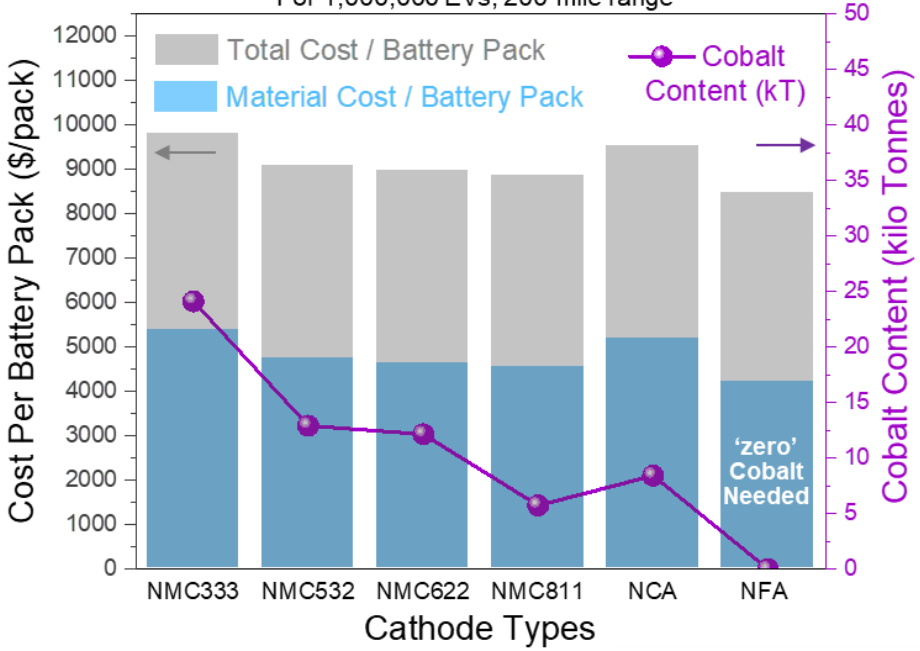
Comparing the NFA class to mainstream NCM and NCA cathodes

Formulation	Specific Capacity (mAh/g)	V_{avg} vs. Graphite (V)	Material Cost ($/kg$_{ore}$)	Wt% Co	Status
NCM-622	170	3.68	$ 22.17	12.2	Currently used
NCM-811	190	3.68	$ 19.00	6.1	Emerging Material
NCA (80:15:5)	195	3.75	$ 21.58	9.2	Used in niche applications
NFA Gen I (80:10:10)	180	3.7	$ 14.63	0	Project Year 1 Goal
NFA Gen II (90:x:y) (x + y = 10)	200	3.7	$ 15.26	0	Project Year 2 Goal





BatPaC Model highlighting the potential of the NFA Cathode
For 1,000,000 EVs, 200-mile range



NFA Gen-2 potentially offers 20% cost reduction when compared to NMC 333

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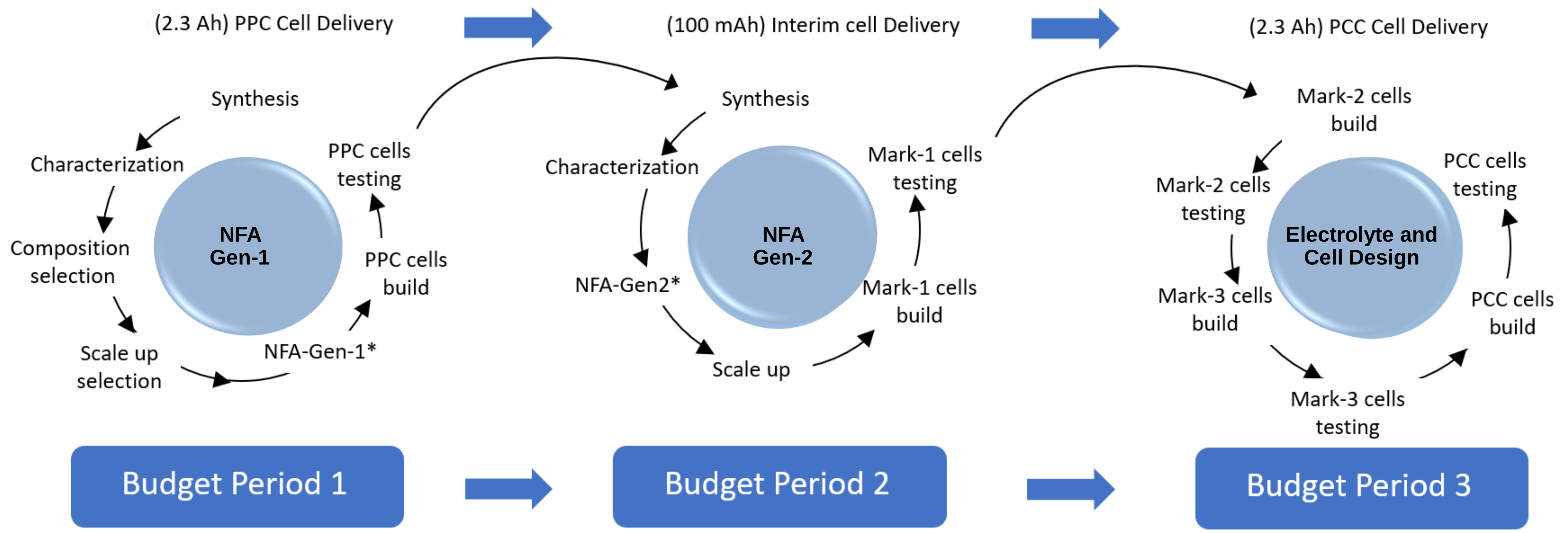
Milestones for FY 20-21

Due Date	Description	Status
03/30/2020 (Q6)	❑ Electrochemical Performance of NFA-Gen-2 in Coin Cells ❑ Down-selection of NFA-Gen-2 Composition	Complete
06/30/2020 (Q7)	❑ Scale-up of NFA-Gen-2 to 1kg	Complete
09/30/2020 (Q8)	❑ Fabrication of NFA Gen-2 Single Layer Pouch Cells (Mark-1 Cells) ❑ Assessment of electrochemical performance of Mark-1 NFA Gen-2 Cells	Complete
12/31/2020 (Q9)	❑ Fabrication of NFA-Gen-2 Single Layer Pouch Cells with Fluorinated Electrolyte (Mark-2 Cells) ❑ Assessment of Electrochemical Performance of Mark-2 NFA Gen-2 Cells	Complete
03/31/2021 (Q10)	❑ Fabrication of NFA-Gen-2 Single Layer Pouch Cells with Optimized Electrode Design (Mark-3 Cells) ❑ Assessment of Electrochemical Performance of Mark-3 NFA Gen-2 Cells	Complete
06/30/2021 (Q11)	❑ Fabrication of (2Ah) NFA-Gen-2 Project Completion Cells	In Progress
09/30/2021 (Q12)	❑ Assessment of Cycle and Calendar Lives Performance of (2Ah) NFA-Gen-2 Project Completion Cells	In Progress

Approach and Strategy

Overall Project Approach FY 19 to FY 21

Novel Lithium Iron and Aluminum Nickelate (NFA) as Advanced Cobalt-Free Cathode Materials for Next-Generation Lithium-Ion Batteries



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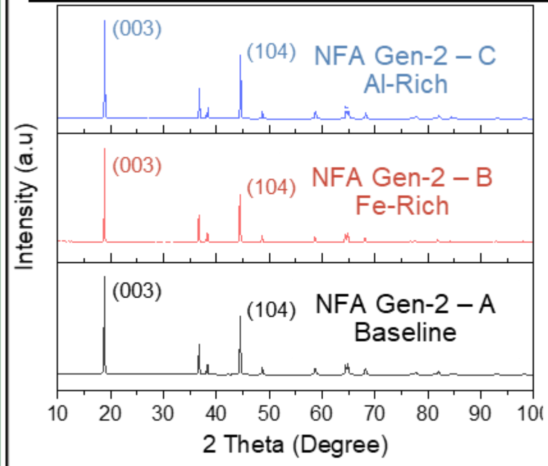
Technical Accomplishments

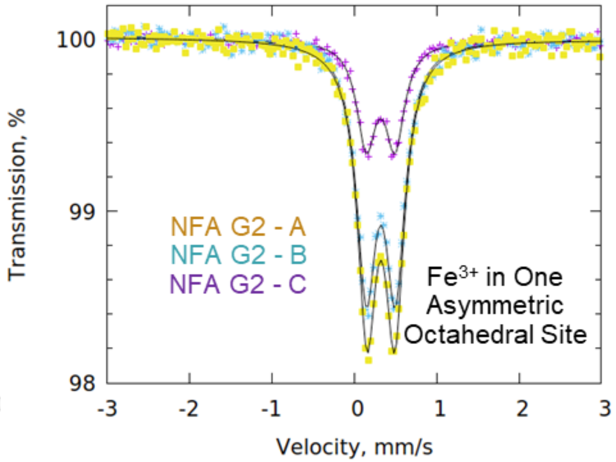
$Li_{1+a}Ni_{0.9}Fe_xAl_yO_2$ (NFA Gen-2) compositional landscape was successfully characterized and electrochemically evaluated

NFA Gen-2 Compositional Landscape – Evaluating Variants A, B and C

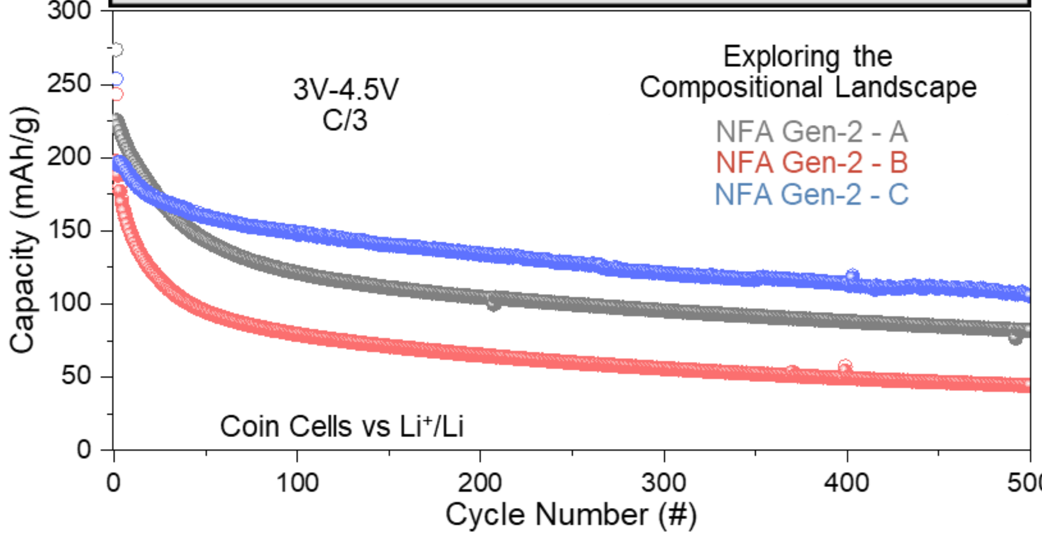
X-Ray Diffractograms



Mössbauer Spectra

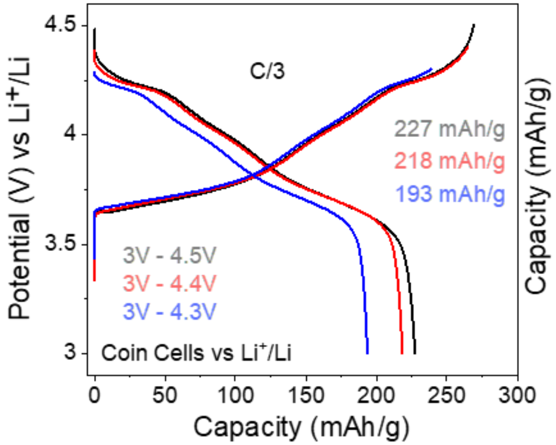


Galvanostatic Charge/Discharge Cycling

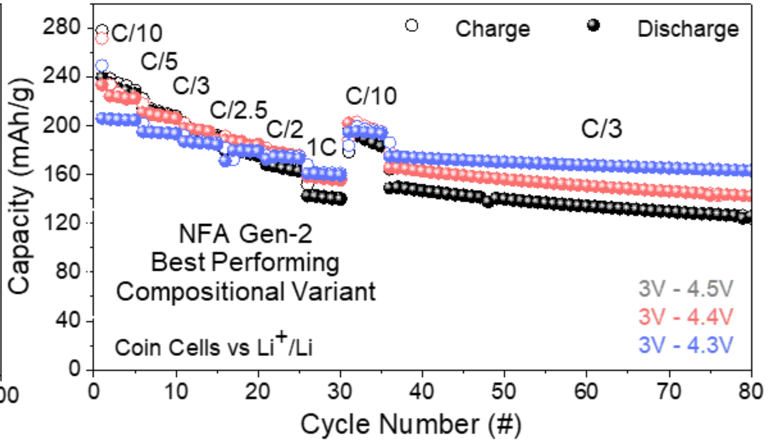


NFA Gen-2 Best Performing Compositional Variant – Electrochemical Performance

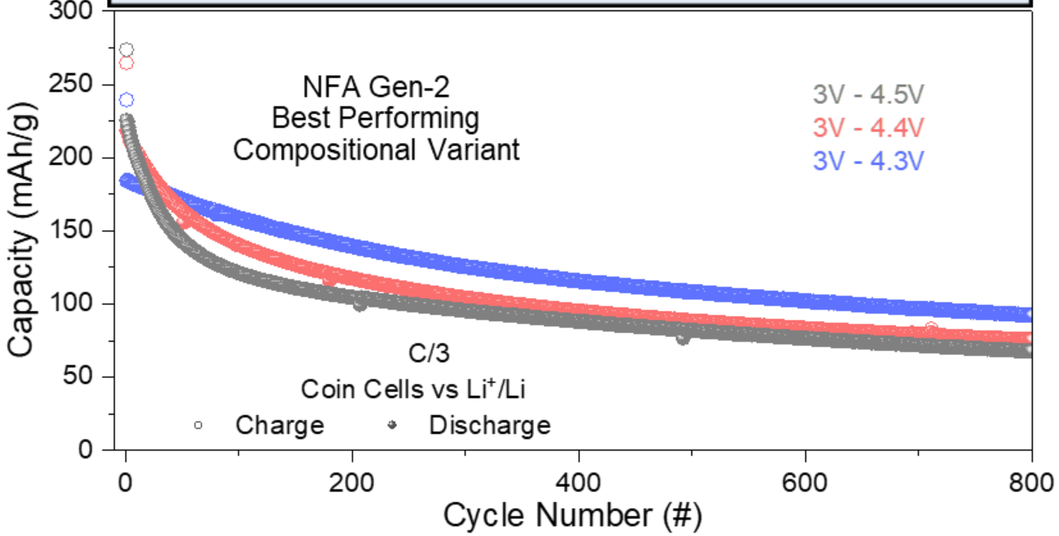
Charge/Discharge Profiles



Rate Performance Assessment



Galvanostatic Charge/Discharge Cycling



Best Performing NFA Gen-2 Variant was identified through electrochemical and material evaluations following which the variant was down selected for upscaling

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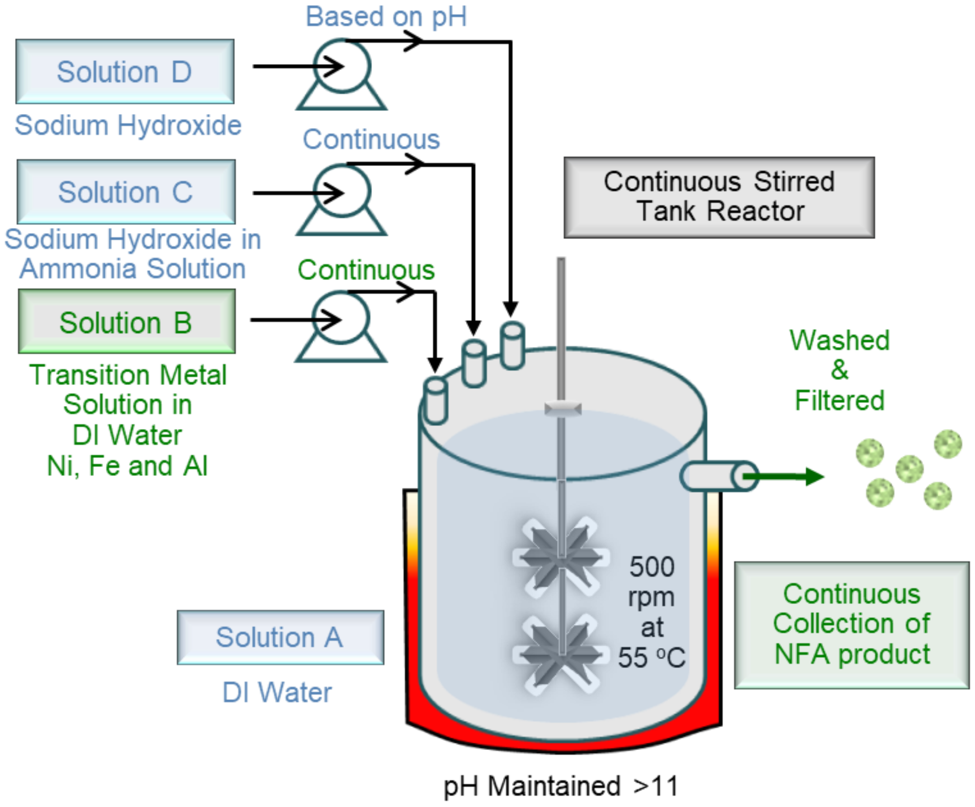
Technical Accomplishments

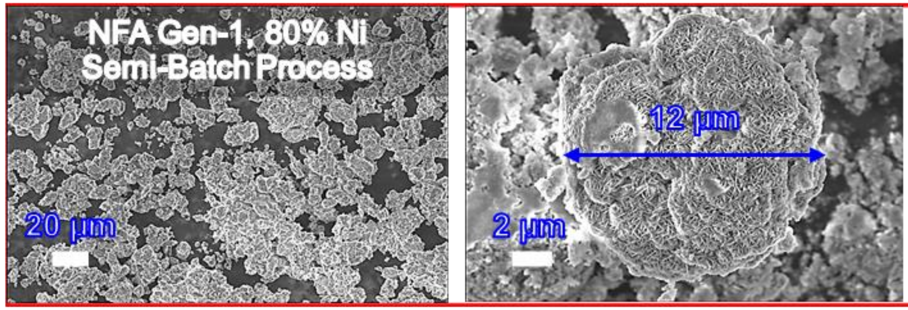
Systematic process optimizations to achieve NFA Gen-2 precursors with desired compositions and morphological homogeneity

Coprecipitation Process for Upscaling NFA Gen-2 Precursors using CSTR

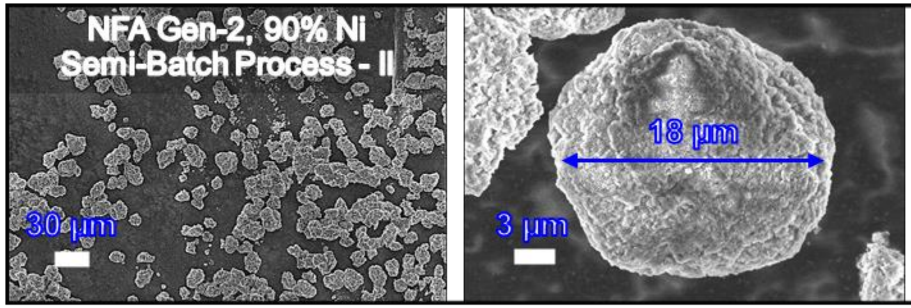


- ❑ Systematic optimizations of the coprecipitation process during the budget periods (FY19-21) yielded NFA precursors with good homogenous spherical morphologies and high compositional purities.
- ❑ During FY20-21, NFA Gen-2 composition was scaled up to kg levels using the optimized coprecipitation process (Continuous Process – II) using the Continuous Stirred Tank Reactor (CSTR) system

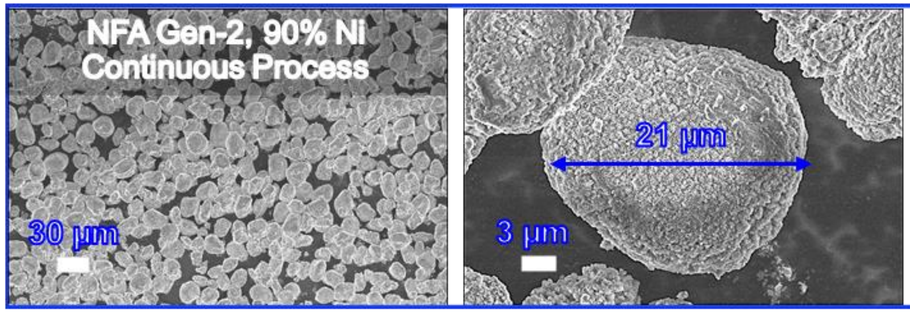
Systematic Process Optimizations (FY19-Fy21)



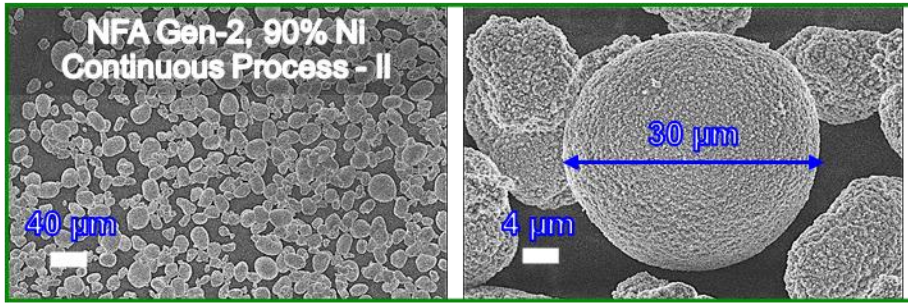
- ❑ Morphological & Compositional inhomogeneities
- ❑ Al deficiency in compositions (ICP)
- ❑ Capacity ~ 160 mAh/g at C/3, 3V-4.3V



- ❑ Morphological & Compositional inhomogeneities
- ❑ Al deficiency in compositions (ICP)
- ❑ Capacity ~180 mAh/g at C/3, 3V-4.3V



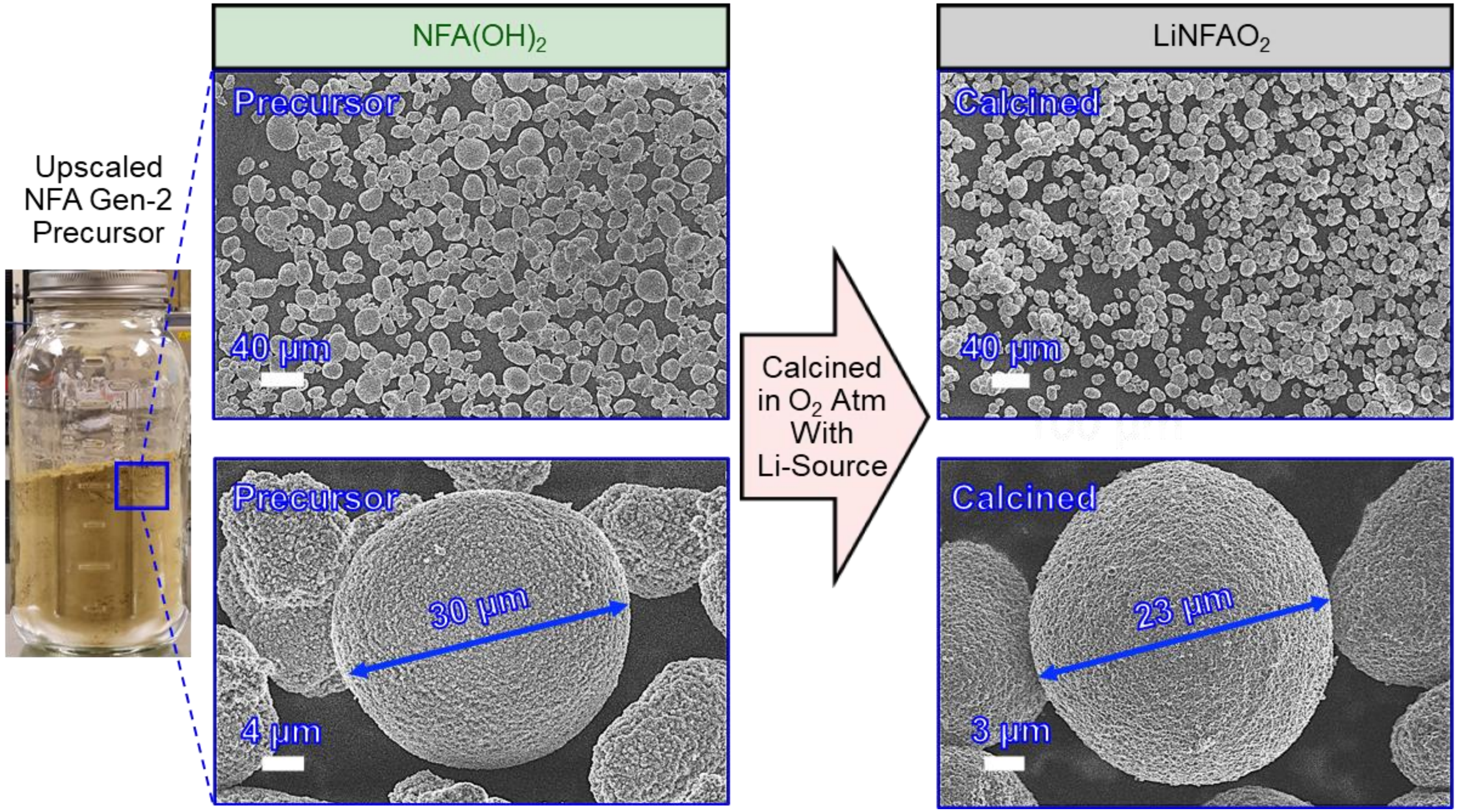
- ❑ Morphological homogeneity
- ❑ Composition was Al deficient (ICP)
- ❑ Capacity ~200 mAh/g at C/3, 4.3V



- ❑ Morphological homogeneity
- ❑ Compositional was exact Gen-2 (ICP)
- ❑ Capacity ~200 mAh/g at C/3, 4.3V

Technical Accomplishments

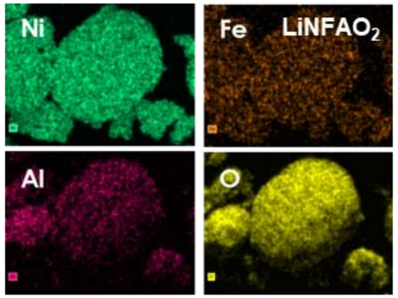
$Li_{1+a}Ni_{0.9}Fe_xAl_yO_2$ (NFA Gen-2) was successfully synthesized, and upscaled to kg levels using CSTR



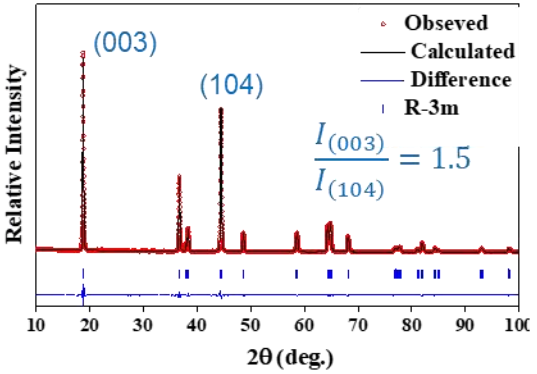
ICP Compositional Analysis

Composition	Li	Ni	Fe	Al
NFA(OH)$_2$		0.89	0.051	0.054
LiNFAO$_2$	1.0	0.89	0.051	0.054

EDS Elemental Mapping

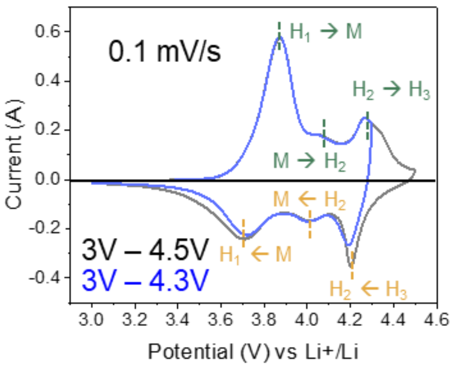


X-Ray Diffractogram

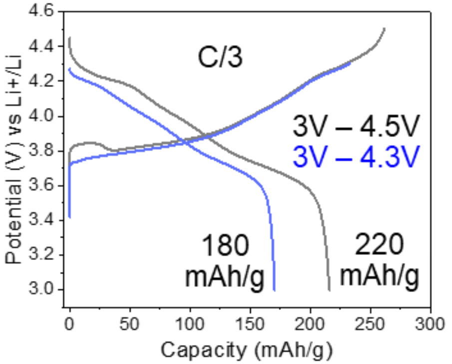


Electrochemical Testing in Coin Cells

Cyclic Voltammogram



Charge/Discharge

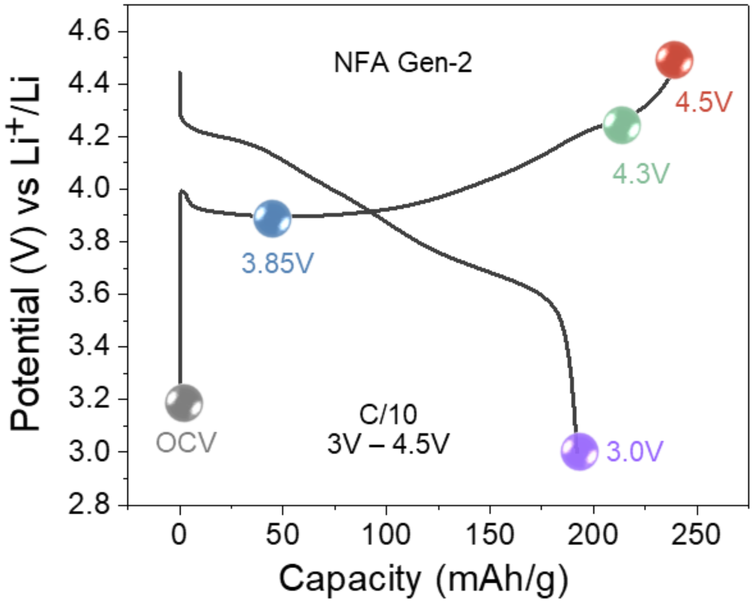


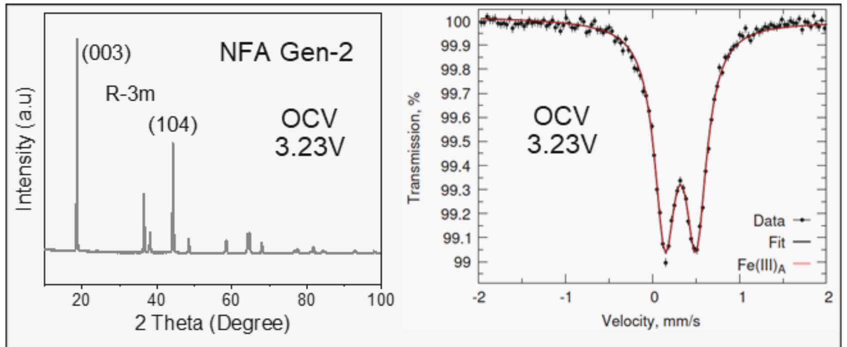
- NFA Gen-2 composition was scaled up to kg levels using the coprecipitation process in a Continuous Stirred Tank Reactor (CSTR)
- Scanning Electron Microscopy, ICP Compositional Analysis, EDS Elemental Mapping and X-Ray Diffractogram of the precursors and calcined product reveals good spherical morphology, compositional purity and good structural ordering, respectively.
- Electrochemical performance assessment in coin cells showed high capacities ~220 mAh/g (3V-4.5V and ~180 mAh/g (3V-4.3V) at C/3. Voltammograms revealed phase transitions similar to cobalt containing NCA and NCM type materials

Technical Accomplishments

$Li_{1+a}Ni_{0.9}Fe_xAl_yO_2$ (NFA Gen-2) – Advanced Characterization using Mössbauer Spectroscopy and X-ray Diffraction

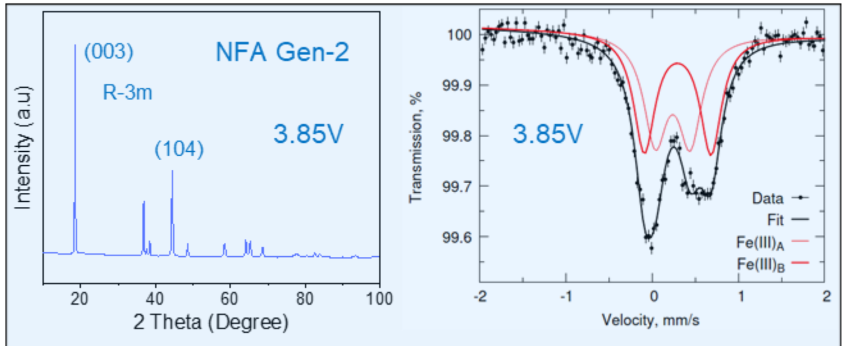
Galvanostatic Charge/Discharge Profile at C/10





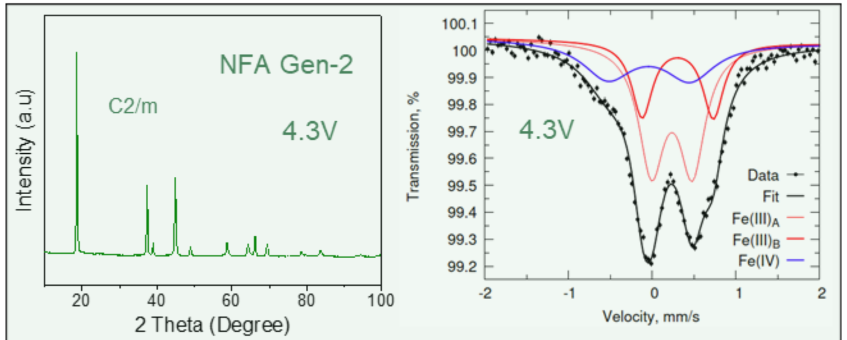
R-3m Space Group

0% Fe_B, Iron in only one site



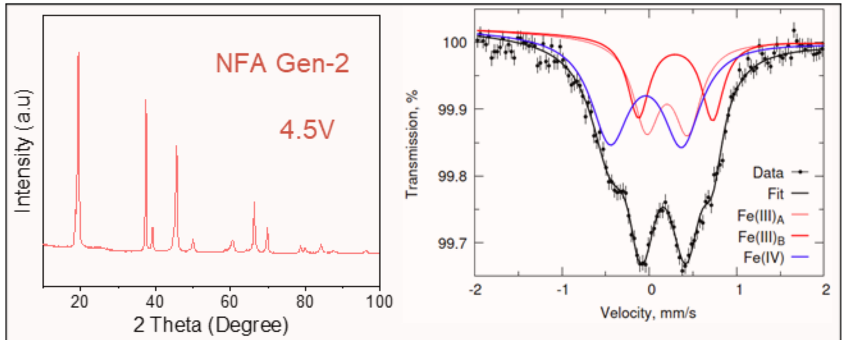
Predominantly R-3m Space Group

50% Fe_B, Iron in two sites



C2/m Space Group

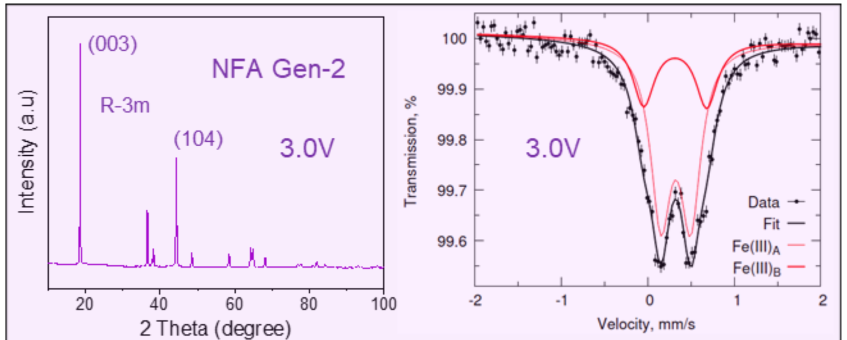
33% Fe(IV), 33% Fe_B, 33% Fe_A
Iron in three sites



Space Group could not be resolved

49% Fe(IV), 25% Fe_B, 25% Fe_A
Iron in three sites

- ❑ Advanced characterization using Mossbauer Spectroscopy and X-Ray Diffraction techniques were employed to characterize the synthesized NFA Gen-2 cathode material at various states of charge
- ❑ Mössbauer spectra obtained at various states of charge for the NFA Gen-2 cathode revealed a reversible redox behavior of iron ($Fe^{3+} \leftrightarrow Fe^{4+}$) in addition to the predominant nickel redox ($Ni^{3+} \leftrightarrow Ni^{4+}$) in NFA materials
- ❑ Mössbauer is especially sensitive to the local environment of iron contained in the NFA crystal structure and thus offers high sensitivities enabling better determination of energy storage behavior of the NFA system



R-3m Space Group

No Fe(IV), 31% Fe_B,
Iron in two sites

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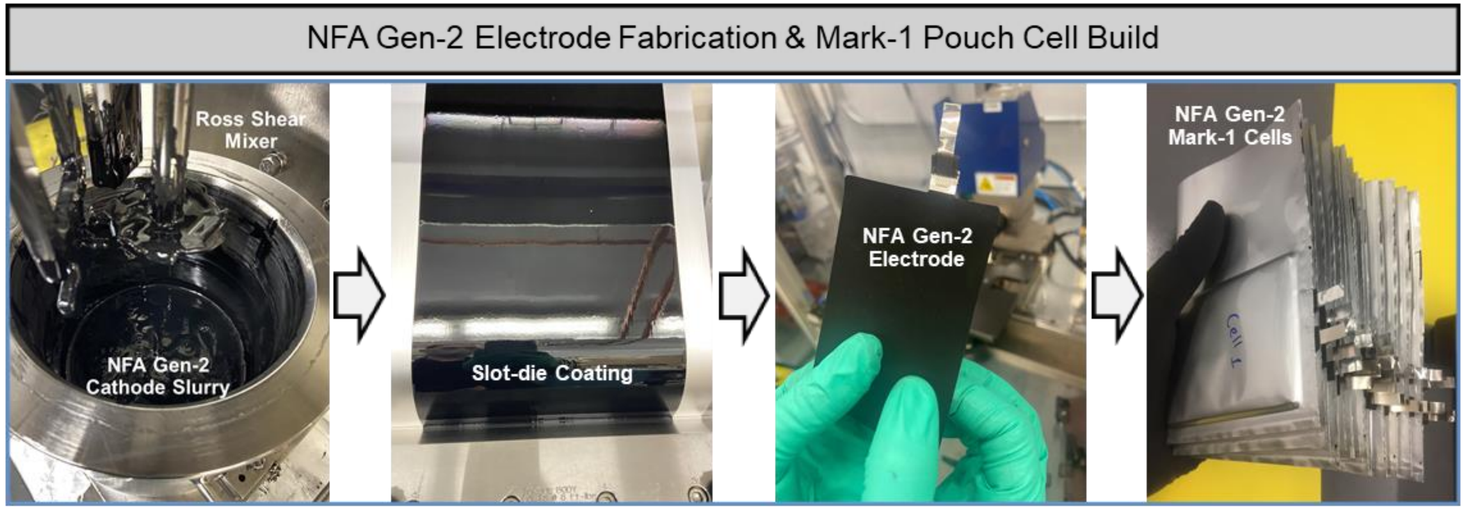
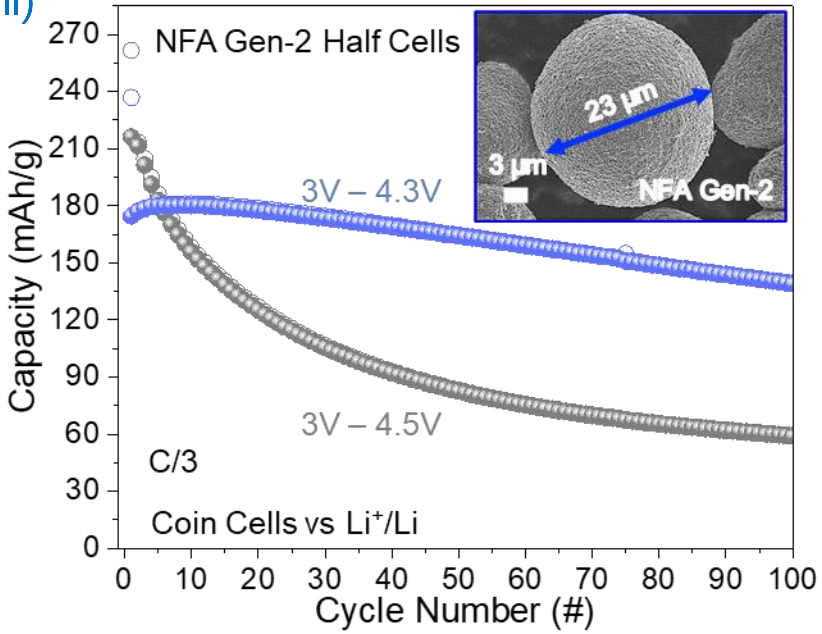
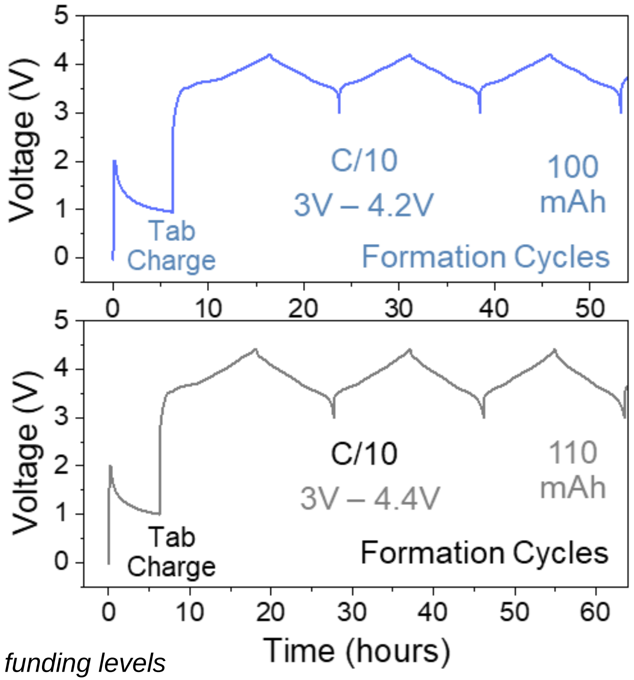
Technical Accomplishments

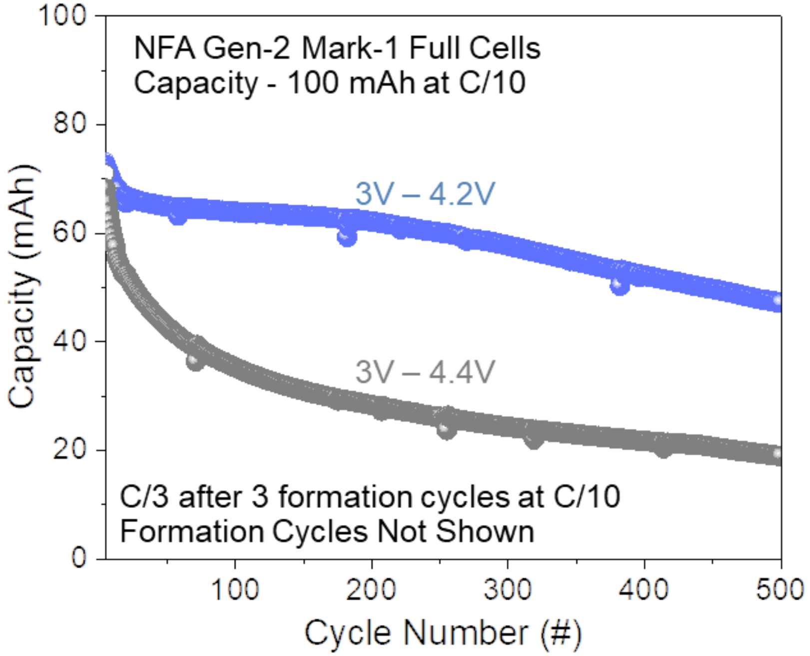
$Li_{1+a}Ni_{0.9}Fe_xAl_yO_2$ (NFA Gen-2) cathode material was slot-die coated and the electrodes were assembled and evaluated in single layer pouch cells (Mark-1 Cell)





- NFA Gen-2 cathode material was successfully cast into electrodes using the slot-die coating technique
- Electrochemical performance of NFA Gen-2 cathode in half-cells with lithium metal as reference demonstrated reasonably stable charge/discharge cycling performance in the voltage window 3V-4.3V, delivering a capacity of ~180 mAh/g (4.3V) and ~214 mAh/g (4.5V).
- NFA Gen-2 cathodes were successfully integrated into single layer 100 mAh (at C/10) Mark-1 pouch cells with graphite as the anode
- Mark-1 cells showed reasonable cycling performance between 3V – 4.2V which can be further improved through the proposed future work within the scope of this project





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Any proposed future work is subject to change based on funding levels

Response to Previous Year Reviewer's Comments

Reviewer Comments

- **Reviewer-1:** The approach the team has taken to making a Co-free nickelate material has been great. The team has addressed technical barriers and overcome them. The one question from the reviewer is if the team is going to improve the electrode loading, percent active in formulation, and porosity during the electrode development.

  Response: We thank the reviewer for the positive feedback. Electrode loading, active material optimization and porosity tailoring would be part of Mark-3 NFA Cell designs that is presently being evaluated in the current budget period. Thank you!

- **Reviewer-2:** The work takes on the interesting task of developing and evaluating the potential of a nanostructured ferritic alloy (NFA)-based, metal-oxide cathode system. This is done in a generally credible way, the reviewer said, and that synthesis aspect of the work appears more accomplished than the performance-evaluation part of the work. To be fair, this is not a high-dollar project and comprehensive evaluation is a very costly endeavor. As with other projects in this subset, there is little benchmarking available at this stage of the work.

  Response: We thank the reviewer for the positive comments regarding our work. With regards to benchmarking we are in the process of comparing the performance of our NFA Gen-2 material with both commercial NMC variants as well as other NMC chemistries developed in other VTO programs through our collaborations during the current budget period. Thank you!

- **Reviewer-3:** Overall, this is a very well managed research project. The reviewer was curious about why Fe was used as a substitute. The amount seems to be very low and since there is no benchmarking versus commercially available materials with the same Ni+Co content, the claim that Fe improves rate capability is not supported. Provided industry "scare" of any Fe in the material, it will be interesting to know the OEM feedback. There have been many publications for the LiNiO2 with Al, Mg, Ti, etc., doping. Why Fe? Is it the mentioned high sensitivity to moisture due to Ni, not Fe? Or both? Why the volumetric energy density is low? Is it due to the synthesis route?

  Response: We thank the reviewer for their positive comment on our work. With regards to Fe, our hypothesis for incorporation lies in the low cost and earth abundance of iron when compared to other elements that are potential candidates. We are in the process of benchmarking our NFA Gen-2 cathode material against both commercial NMC variants as well as other NMC chemistries developed in other VTO programs through our collaborations during the current budget period. Additionally, with regards to volumetric energy densities, we expect to see improvements through our synthesis optimizations as well as using optimized electrode designs which would be incorporated in the Mark-3 NFA cells are being evaluated during the current budget period. Thank you!

Collaboration and Coordination with other institutions

Battery Manufacturing Facility

Overall project lead, electrochemical, spectroscopic and material characterization

Contributors and Collaborators: Dr. Nitin Muralidharan, Dr. Rachid Essehli, Dr. Zhijia Du, Dr. Ethan Self, Dr. Hermann Raphael
Participation in Bi-Weekly Update Meetings and Quarterly Update Meetings

Microstructural and Crystallographic characterization

Independent Battery Performance Evaluation
Collaborator: Dr. Sergiy Sazhin

Nissan Technical Center

Li-ion battery performance assessment and validation
Participation in Bi-Weekly Update Meetings and Quarterly Update Meetings

Electrochemical benchmarking, process feasibility and cost modeling of materials for Li-ion batteries Participation
in Bi-Weekly Update Meetings and Quarterly Update Meetings

Remaining Challenges and Barriers in FY-21

Technical Challenges

- Li source and stoichiometry, mixing conditions, pretreatment temperatures and profiles, oxygen flow rates and powder packing during annealing are among the most important synthesis conditions and processes that still require optimization.

- Slurry formulation and electrode engineering, choice of conductive carbon and binders, choice of suitable graphite anode, N/P ratio and added electrolyte amount in nickel rich cathodes need to be further explored and optimized.

- Stabilizing the NFA nickel rich, cobalt free system at high voltages (>4.3V vs Li^+/Li) requires systematic investigations into surface coating and electrolyte additive approaches. Such studies would enable accessing additional capacities from these novel cathodes

- The storage conditions and stability of high nickel rich cathode materials during the slurry preparation and coating (humidity, Li_2CO_3 formation)

Any proposed future work is subject to change based on funding levels

Proposed Future Research

Completed

FY 20-21

- ❑ Selection of the NFA-Gen-2 cathode that will be scaled up
- ❑ Scale up of NFA-Gen-2 to 1 kg by the process selected in budget year 1
- ❑ Build of Mark-1 cells with NFA-Gen-2*, and inhouse testing of Mark-1 cells
- ❑ Build of Mark-2 cells with NFA-Gen-2 and 3 FEC-based electrolytes, and inhouse testing of Mark-2 cells
- ❑ Selection of the best electrolyte that will be used in the build of Mark-3 cells
- ❑ Build of Mark-3 cells with NFA-Gen-2, selected electrolyte and 3 cell designs, inhouse testing of Mark-3 cells
- ❑ Selection of the best cell design that will be used in the build of the Project Completion Cells

Ongoing

FY 21

- ❑ Build of 2.3 Ah Project Completion Cells with the NFA-Gen-2* optimized cell chemistry, and inhouse testing of 15 PCC cells
- ❑ Delivery of 2.3 Ah PCC cells to DOE

Any proposed future work is subject to change based on funding levels

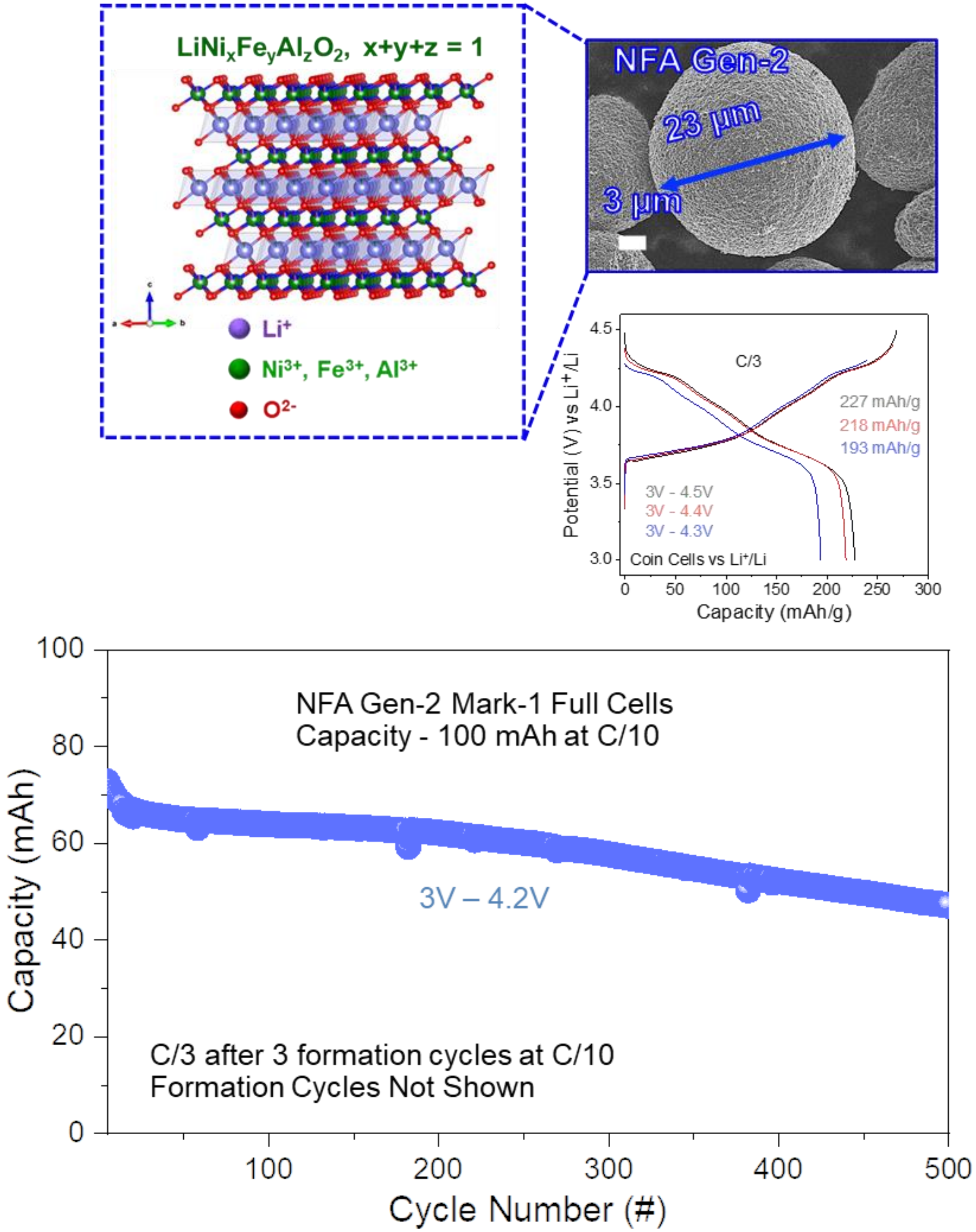
Summary

Accomplishments:

- Successfully *investigated the NFA Gen-2* cathode compositional landscape using advanced material and electrochemical in-situ, ex-situ and operando characterization techniques and down selected the best compositional variant for upscaling

- Successfully *scaled-up* the down selected NFA Gen-2 cathode composition to kg levels and *evaluated material and electrochemical characteristics and performance*

- Fabricated electrodes of *NFA Gen-2 cathode material, assembled single layer Mark-1 full pouch cells* and performed *electrochemical assessment*



Ongoing Work:

- Build of 2.3 Ah Project Completion Cells with the NFA-Gen-2 cathode followed by in-house testing

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