High Energy Density Li-ion Cells for EV's Based on Novel, High Voltage Cathode Material Systems

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Project ID: # ES213

Overview

Timeline

- Start Date: October, 2013
- End Date: October, 2015
- Percent Complete – 75%

Barriers

- Insufficient energy density of Li-ion battery systems for PHEV and EV applications.
- Insufficient cycle and calendar life of Li-ion battery systems.
- Accelerated energy loss at elevated voltages for Li-ion technology.

Budget

- Total Project Funding: $3,480,000
  - -DOE Share: $2,160,000
  - -FFRDC: $600,000
  - -Contractor Share: $720,000
- 2014 Funding: ~$1,400,000
- 2015 Funding: ~$1,780,000

Partners

- Argonne National Laboratory:
  - ➢ Advanced Cathode Materials Development
- Lawrence Berkeley National Laboratory:
  - ➢ Advanced Cathode Materials Development
- DuPont:
  - ➢ High Voltage Electrolyte, Separator Development
- Nanosys/OneD Material, LLC:
  - ➢ High Capacity Anode Materials Development

Relevance

- New cathode and anode electrode materials and Li-ion cell components are required to enable major advances in the energy density of battery systems for transportation technologies.
- The layered and layered-layered "NMC" class of cathode materials paired against a silicon based anode offer the greatest potential to meet the PHEV and EV performance goals.
- Utilization of the inherent capacity in these systems can be greatly increased if higher voltage operation can be enabled.
- There are multiple interacting failure mechanisms at the materials and cell level that are barriers to achieving the system level battery performance goals.
- A focus on cell level development utilizing advanced materials and components is critical to achieving major breakthroughs in battery performance.

Relevance - Project Objectives

Project Goal:

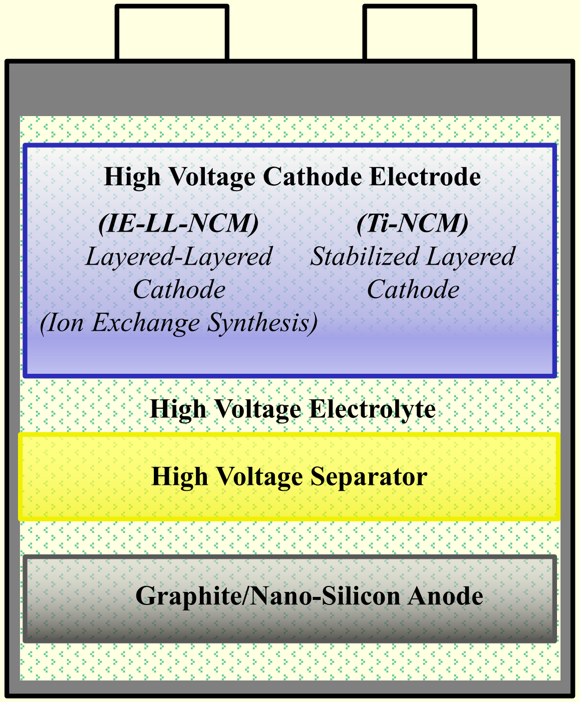
The goal of this project is to develop and demonstrate new high energy, high voltage capable Li-ion materials and cell components to enable high energy, high power Li-ion cells that have the potential to meet the performance goals of PHEV40 and EV light-duty vehicles.

Performance Objective:

The objective is to demonstrate a PHEV40 cell with an energy density of 250 Wh/kg and an EV light duty cell with an energy density 350 Wh/kg that can meet the cycle life goals for those applications.

Cell Level Goals:

Energy Storage Requirements			
Characteristics	**Unit**	**PHEV40**	**EV**
Specific Discharge Pulse Power	W/kg	800	800
Discharge Pulse Power Density	W/l	1600	1200
Specific Regen Pulse Power	W/kg	430	400
Regen Pulse Power Density	W/l	860	600
Recharge Rate		C/3	C/3
Specific Energy	Wh/kg	200	400
Energy Density	Wh/l	400	600
Calendar Life	Year	10+	10
Cycle Life (at 30°C with C/3 charge and discharge rates)	Cycles	5,000	1,000
Operating Temperature Range	°C	-30 to +52	-30 to +65



Project Technical Targets

Year 1 (Gen 1):
Cell Level 230 Wh/kg, 1000 cycles (PHEV)

Year 2 (Final Deliverable Cells):
Cell Level 250 Wh/kg, 5000 cycles (PHEV), Cell Level 350 Wh/kg, 1000 cycles (EV)

Second Year Technical Milestones

- Milestones leading to final deliverable cell build incorporating high-energy active materials, advanced electrolytes, and optimized cell designs.

Cell Build Progression:

Year 1 | Year 2

Baseline (LL-NCM/Graphite) → Gen 0 (NCM/Graphite) → Gen 1 (Advanced Materials) → Gen 2 (Advanced Materials) → Final Deliverables (Optimized System)

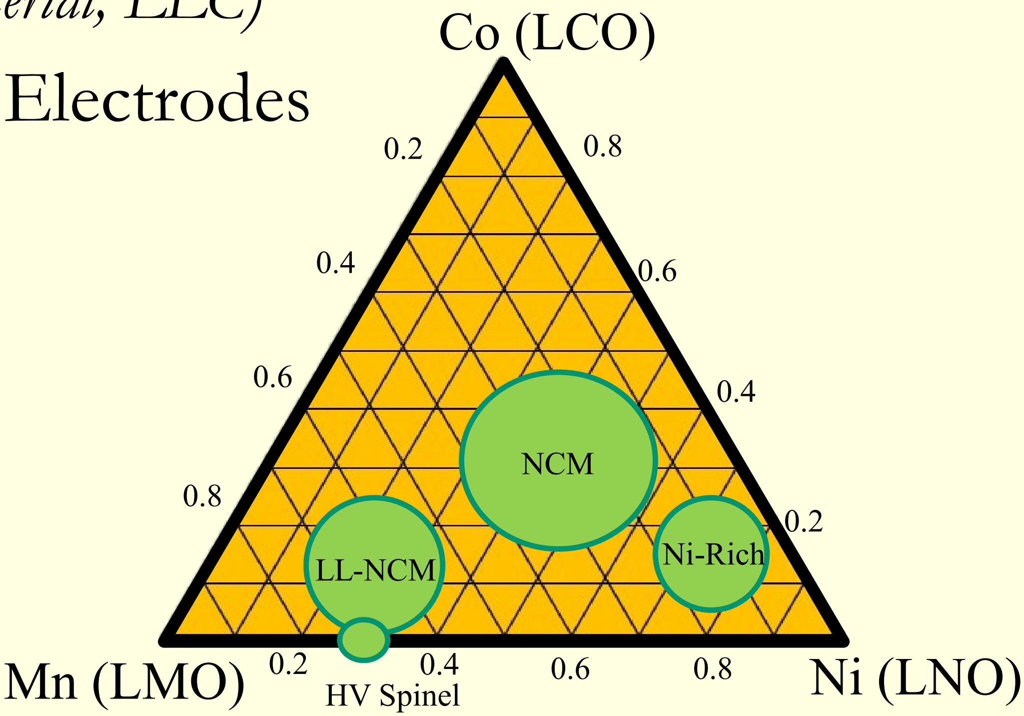
Second Year Milestones and Status

Milestone	Type	Description	Status
Selection of GEN 2 Cathode Materials	Technical	Physical and chemical characterization of Li-ion battery materials	Complete
Completion of GEN 2 Small Cell Testing	Technical	Projected Cell Performance Information, and Cell Test Plan	In progress
Provide Initial Testing Data and Deliver Cells to DOE	Technical	Test plan coordinated with the DOE and test cells delivered to directed site.	Pending final cell build in Q4

Technical Approach

Development focused on addressing key current barriers to achieving high capacity long life Li-ion cells.

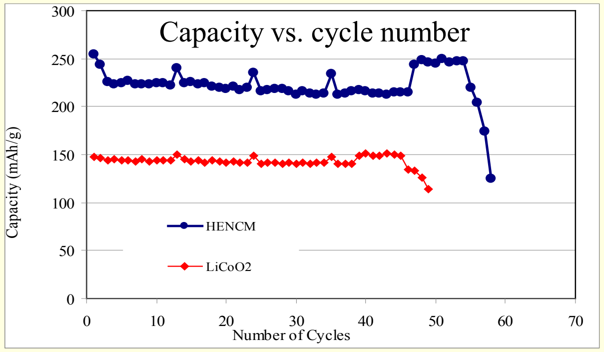
- Higher Capacity, Higher Voltage Active Materials
  - IE-LLS-NCM *(Argonne National Laboratory)*
  - Stabilized-NCM *(Lawrence Berkeley National Laboratory)*
  - Si-Graphite Composite *(OneD Material, LLC)*
- Higher Rate Capability Cathode Electrodes
  - Ion Exchange Synthesis
  - Composite Cathode Formulations
- Higher Voltage Operation
  - Cathode Surface Stabilization
  - Stable Electrolytes *(DuPont)*
  - Stable Separator *(DuPont)*

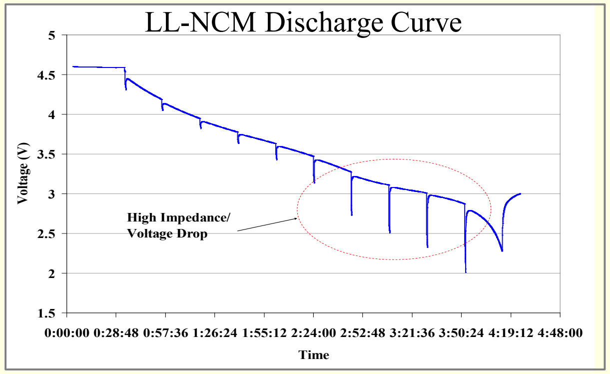


Technical Approach
High-Energy "Layered-Layered" NCM

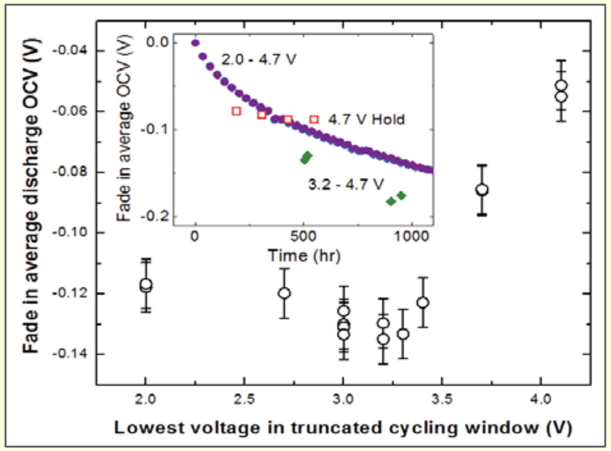
Advantages:
- High specific capacity – 230-250 mAh/g.
- Greater stability at high voltages.

Barriers:
- High impedance.
- State of charge dependent impedance and impedance growth.
- Voltage fade mechanism.
- Accelerated capacity loss if not stabilized.
- Low utilization in full cells.
- Low tap density.
- Wide voltage window.





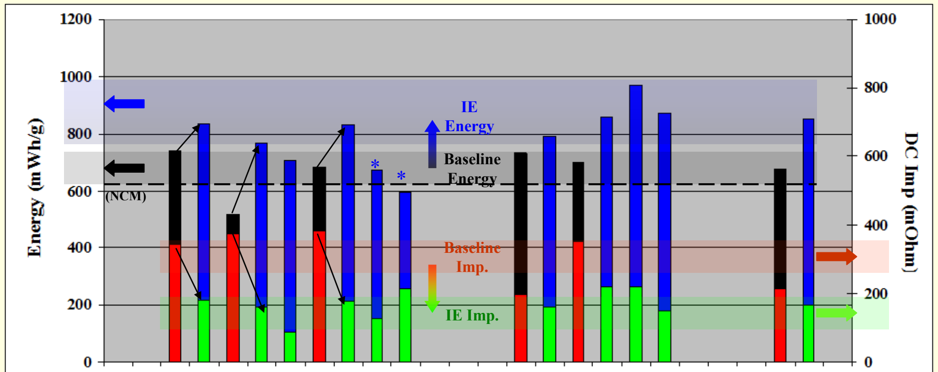
OCV drop during cycling LL-NCM within different voltage windows



Technical Approach
High-Energy "Layered-Layered" NCM

- Development strategy based on initial work done by Dr. Chris Johnson at Argonne National Laboratory and continued at Farasis Energy.
- Ion-Exchange Synthesis Approach
  - Na based LL-NCM material is used as a precursor to form Lithium LL-NCM through an ion-exchange process with Lithium (IE-LL-NCM)
  - Composition and synthetic conditions can be tuned to produce a high voltage spinel component to the LL materials → Layered-Layered-Spinel NCM (LLS-NCM)
  - Initial work indicates synthetic approach leads to materials with lower impedance and greater utilization.
- Potential for New Structural and Performance Characteristics
  - Potential to avoid O3 stacking and transition metal movement during cycling.
  - Route to creation of materials with larger interlayer spacings.
  - Route to introduce disorder into materials.
  - Route to materials with different surface morphology, stacking faults.

Comparison of energy and impedance measured for a number of IE and conventional LL-NCM compositions synthesized



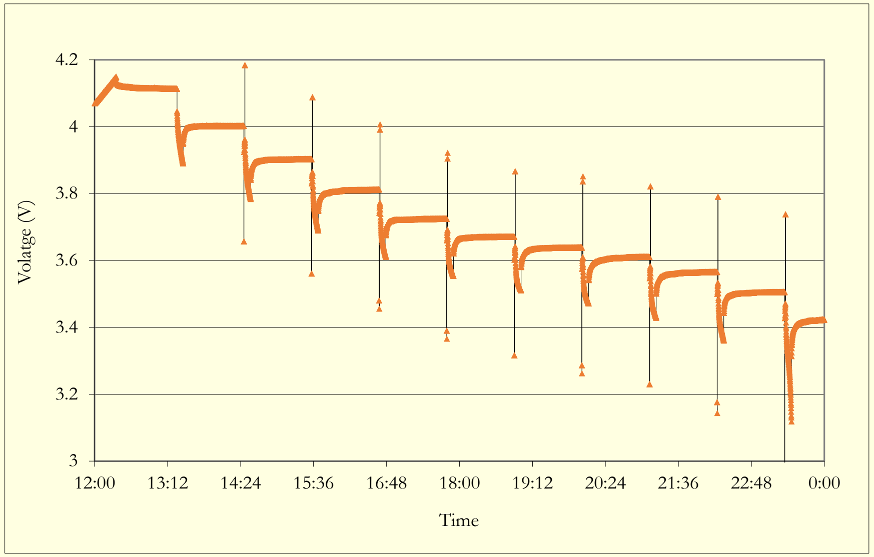
IE-LL Material Compositions
Energy - IE/Conventional – Blue/Black
Impedance – IE/Conventional – Green/Red

Technical Approach
Layered NCM Materials

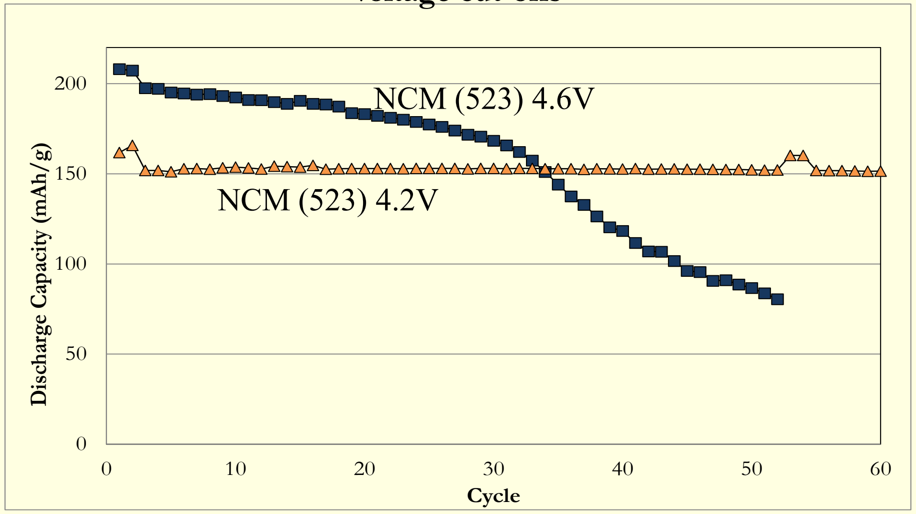
Advantages:
- Good rate capability
- High tap density
- Good stability at moderate voltages
- Reasonable average voltage

Barriers:
- Stability at high voltages.

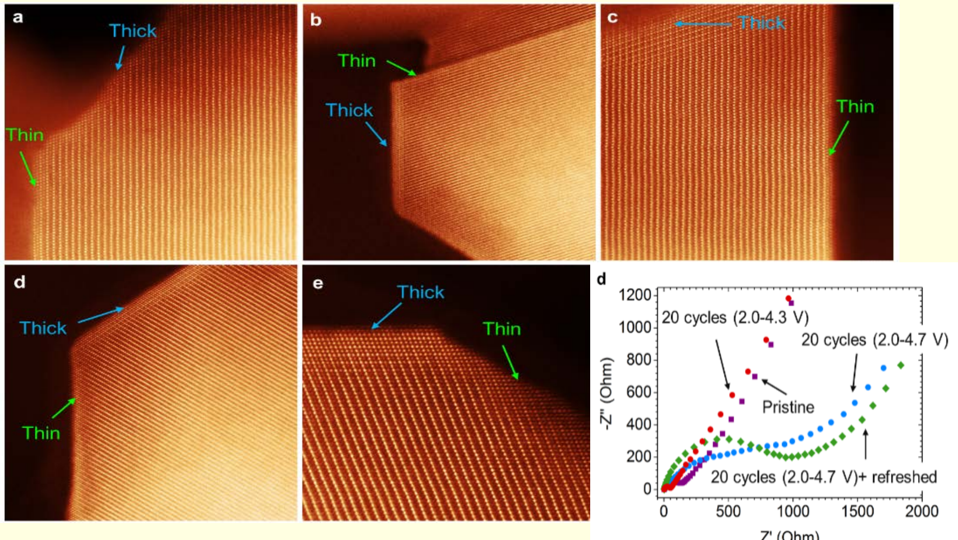
NCM/Graphite Cell HPPC test



Relative stability of NCM (523) cathode to different upper voltage cut-offs



Rock-salt surface reconstruction occurs upon electrolyte exposure alone, but is more severe when electrodes are cycled to 4.7V



Lin, F., *et al.*, Nature Communications, March 2014

Technical Approach
Layered NCM Materials

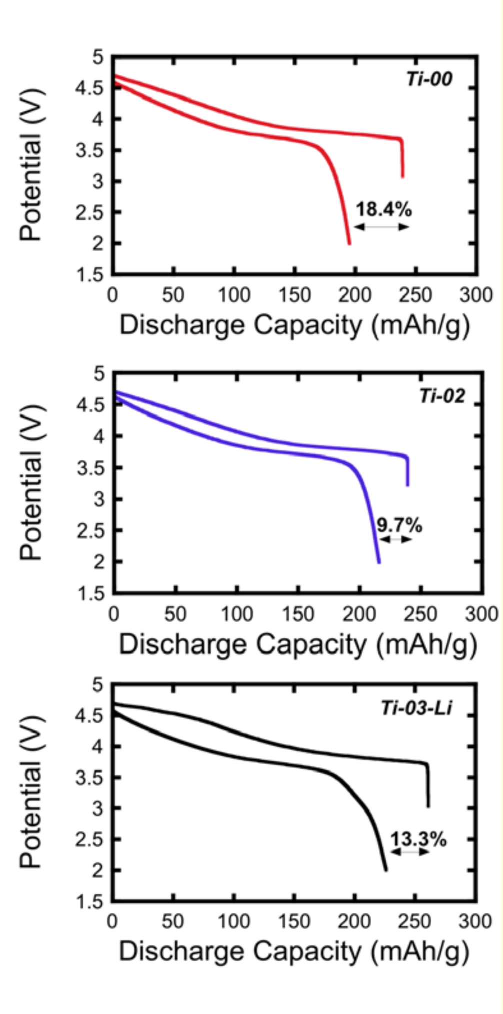
Surface Stabilization:

- Coatings/surface treatments.
- Decrease active material surface reactivity to electrolyte.

Doping:

- Bulk addition of elemental dopants to NCM composition.
- Stabilize layered structure in highly charged state.
- Aliovalent substitution to limit oxygen loss/surface reconstruction.

High Voltage Formation Curves of Ti-Doped NCM(424)

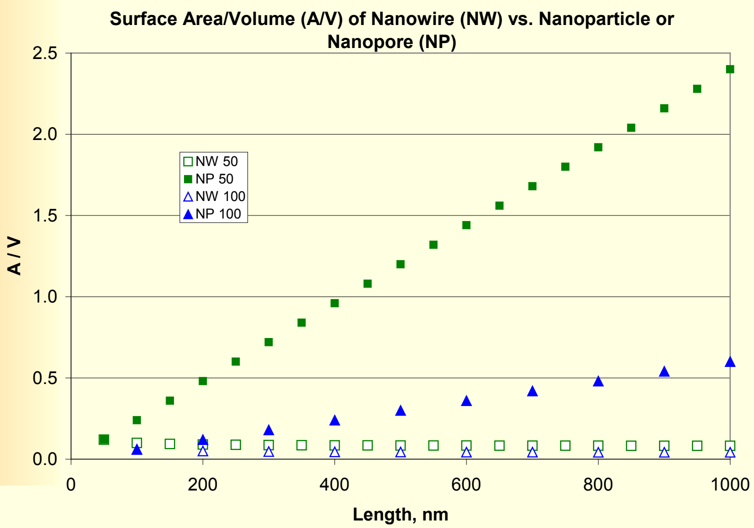


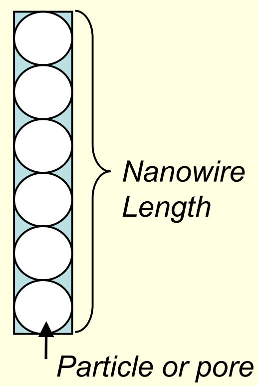
Kam, Kinson C., et. Al, J. Mater. Chem, 2011, 21 9991.

Technical Approach
Nano-Silicon Anode Materials

Nanosys SiNANOde Approach vs. Hollow/Porous Approach

SiNANOde	Hollow/Porous Si
Low A/V & Intact NW after cycling	High A/V; defects
Pack density similar to graphite	Pack density lower than graphite
Mass-produced with a competing cost * high Si utilization	Difficult and expensive to commercialize

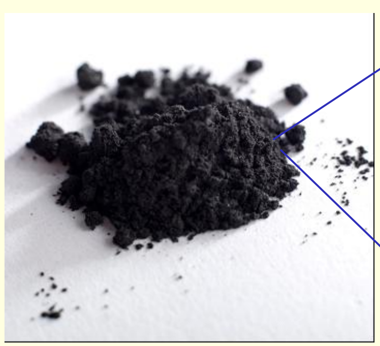


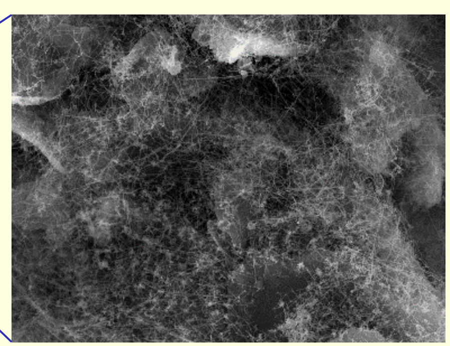


- A Si nanowire is equivalent to several Si particles or pores with an identical diameter.
- Si nanowire has lower surface area/volume ratio (A/V) and hence less side-reaction with electrolyte and better cycle life

SiNANOde production process: Directly grow Si nanowires on graphite powders

- Cost effective and high Si utilization
- Improves dispersion in slurry and drop in process (just replace graphite powders)
- Si-C conductivity improvement
- Si% or anode specific capacity is controllable, focusing on **500 ~ 1600 mAh/g**
- High electrode loading, as high as $1.5 g/cm^3$
- Good cycling performance, cycled >1000 times





Technical Approach
High Voltage Li-ion Cell

- Develop high voltage capable fluorinated electrolytes with proper battery system design to enable operation up to 4.7 V:
  - ➢ Increase cell **Energy Density** by enabling higher voltages
  - ➢ Increase cell **Power Density** by maintaining/improving conductivity
  - ➢ Lower System **Costs** by enabling higher voltages, reducing number of cells needed and potentially simplifying packaging requirements
  - ➢ Good wettability will drive similar manufacturing processes
- Incorporation of separators that are inherently stable to high voltage operation.
- Improve adhesion stability of electrode laminates.
- Incorporation of low reactivity electrode laminate components.

Technical Accomplishments: Baseline Deliverable Cells

Milestone 1: Completion of Baseline Cell Deliverables

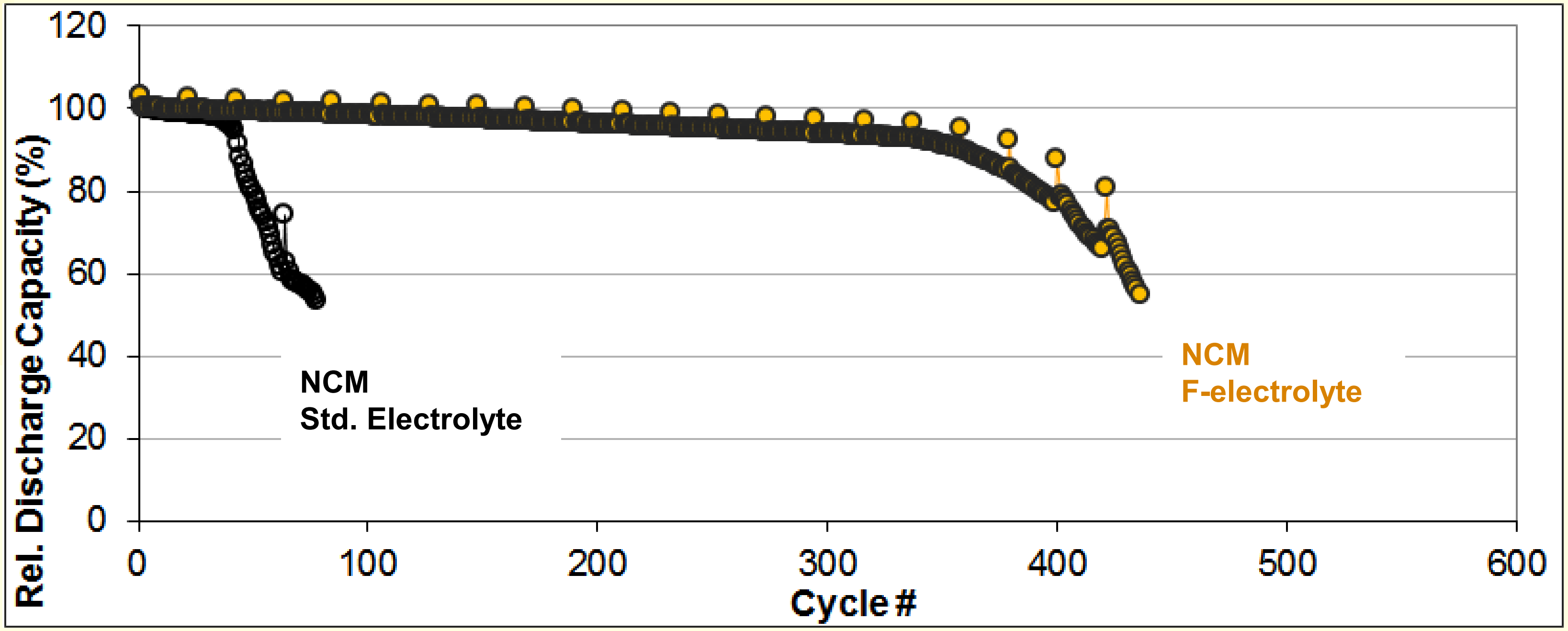
- HE-NCM//Graphite Li-ion Pouch Cells using “standard” electrolyte.
- 1.6 Ah capacity
- Test plan developed with INL and DOE program managers.
- **Fourteen cells being tested at Idaho National Laboratory since August 2014 will serve as a point of comparison for the final deliverable cells.**

Baseline Pouch Cell

Technical Accomplishments: High Voltage Electrolyte Development

Milestone 2: Completion of Round 1 Electrolyte Evaluation

- Novel electrolytes used in this program were screened in both 18650 and pouch cells formats using conventional NCM//Graphite based chemistries.
- Ongoing work involves formulation optimization, formation protocol studies, failure mode analysis, and gas generation measurements.



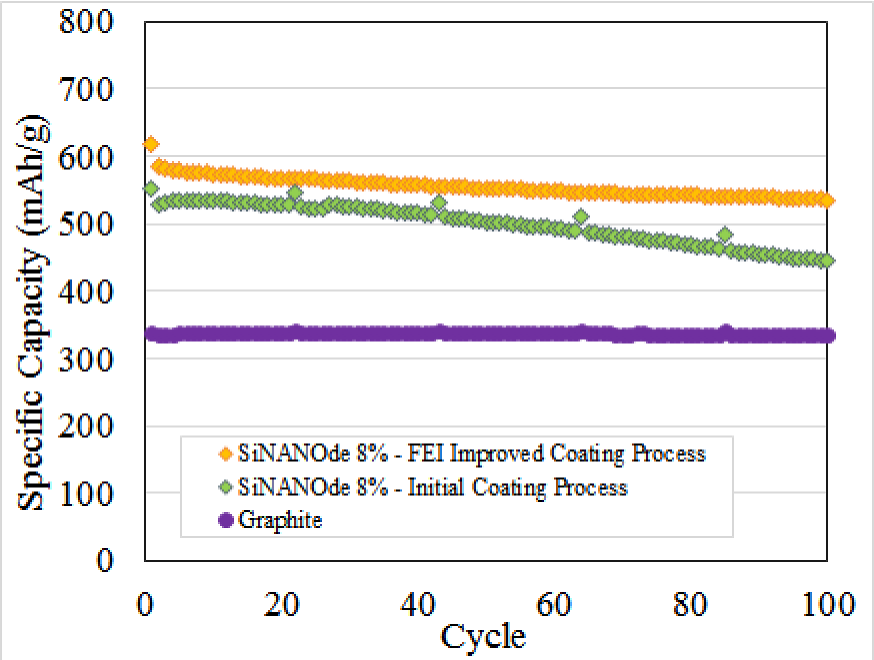
"Gen 0" Cells

Testing in 2 Ah
18650 cells
3.0 – 4.4 V
0.5C charge
0.5C discharge

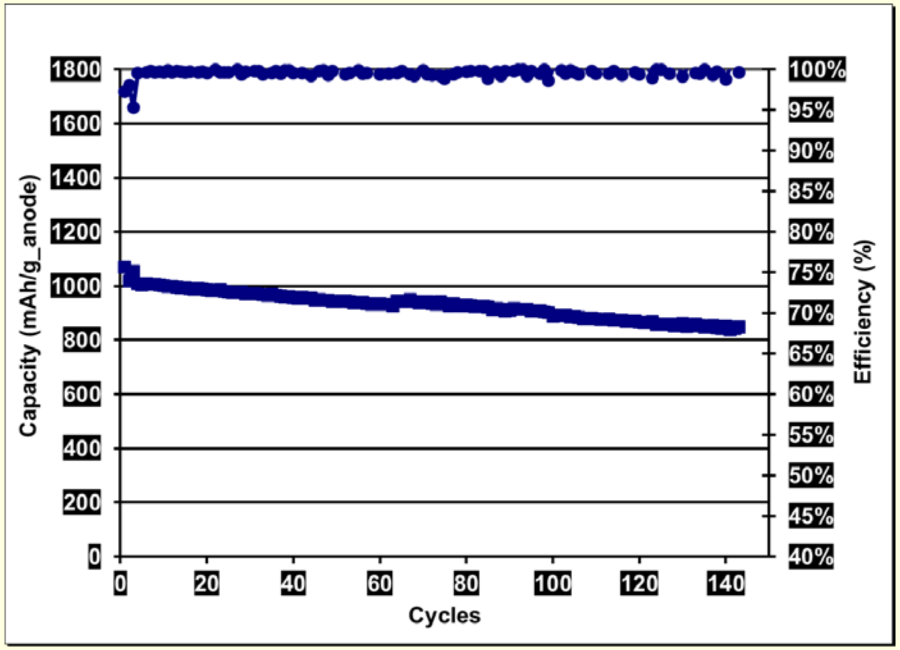
Significant improvements in stability at high voltages relative to baseline carbonate electrolytes have been observed for the best-performing novel electrolytes.

Technical Accomplishments
Si@C Negative Electrode Development

- Development carried out in conjunction with subcontract to OneD Materials.
- Si nanowire / Graphite composite materials.
  - Examined multiple binders, alone and some in combination, to optimize electrode adhesion.
  - Novel slurry processing conditions were developed and optimized to ensure uniform electrode coatings.
  - The new process was scaled for production of Gen 1 negative electrodes (based on 8 % Si material).
- **Capacity is much higher than graphite, but capacity retention still lags behind that of carbon based anodes.**



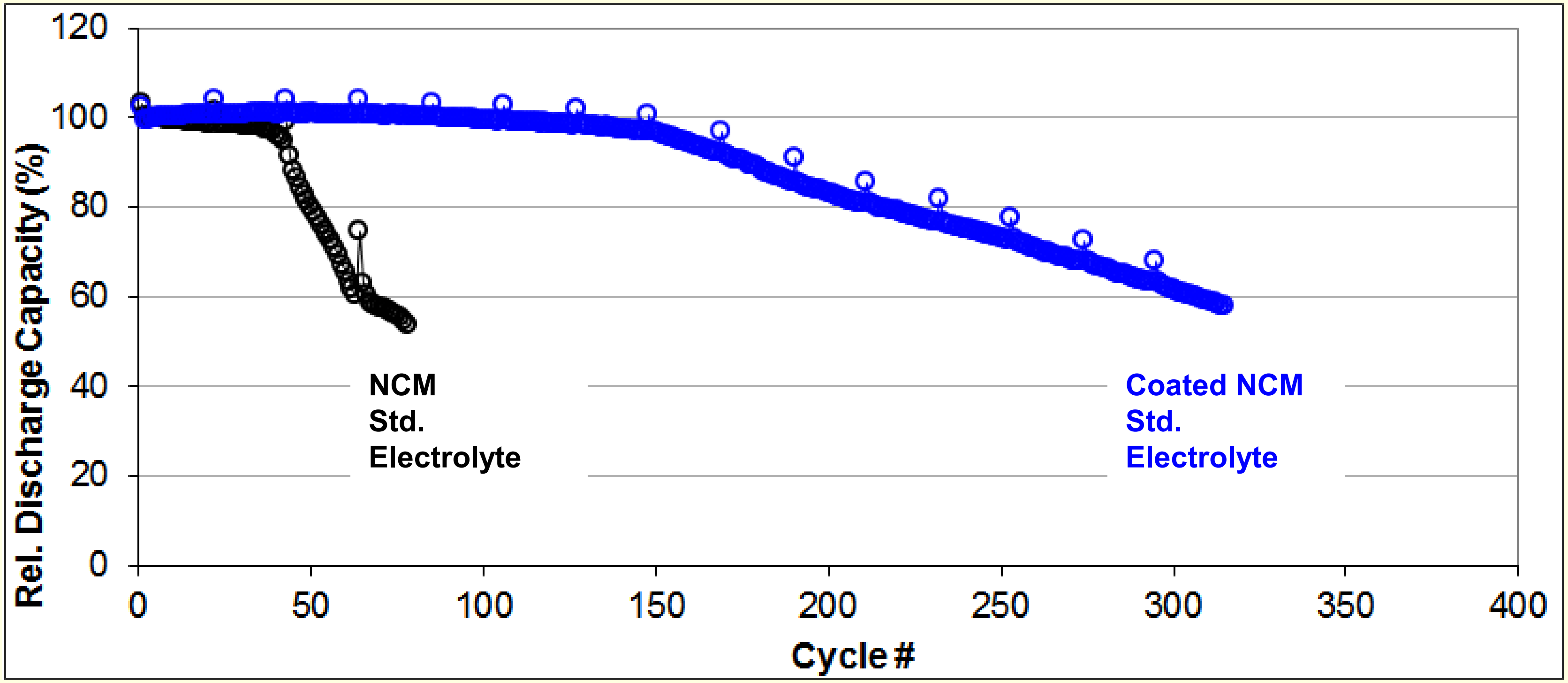
Li half-cell cycling data shows improved capacity retention for improved coating process.



Gen 2 cell build will make use of higher Si content composites to increase energy density.

Technical Accomplishments NCM Materials Development

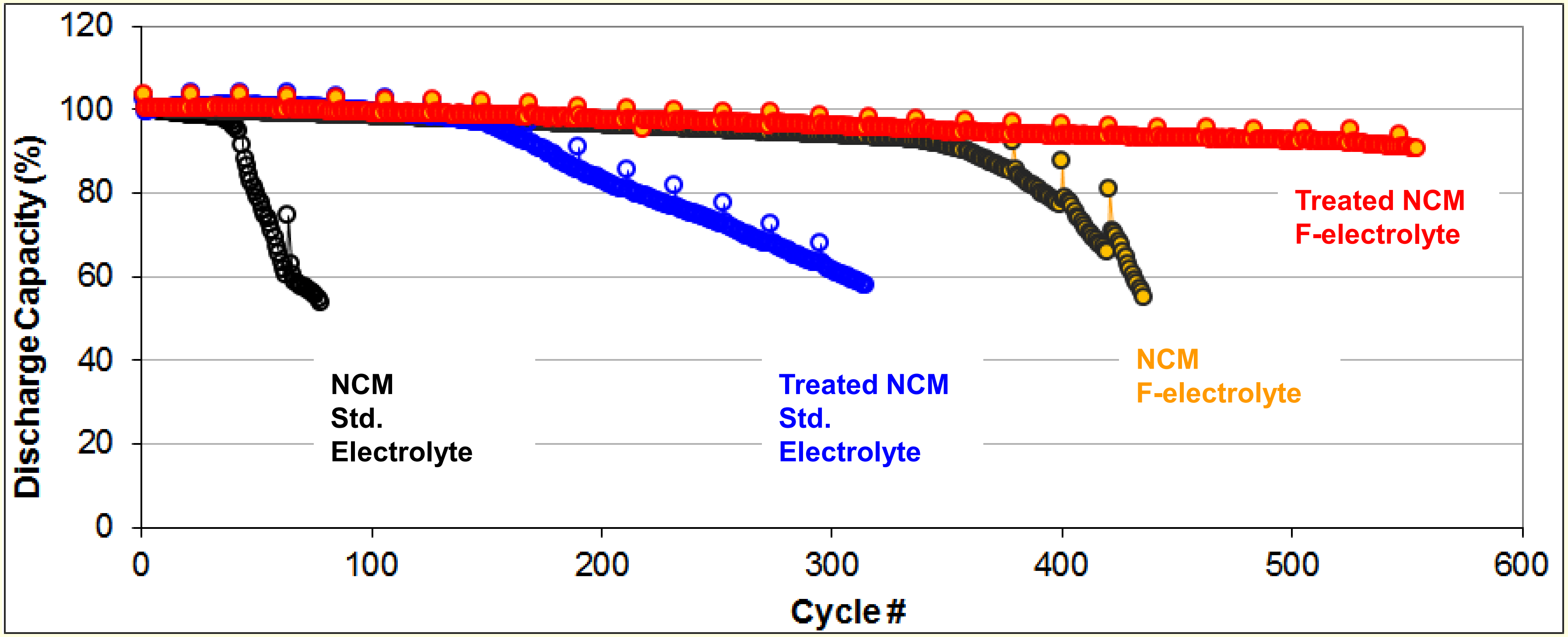
- Bulk-substitution (see poster ES-258)
  - Performed initial experiments to evaluate feasibility of low cost synthetic routes of doped NCM compositions.
  - Initial process development of surface stabilization for several NCM cathode compositions.
  - Cell design and initial evaluation of stabilized NCM materials at high voltage in full pouch cells.
- Surface coatings
  - Evaluated multiple coating chemistries including conventional and Farasis proprietary technology.



Testing in 2 Ah
18650 cells
3.0 – 4.4 V
0.5C charge
0.5C discharge

Coatings show great promise in impeding deleterious reactions responsible for impedance rise and capacity fade.

Technical Accomplishments
Interplay of Coatings and HV-Electrolytes



Testing in 2 Ah 18650 cells, 3.0 – 4.4 V, 0.5C charge, 0.5C discharge

- **Coatings work in tandem with HV-stable solvents to increase cell cycle life.**
- A proposed mechanism is that the HV-electrolyte minimizes reactivity at fresh electrode surfaces that become exposed within the cell due to mechanical fatigue or other material changes.

Technical Accomplishments
Generation 1 Cell Build

Milestone 3: Selection of Gen 1 Cathode Materials

- **Based on over 50 compositions examined in the first year of this project, the best-performing cathode materials prepared during this project, one composition for IEx-HE-NCM and two different coated NCM materials were selected for inclusion in Gen 1 cell testing with advanced anodes and electrolytes.**
- Scaled-up coating of commercial NCM materials was performed at the multi-kg level by Farasis.
- Synthesis of the chosen IEx-HE-NCM material was scaled-up at Farasis to the kg-level to provide sufficient material for preparation of electrodes for the Gen 1 cell build.

Technical Accomplishments Generation 1 Cell Build

Milestone 4: Completion of Generation 1 Cell Build

- **The Gen 1 cell build consisted of 28 designs incorporating advanced cathodes, anodes, and electrolytes developed in the first year of the project.**
- Cycle life testing is ongoing.
- A conventional, uncoated NCM was used as a cathode control to isolate the influence of coatings.
- Full factorial design was not used due to material constraints.

Cathode	Anode	Electrolyte
Coated NCM 1	Graphite	Std.
		F1
		F2
	3 % Si@Graphite	Std.
	8 % Si@Graphite	Std.
		F1
		F2
Coated NCM 2	Graphite	Std.
		F1
		F2
	3 % Si@Graphite	Std.
	8 % Si@Graphite	Std.
		F1
		F2
IEx-HE-NCM	Graphite	Std.
		F1
		F2
	3 % Si@Graphite	Std.
	8 % Si@Graphite	Std.
		F1
		F2
Blend of Coated NCM 1 and IEx-HE-NCM	Graphite	Std.
		F1
		F2
	3 % Si@Graphite	Std.
	8 % Si@Graphite	Std.
		F1
		F2
Uncoated NCM control	Graphite	Std.
		F1
		F2
	3 % Si@Graphite	Std.
	8 % Si@Graphite	Std.
		F1
		F2

Collaborations and Coordination with Other Institutions

Argonne National Laboratory (Chris Johnson)

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- Layered-Layered-(Spinel) *(LL-S)* NCM Cathode Material Development – Developing an ion-exchange synthetic approach to address the impedance and voltage fade barriers of high capacity LL-NCM cathode materials.

Lawrence Berkeley National Laboratory (Marca Doeff):

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- High Voltage Stabilized NCM Cathode Material Development – Develop and optimize doping and advanced coating methods to stabilize high capacity NCM materials to operation at high voltages.

Nanosys/OneD Material, LLC (Yimin Zhu):

Industry – Subcontractor providing materials and development guidance for project.

- Nano-Silicon Graphite Composite Anode Material Development – Optimize nano-silicon graphite composites for long term cycling stability.

DuPont (Srijanani Bhaskar):

Industry – Partner providing materials and analytical work for project.

- High Voltage Capable Electrolytes and Cell Components- Develop new fluorinated electrolyte systems, additives and separators with exceptional high voltage stability to advanced active materials.

Proposed Future Work

- Continue to develop and optimize ion-exchange LL-NCM compositions for capacity, rate capability, and stability focusing on Na/Li ratio in precursor.
- Perform detailed structural and electrochemical characterization of new materials and impact of compositional and synthesis variables on material.
- Evaluate new IE-LL-NCM materials using "voltage fade" protocols.
- Develop synthetic methods for making aliovalent doped high-Ni-content NCM materials.
- Select and scale synthesis of best materials for Gen 2 cell build.
- Optimization of Silicon anode electrode for final deliverable cell build.
- Test cell component lightweighting strategies to increase energy density (*e.g.*, thinner separators or lighter current collectors).
- Incorporate high-Li content additives in cathode to help offset irreversible capacity loss and thereby increase energy density.
- Plan final deliverable cell build and design, build and test cells.

Responses to Reviewer Comments

- Question 1: Reviewer 2 noted that it is “important to produce Generation 1 cells with a more traditional anode,” to serve as a baseline. We have included this suggestion in the Gen 1 cell build and also included an unmodified-NCM as a cathode baseline.
- Question 2: Reviewer 4 commented that “the project team should show actual numbers in the capacity instead of normalized values.” In this presentation, any graphs using normalized capacity numbers have been annotated with the actual cell capacity for reference.

Summary Slide

- Project is relevant to the development of high energy Li-ion cells capable of meeting the PHEV40 and EV performance goals set by DOE.
- Approach to addressing current cell level performance barriers based on strong advanced materials technical foundation.
  - Improvements in capacity and rate capability were achieved for “layered-layered” cathode materials synthesized via the ion-exchange synthetic route.
  - Bulk-doping of NCM materials with Ti improves stability when cycling at high voltage.
  - Cell component development aimed at enabling long term high voltage operation.
- Strong coordination with subcontractors and partners with steps taken to allow parallel development of multiple cell components for incorporation into high performance cells.
- Future work will continue advanced cell development and optimization culminating in the final deliverable cell build at the end of Year 2 with a target energy density of 350 Wh/kg.

Technical Back-up Slides

Mechanistic Aspects of Ion-Exchange Synthesis of Layered-Layered NCM

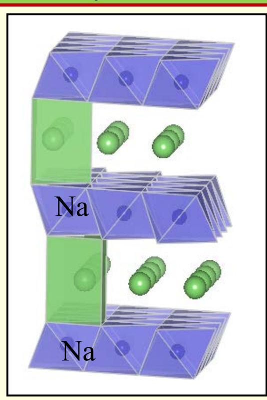
Impact of ion-exchange route on structure of high energy materials:

Mixed Metal Hydroxide Precursor

Li_2CO_3

Na_2CO_3
Li_2CO_3

Na(Li)-based layered $Ni_xCo_yMn_z$ oxide

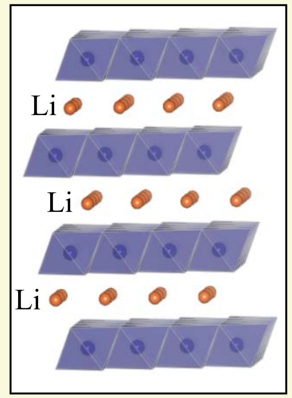


P2 stacking created due to preference of Na for this coordination geometry

LiX / ROH

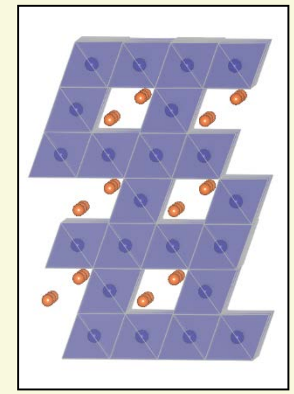
Low temperature ion-exchange: relative sliding of TM slabs, but no gross reorganization of oxide matrix

Li-rich Layered $Ni_xCo_yMn_z$ oxide (LL-NCM)

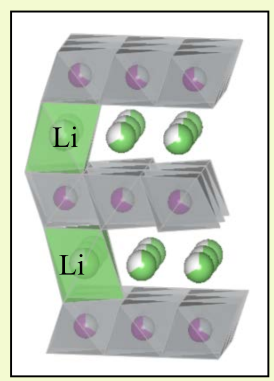


O3 Stacking

Cycling

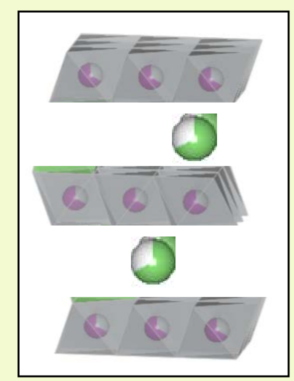


O3 (Spinel)



Stacking Faults, "O2"

Cycling

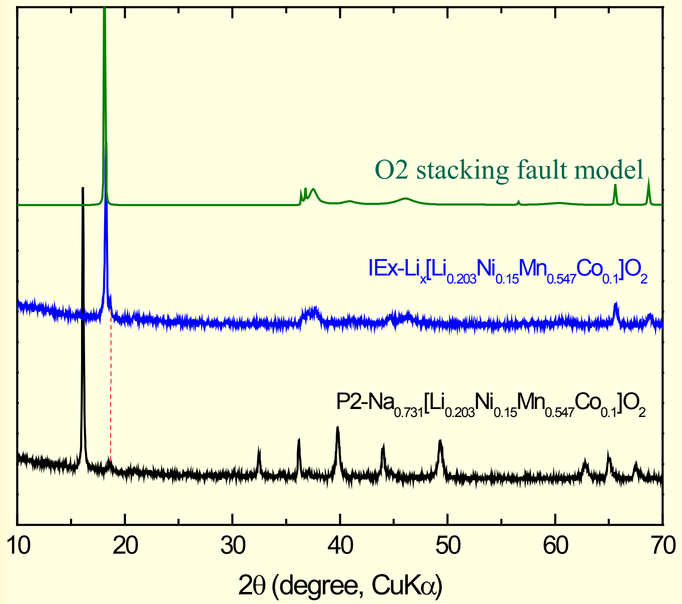


Stacking Faults, "O2"

Ion-Exchanged Li-rich Layered $Ni_xCo_yMn_z$ oxide (IEx-LL-NCM)

Ion-Exchange Synthesis of Layered-Layered NCM

- X-ray diffraction indicates good layering order but significant disorder in other crystallographic directions suggesting presence of stacking faults.



- Faults in shear order of crystal lattice during ion exchange
- Still strongly layered
- Local c-axis disorder
- Structural modeling indicates presence of extensive stacking faults with O2 layering characteristics.