Lithium Iron and Aluminum Nickelate (NFA), an Advanced Co-free Cathode Material

PI: Ilias Belharouak (belharouaki@ornl.gov)

N. Muralidharan, R. Essehli, E. Self, J. Li, Z. Du, D. Wood, J. Nanda (All ORNL)
J. Camardese (Xalt Energy) and T. Han (Nissan Technical Center)

Oak Ridge National Laboratory

2019 U.S. DOE Vehicle Technologies Office
Annual Merit Review

June 11, 2019 **Project ID: BAT412**

ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 15%

Barriers

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

Budget

- FY19 Funding: $ 710,000

Partners/Collaborators

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

Relevance

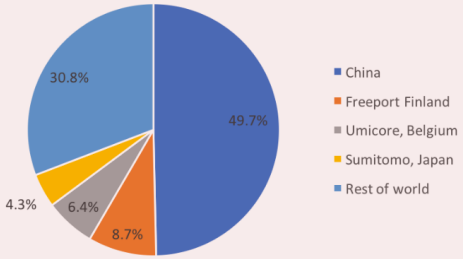
Cobalt is the key limiting factor in the production of next generation electric vehicles

Cobalt Mining

Source: https://www.theglobeandmail.com/globe-investor/scarce-expensive-cobalt-essential-for-electric-cars/article38126326/

- Cobalt mining is driving a humanitarian crisis

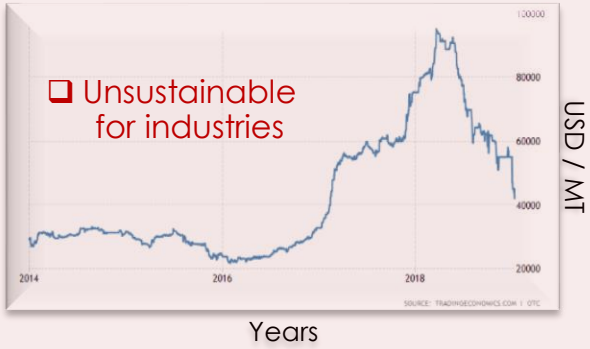
Global Cobalt Refining



Source: http://www.resourcefulpaths.com/blog/2017/3/6/cobalt-for-batteries-who-will-control-supply-how-ethical-and-sustainable-will-it-be

- US is not a dominating player

Cobalt Price Fluctuations



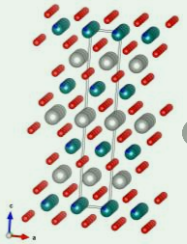
Commercially available Present-day cathodes are cobalt dependent

Formulation	Specific Capacity (mAh/g)	V_{avg} vs. Graphite (V)	Material Cost ($/kg$_{ore}$)	Wt% Co
NCM-622	170	3.68	$ 22.17	12.2
NCM-811	190	3.68	$ 19.00	6.1
NCA (80:15:5)	195	3.75	$ 21.58	9.2

The Solution

Cobalt Free Iron, Aluminum Nickelate (NFA)

Formulation	Specific Capacity (mAh/g)	V_{avg} vs. Graphite (V)	Material Cost ($/kg$_{ore}$)	Wt % Co
NFA Gen-1	180	3.7-4.2	$14.63	0
NFA Gen-2	200	3.7-4.2	$15.26	0



Li^+ Ni^{3+}, Fe^{3+}, Al^{3+} O^{2-}

Iron, Aluminum Nickelate

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 2.3 Ah cells.
- Less than $100 per kWh at the cell level.

Milestones for FY 19

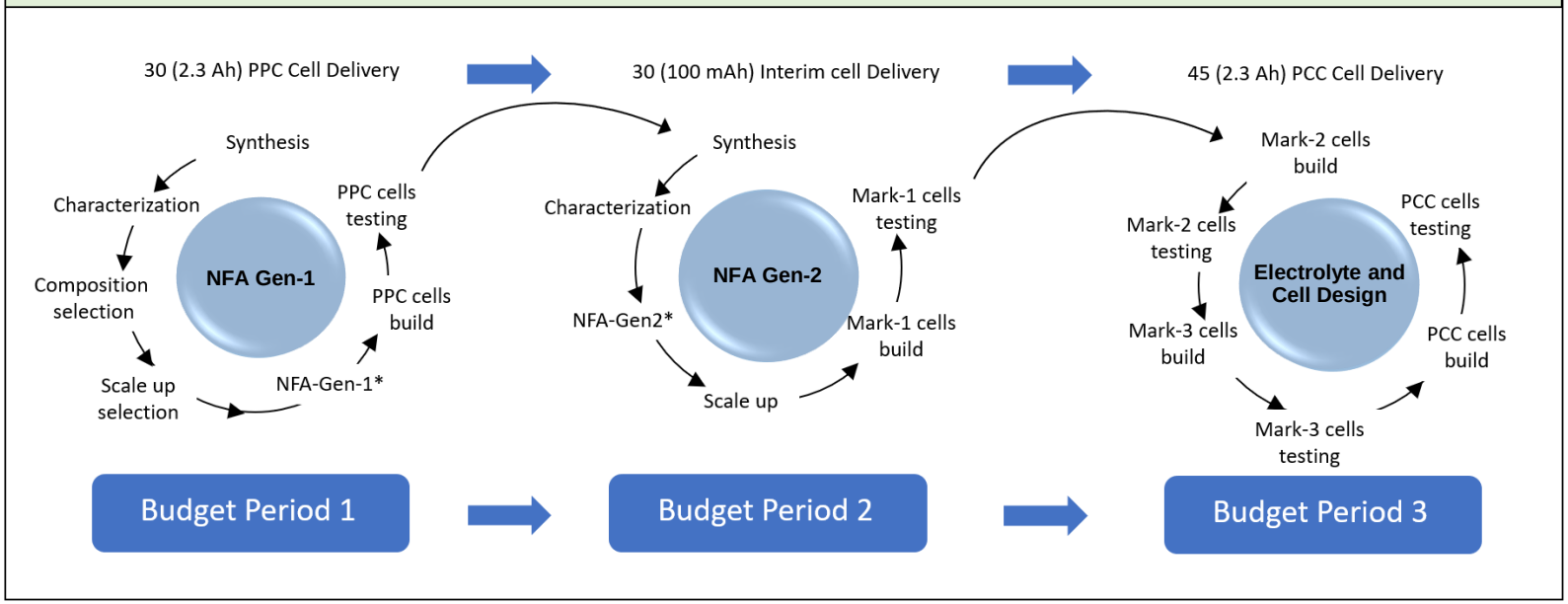
Due Date	Description	Status
12/31/2018 (Q1)	❑ Synthesis of $Li_{1+a}Ni_xFe_yAl_zO_2$, NFA Gen-1 by Sol-Gel Method ❑ Structural Characterization of NFA Gen-1 Cathodes	**Complete**
03/31/2019 (Q2)	❑ Scale up of NFA-Gen 1 in 500g batches ❑ Phase purity, particle size and packing density checks	**In Progress**
06/30/2019 (Q3)	❑ Fabrication of NFA Gen-1 single layer cells ❑ Electrochemical performance of NFA Gen-1 Batches ❑ Down selection of NFA Gen-1 batches ❑ Down selection of the scale-up process	**In Progress**
09/30/2019 (Q4)	❑ Fabrication of 30 (2Ah) NFA Gen-1 Project Progress Cells ❑ Assessment of performance of 15 (2Ah) NFA Gen-1 Project Progress Cells	**In Progress**

OAK RIDGE National Laboratory

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

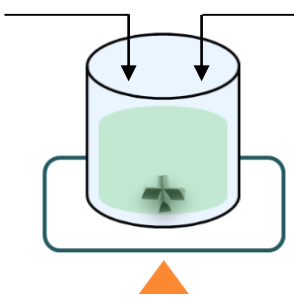


Approach and Strategy for FY 19

Investigate the NFA system Using Sol-Gel Process

Scale-up of the best NFA system Using Co-precipitation Process

Fabricate 2.3Ah Project Progress Cells



Continuous Stirred Tank Reactor (CSTR)

Image Source: https://syrris.com/product/atlas-hd-potassium/

Project Progress Cells

Image Source: BMF (ORNL)

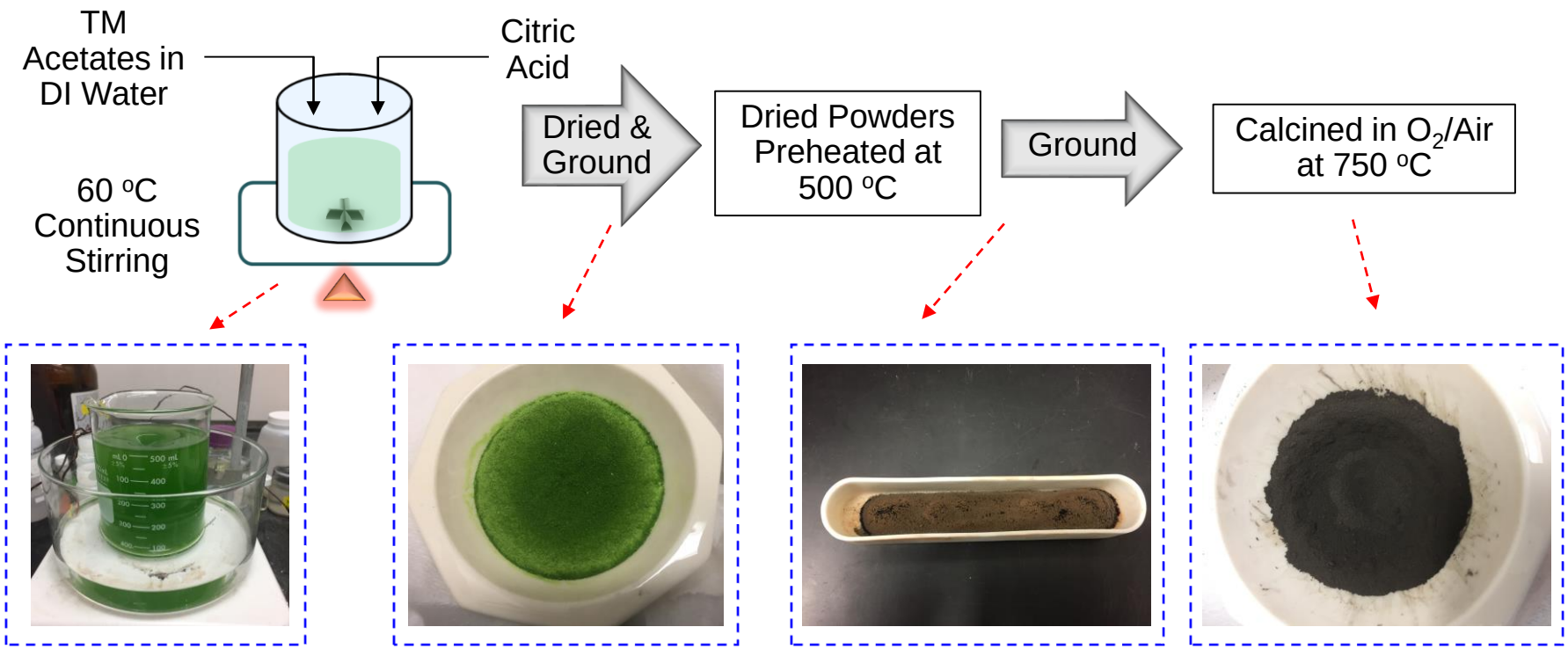
OAK RIDGE National Laboratory

Technical Accomplishments

NFA $Li_{1+a}Ni_xFe_yAl_zO_2$ (NFA Gen-1) was successfully synthesized using the sol-gel process

Our selection of the sol-gel process to synthesize these cathode powders enables fast characterization, fine tuning morphological and electrochemical characteristics prior to scale up using the co-precipitation process.

Sol-Gel Process for the synthesis of NFA cathode powders



TM Acetates in Solution

NFA Precursor Powder

After Pre-treatment

NFA Cathode Powders

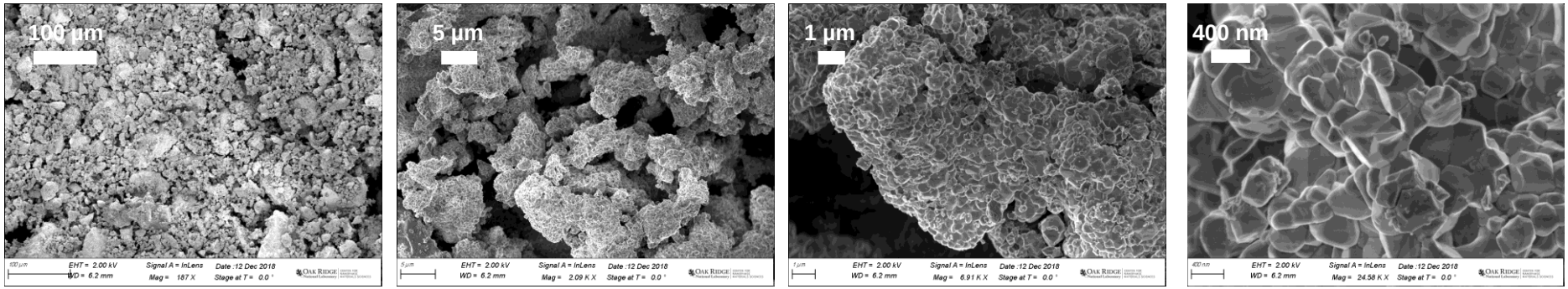
OAK RIDGE National Laboratory

Technical Accomplishments

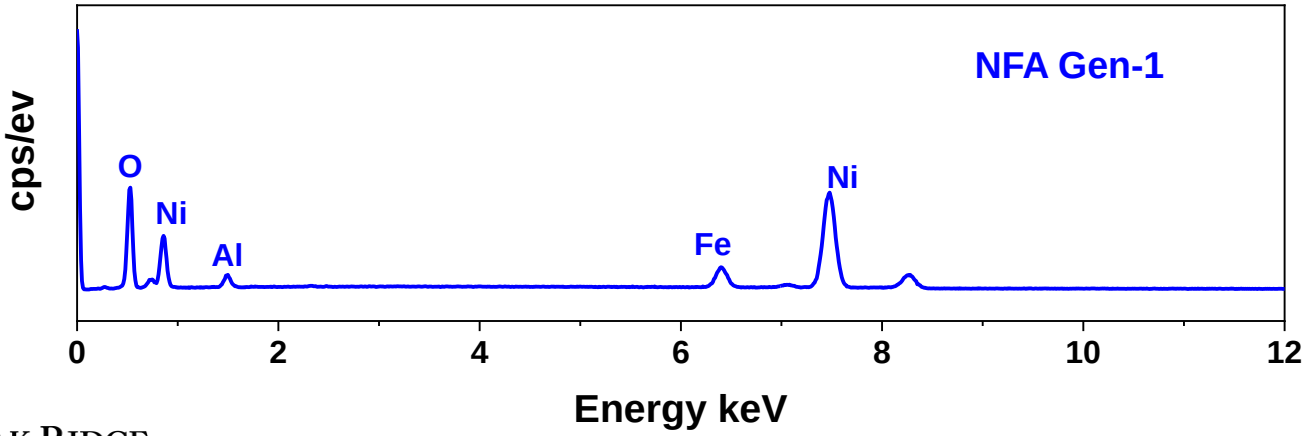
SEM Micrographs and EDS spectra of the NFA $Li_{1+a}Ni_xFe_yAl_zO_2$ (NFA Gen-1) reveal that no elemental impurities are present after the sol-gel synthesis and calcinations

Morphological tuning can be achieved by synthesizing NFA Gen-1 powders using an optimized coprecipitation protocol in a Continuous Stirred Tank Reactor (CSTR)

SEM Micrographs of the sol-gel synthesized NFA Gen-1 powders



EDS Spectra – Identifying Elemental Compositions and Impurities if any



EDS Map
Quantitative analysis

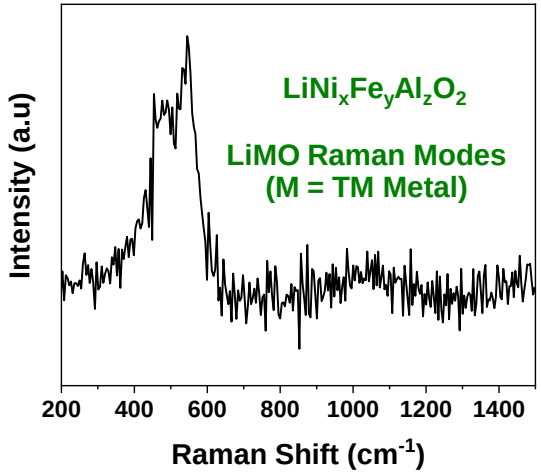
Element	Atom [%]
Oxygen	68.61
Nickel	19.47
Iron	3.87
Carbon	4.37
Aluminium	3.68
	100.00

OAK RIDGE National Laboratory

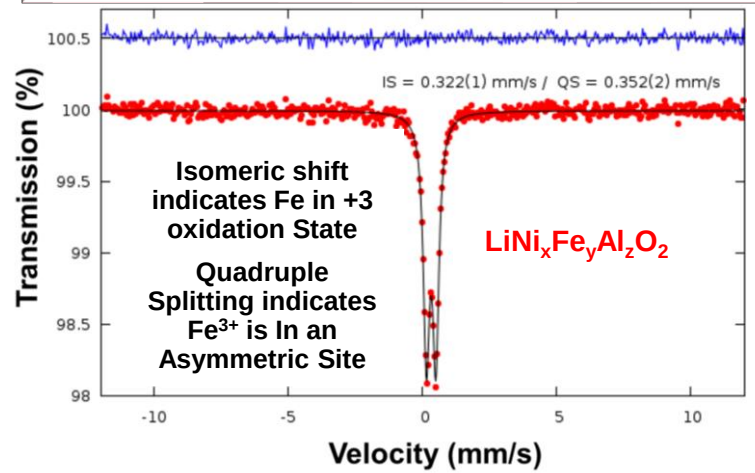
Technical Accomplishments

Raman, Mossbauer and XRD characterization performed on the NFA $Li_{1+a}Ni_xFe_yAl_zO_2$ (NFA Gen-1) powders

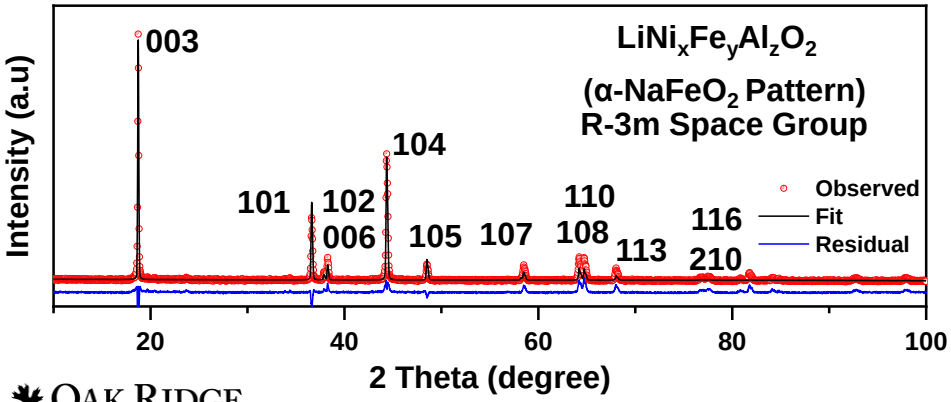
Raman Spectra – Information about Bonding Environment

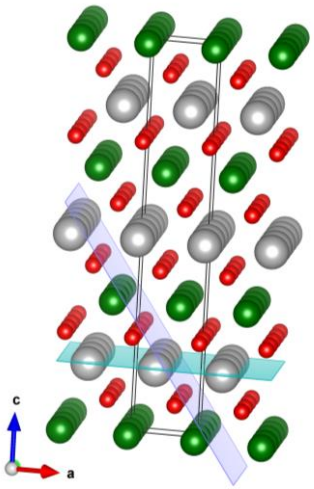


Mossbauer Spectra – Information about Fe oxidation state and local environment



X-Ray Diffractogram – Crystallographic Assessment





Li^+

Ni^{3+}, Fe^{3+}, Al^{3+}

O^{2-}

NFA Crystal Structure
R-3m Phase

Sol-Gel Synthesized NFA Gen-1:

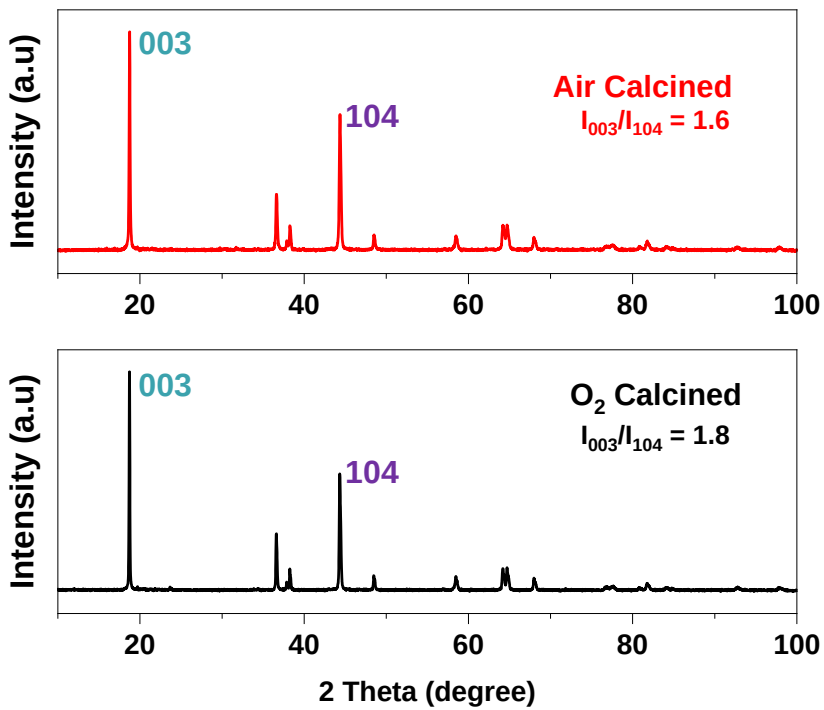
- ❑ Phase Pure
- ❑ R-3m Space Group
- ❑ Fe in 3+ oxidation state

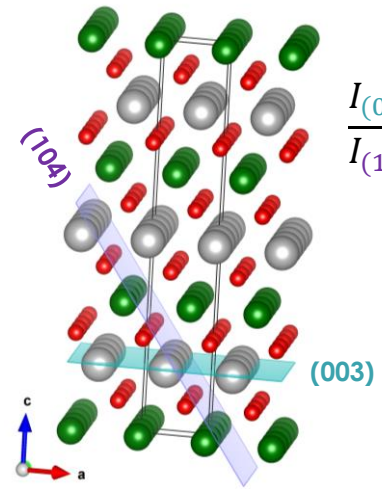
OAK RIDGE National Laboratory

Technical Accomplishments

Investigating the influence of Calcination Atmosphere

- In the case of Nickel rich cathodes, intermixing of cations (Nickel and Lithium) can occur owing to the similar ionic radii of Ni^{2+} and Li^{+}.
- This intermixing causes blocking of lithium diffusion pathways which result in lowered capacities
- The choice of calcination atmosphere is of utmost importance to minimize this issue





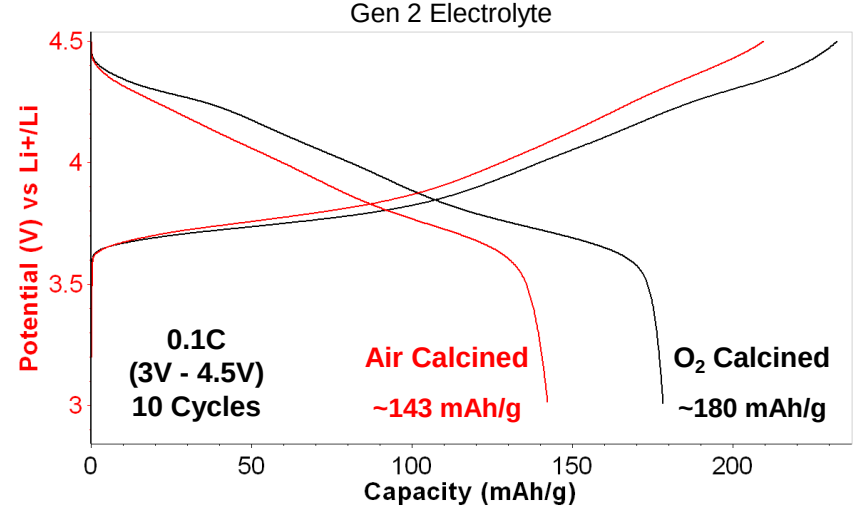
$$\frac{I_{(003)}}{I_{(104)}} \approx \textit{Degree of cation mixing}$$

Higher this ratio, lower the mixing of Ni^{2+} and Li^{+} ions

Electrochemical performance of the air and oxygen calcined NFA Gen-1 Powders

Active Material: Binder: Carbon Black (Denka) - 80:10:10

Gen 2 Electrolyte



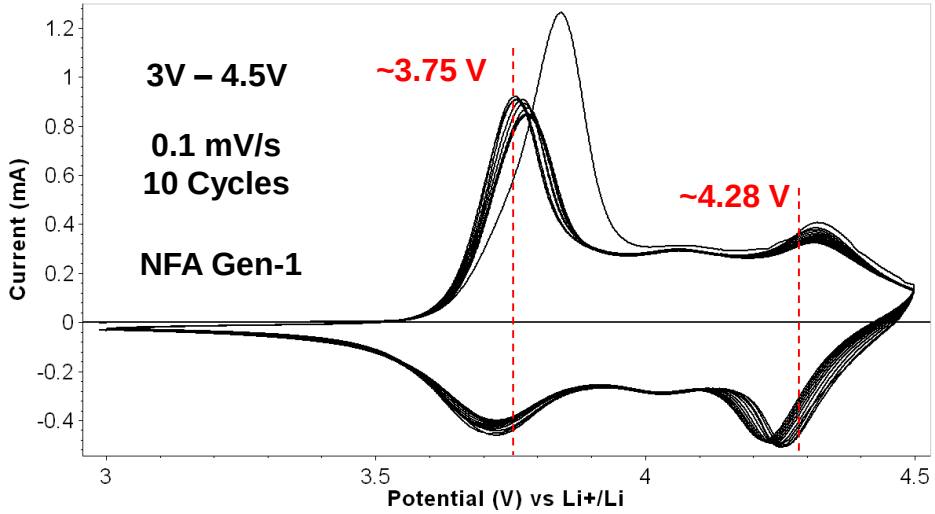
- O_2 atmosphere is critical to achieve minimal cation mixing between the TM ions and lithium
- As a result, higher capacities for NFA powders calcined in O_2 atmospheres were achieved

OAK RIDGE National Laboratory

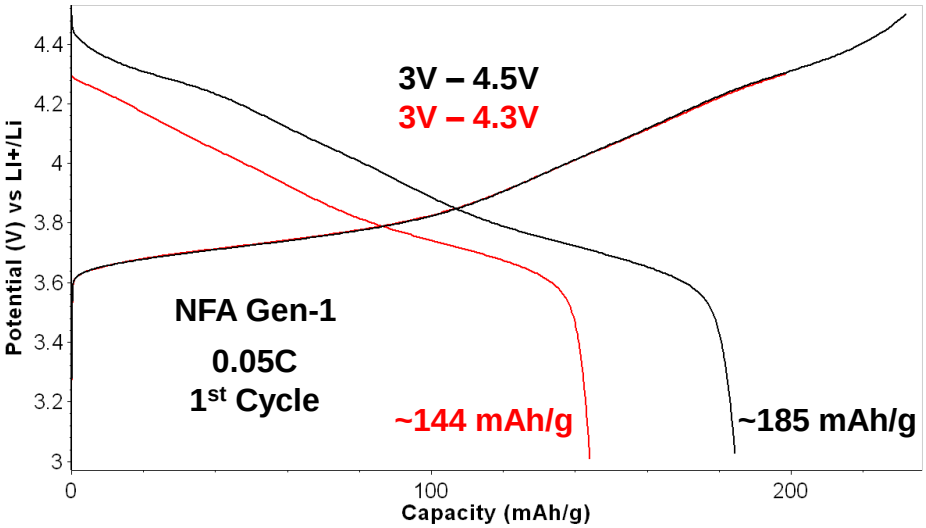
Technical Accomplishments

Electrochemical Performance of O_2 Calcined, NFA Gen-1 cathodes

Cyclic Voltammogram

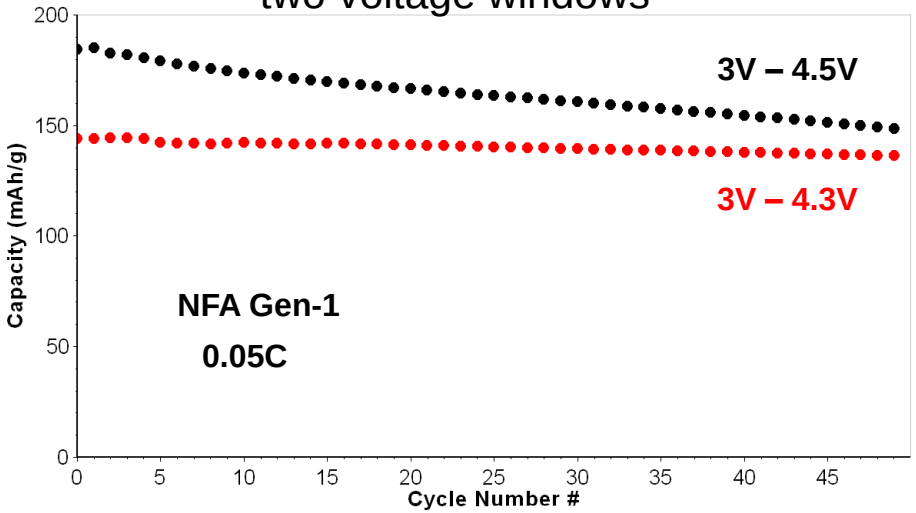


Charge/Discharge



- O_2 calcined NFA 811 powders synthesized using sol-gel process gave ~185 mAh/g when charged up to 4.5V
- When the voltage cutoff was lowered to 4.3V, the capacity delivered was ~144 mAh/g
- Further improvements to capacity can be achieved by controlling the morphology of the particles through the co-precipitation process in a CSTR

Charge/Discharge Cycling in two voltage windows



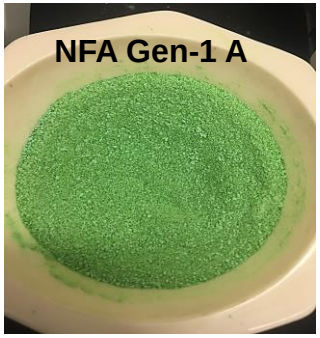
OAK RIDGE National Laboratory

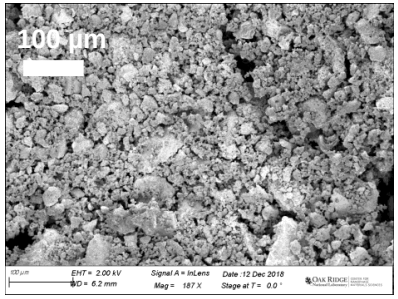
Technical Accomplishments

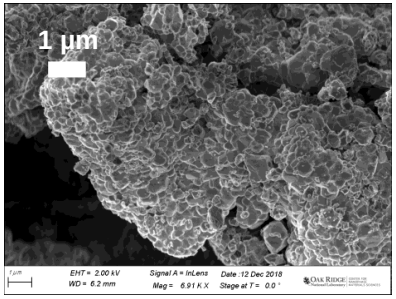
Investigating the compositional landscape – NFA Variants

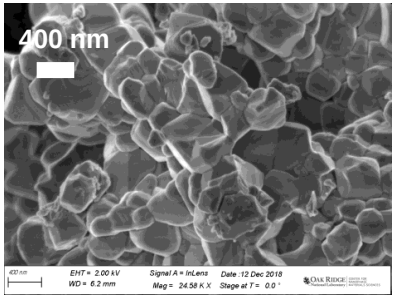
The compositional variants of NFA were successfully synthesized using the sol-gel process

NFA Gen-1 Baseline Variant (NFA Gen-1 A)





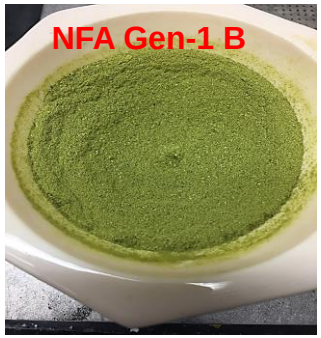


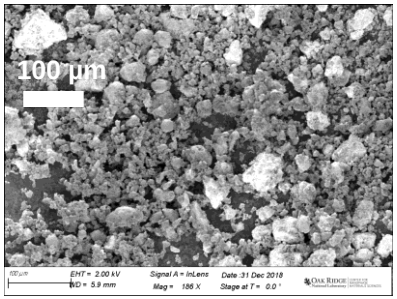


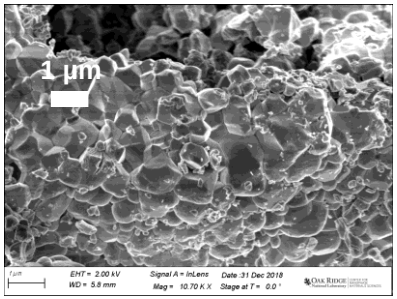
EDS Map
Quantitative analysis

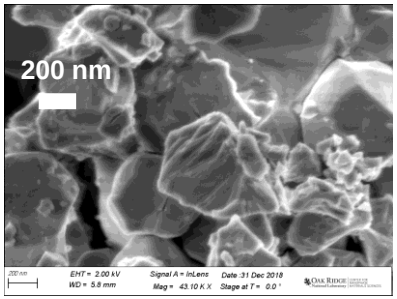
Element	Atom [%]
Oxygen	68.61
Nickel	19.47
Iron	3.87
Carbon	4.37
Aluminium	3.68
	100.00

NFA Gen-1 Iron Rich Variant (NFA Gen-1 B)



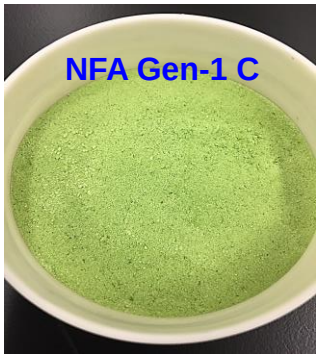


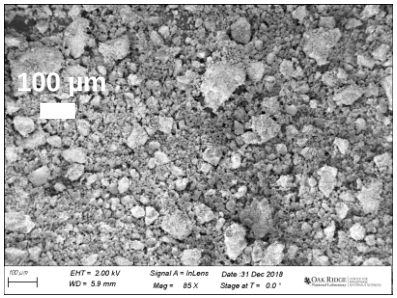


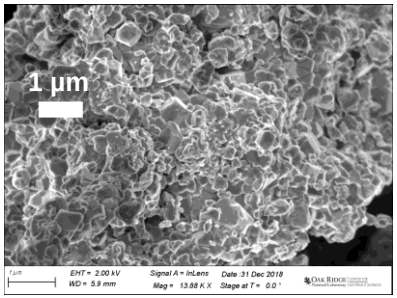


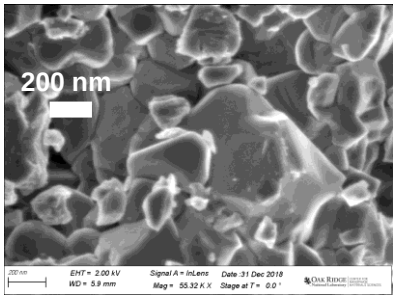
Element	Atom [%]
Nickel	19.77
Iron	10.78
Aluminium	2.24
Carbon	0.00
Oxygen	67.21
	100.00

NFA Gen-1 Aluminum Rich Variant (NFA Gen-1 C)





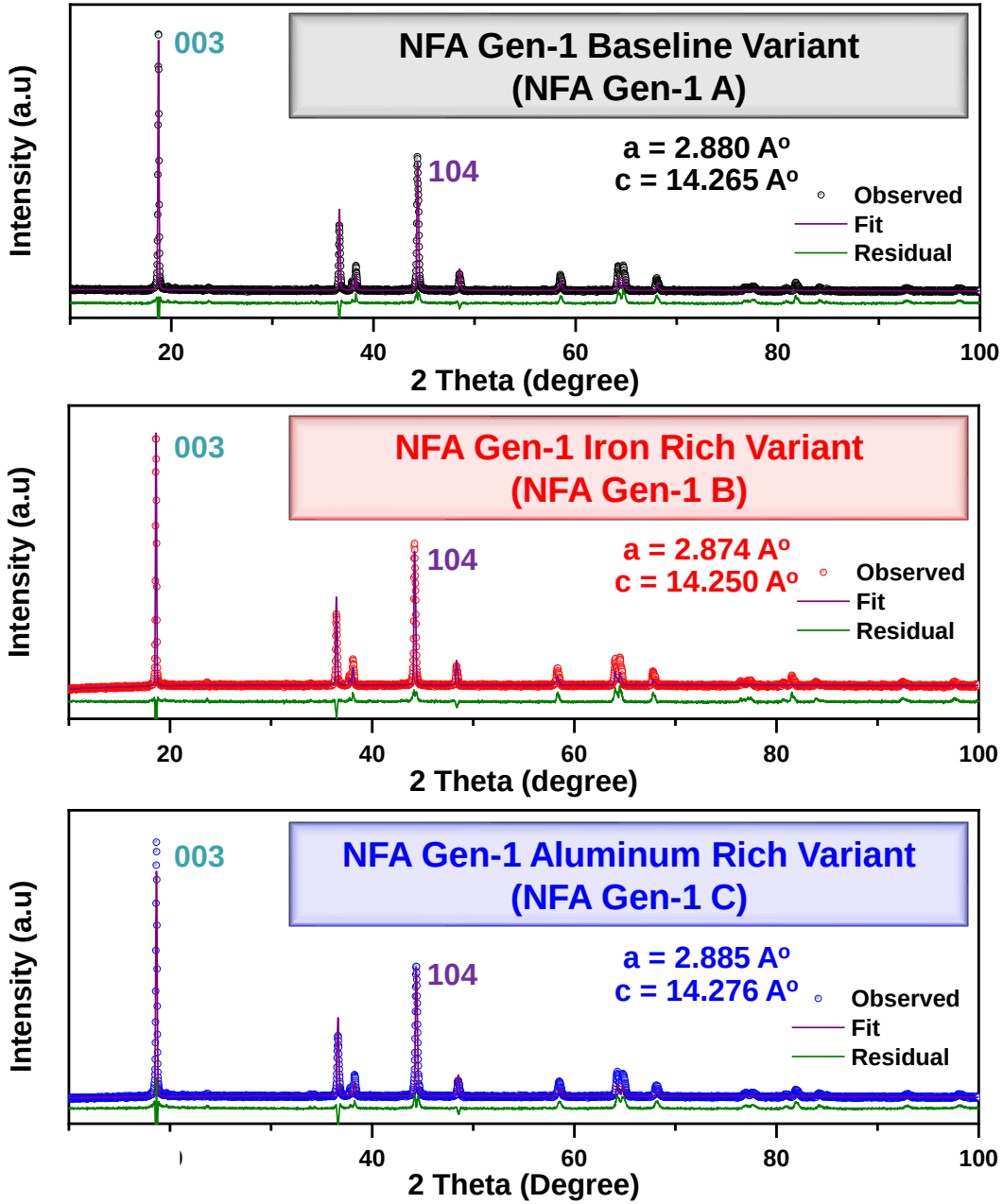




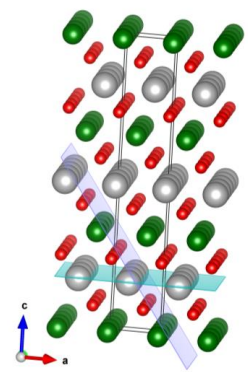
Element	Atom [%]
Nickel	20.09
Iron	2.47
Aluminium	5.85
Carbon	0.60
Oxygen	70.99
	100.00

Technical Accomplishments

Crystallographic Characterization of NFA Compositional Variants



- NFA variants with varying atomic % of aluminum and iron were synthesized using the sol-gel process
- These powders calcined in oxygen atmosphere when subjected to XRD measurements showed very good ordering with I_{003}/I_{104} ratios around ~ 1.8
- Efforts are underway to study the subtle differences in the crystal structure of these NFA variants



Li^{+}

Ni^{3+}, Fe^{3+}, Al^{3+}

O^{2-}

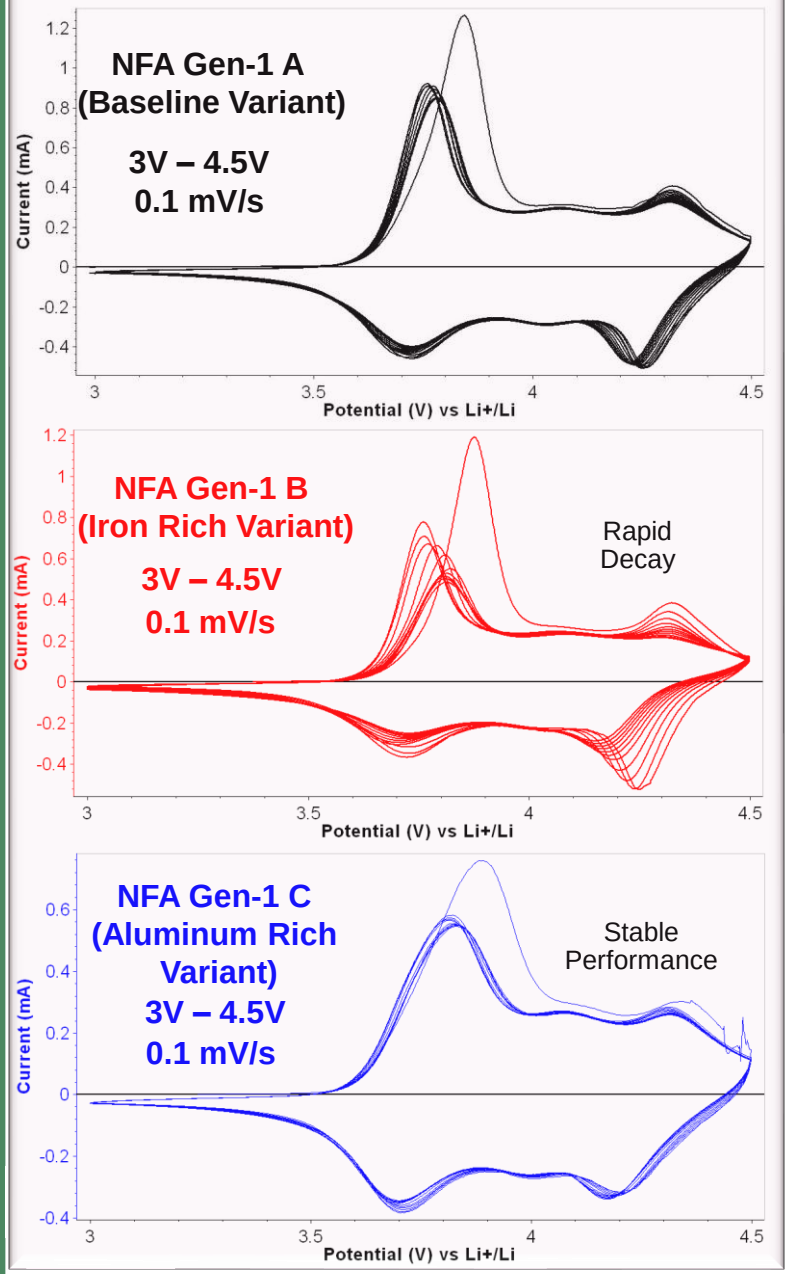
In all cases, R-3m phase was preserved

NFA Gen-1 Compositional Variants synthesized using sol-gel technique showed good phase purity

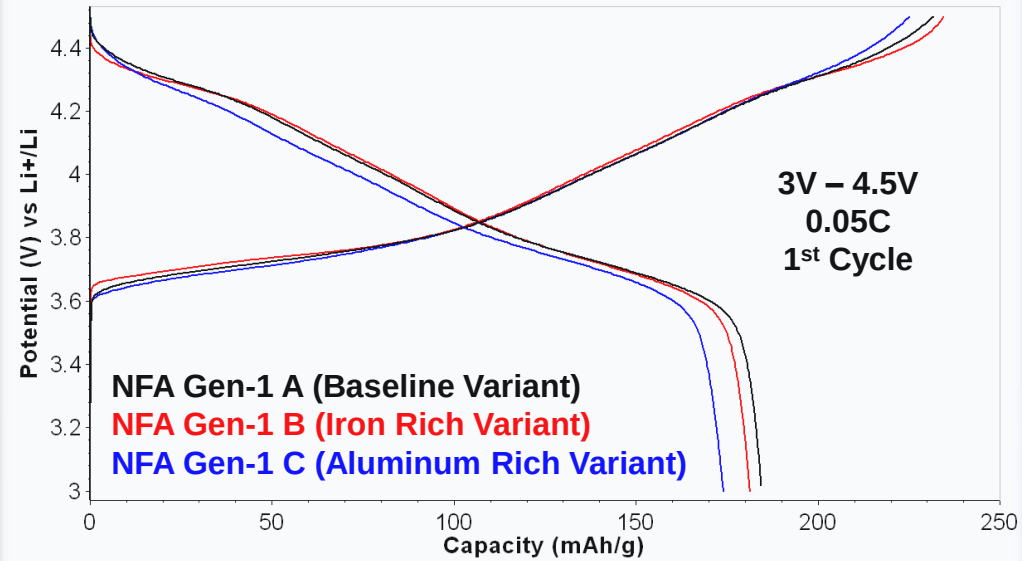
Technical Accomplishments

Electrochemical Performance of the NFA Compositional Variants

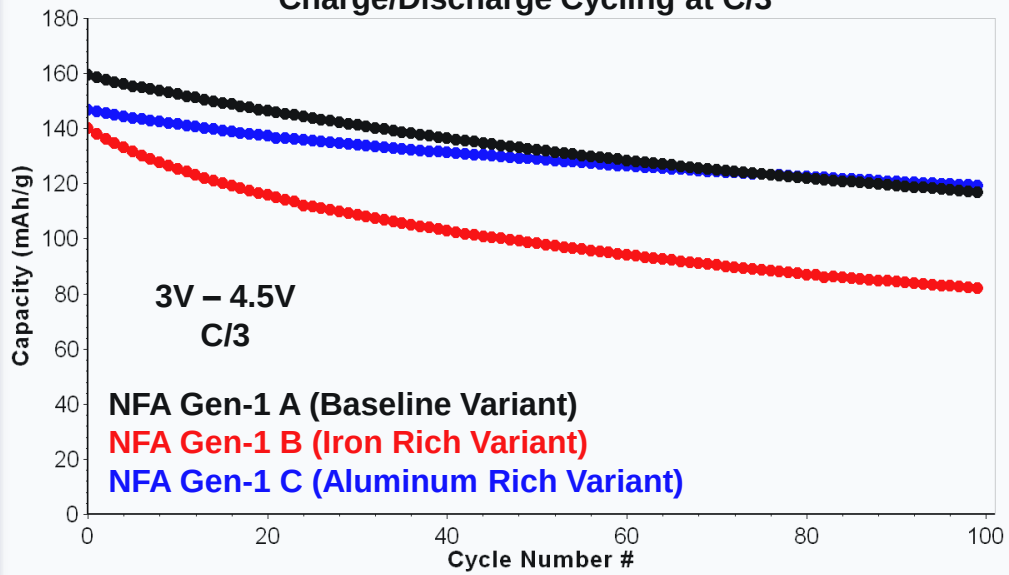
Cyclic Voltammograms (First 10 Cycles)



Charge/Discharge Tests at C/20



Charge/Discharge Cycling at C/3



Response to Previous Year Reviewer's Comments

This project was not reviewed the previous year as it only started on 10/01/2018

OAK RIDGE National Laboratory

Collaboration and Coordination with other institutions

Oak Ridge National Laboratory
Battery Manufacturing Facility

Overall project lead, electrochemical, spectroscopic and material characterization

Contributors and Collaborators: Dr. David Wood, Dr. Jianlin Li, Dr. Zhijia Du, Dr. Rachid Essehli, Dr. Ethan Self, Dr. Hermann Raphael
Participation in Bi-Weekly Update Meetings and Quarterly Update Meetings

Oak Ridge National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

Microstructural and Crystallographic characterization

Nissan Technical Center

Nissan
Innovation that excites

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

XALT Energy a brand of FREUDENBERG

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-19

- Implement co-precipitation process using the CSTR system to scale up the NFA materials, and investigate/optimize the process parameters such as pH, concentration, flow rate, time, temperature and mixing conditions.

- Nickel cationic mixing in the lithium slab along with the control of the physical properties of the NFA materials could have an impact on both the energy density and long term cycle life.

- Employ advanced characterization techniques such as Neutron Diffraction, TXM-XANES, HR-TEM, Elemental Depth Profiling to further characterize the NFA class of cathodes to enable a thorough investigation of the various properties.

OAK RIDGE National Laboratory

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

Proposed Future Research

Ongoing — **FY 19**

- Scale up of NFA-Gen-1 to 2 x 500 g quantities by CSTR and batch processes
- Selection of the scale up process that will yield the NFA Gen-1 cathode
- Build of 30 (2.3 Ah) Project Progress Cells (PPC) with NFA Gen-1 cathodes
- In-house testing of 15 PPC cells
- Delivery of 15 (2.3 Ah) PPC cells to DOE

Planned — **FY 20**

- Synthesis of NFA-Gen-2 cathode by sol-gel
- Material and electrochemical characterization of NFA-Gen-2
- 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 30 Mark-1 cells with NFA-Gen-2*, and inhouse testing of Mark-1 cells

Planned — **FY 21**

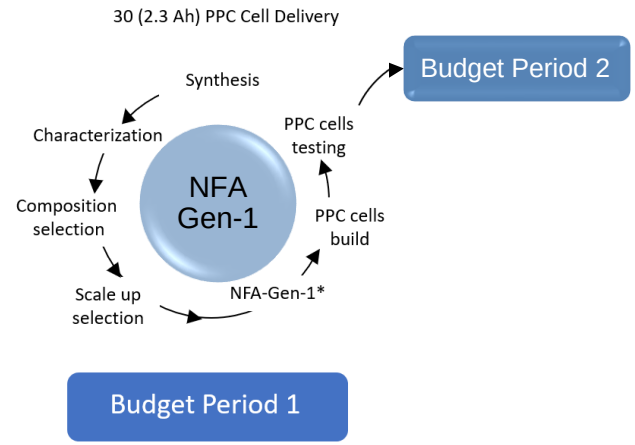
- Build of 30 Mark-2 cells with NFA-Gen-2 and 3 FEC-based electrolytes, and inhouse testing of Mark-2 cells.
- Selection of the best electrolyte that will be used in the build of Mark-3 cells.
- Build of 30 Mark-3 cells with NFA-Gen-2, selected electrolyte and 3 cell designs, and inhouse testing of Mark-3 cells.
- Selection of the best cell design that will be used in the build of the Project Completion Cells.
- Build of 45 (2.3 Ah) Project Completion Cells with the NFA-Gen-2* optimized cell chemistry, and inhouse testing of 15 PCC cells.
- Delivery of 30 (2.3 Ah) PCC cells to DOE.

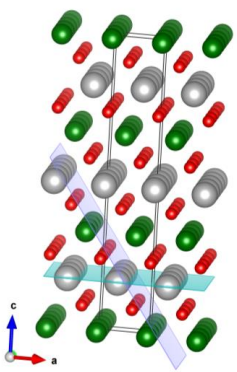
Any proposed future work is subject to change based on funding levels

Summary

Technical Approach:

- ❑ Investigate the material and electrochemical properties of novel cobalt free NFA class of cathodes using the sol-gel synthesis process
- ❑ Scale-up the best NFA composition using co-precipitation process in a CSTR
- ❑ Fabricate 30 project performance cells utilizing the NFA class of cathodes





Li^+

Ni^{3+}, Fe^{3+}, Al^{3+}

O^{2-}

NFA Crystal Structure
R-3m Phase

Accomplishments:

- ❑ Successfully *synthesized NFA Gen-1* cathodes using sol-gel process
- ❑ Performed *material characterization* (XRD, Raman, Mossbauer, SEM and EDS) and *electrochemical assessment* of the NFA Gen-1 cathodes synthesized using sol-gel process
- ❑ Successfully synthesized *NFA Gen-1 compositional variants* using sol-gel process and performed *material and electrochemical characterizations*

Ongoing Work:

- ❑ Scale-up of the best NFA composition using co-precipitation process in a CSTR
- ❑ Build of 30 (2.3 Ah) Project Progress Cells (PPC) with NFA Gen-1 cathodes and in-house testing of 15 PPC cells
- ❑ Delivery of 15 (2.3 Ah) PPC cells to DOE

Continuous Stirred Tank Reactor (CSTR)

Image Source: https://syrris.com/product/atlas-hd-potassium/

Project Progress Cells

Image Source: BMF (ORNL)