Tailoring Spinel Electrodes for High Capacity Li-Ion Cells

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Annual Merit Review
DOE Vehicle Technologies Program
Washington, DC
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ES049

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete:
  - 15%

Budget

- Total project funding
  - 100% DOE
- Funding in FY16: $500K

Barriers

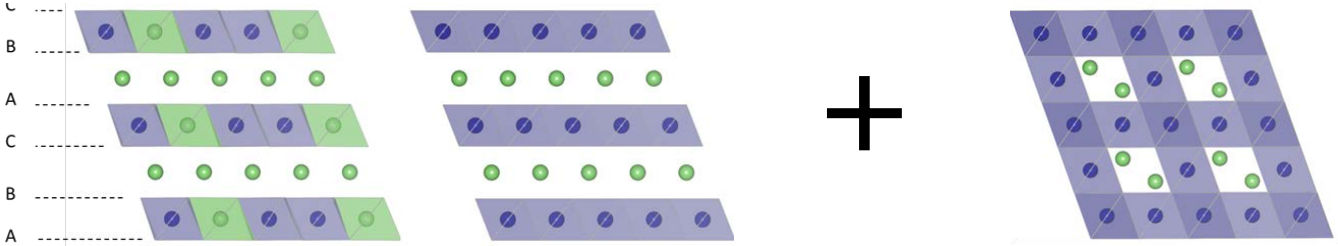
- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason R. Croy
- Collaborators:
  - CSE, Argonne: Eungje Lee, Joong Sun Park, Bryan Yonemoto, Roy Benedek, Fulya Dogan Key
  - APS: Mali Balasubramanian (XAS)
  - PNNL: Chongmin Wang (TEM)
  - NUANCE, Northwestern University: Vinayak Dravid (TEM)
  - Northwestern University: Christopher Wolverton (Theory)
  - Industry: Argonne licensees and collaborators

Objectives

- Improve the structural stability of high energy ‘layered-layered’ cathodes by introducing a stabilizing spinel component into the composite electrode structure with a particular emphasis on employing lithium-cobalt-nickel-oxide spinel components that can accommodate lithium at approximately 3.5 V vs. metallic lithium.

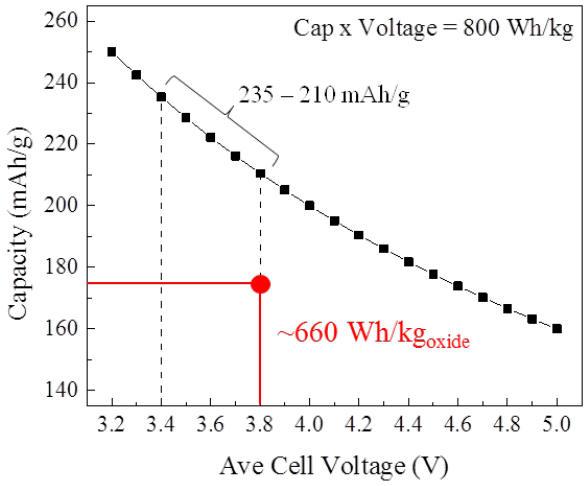


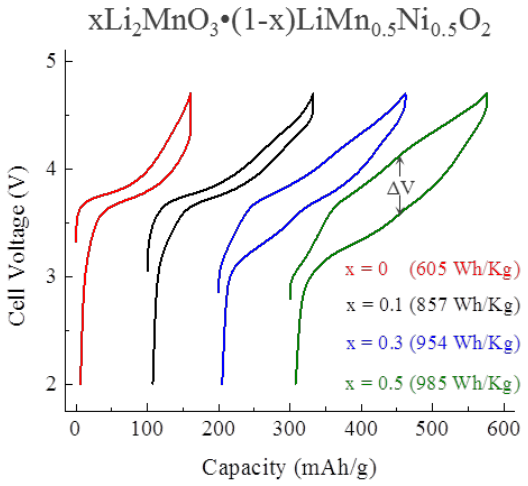
Layered-Layered
(High energy)

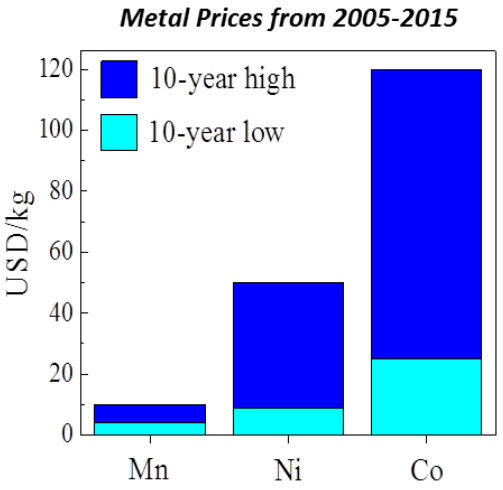
Li-Co-Ni-O spinel
(High stability)

Relevance (see ES235)

- Current lithium-ion cathodes deliver a cell energy that is limited to less than 700 Wh/kg_{oxide} (●).
- Lithium- and ***manganese-rich*** cathodes can deliver considerably higher cell energies.
- Complex atomic-scale structures govern performance and stability: Insights and understanding are critical to successful development.







Approach

- Design, synthesize and screen spinel compositions and structures comprising cobalt and/or nickel that operate above 3 V and below 4 V and determine their structural and electrochemical properties.

- Evaluate and identify the most promising spinel structures and compositions as stabilizers for high energy, composite ‘layered-layered-spinel’ cathode materials.

- Develop synthesis methods to incorporate a stabilizing spinel component within high energy composite cathode structures.

- Perform complementary computational studies to aid the compositional and structural design of Li-Co-Ni-O spinel electrodes.

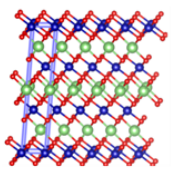
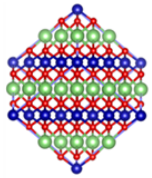
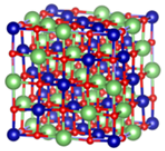
Milestones (FY15/16)

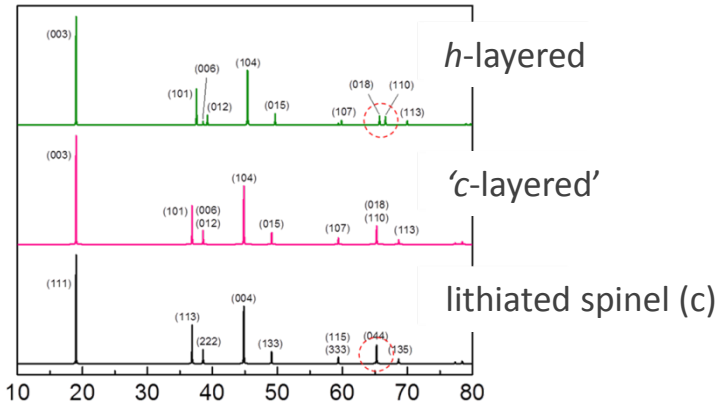
- Synthesize and optimize lithiated Li-Co-Ni-O spinel compositions and structures and determine their structural and electrochemical properties.
- Devise synthesis techniques to embed the most promising spinel compositions into layered structures.
- Determine the impact of embedding lithiated Li-Co-Ni-O spinel components on the electrochemical properties and cycling stability of composite ‘layered-spinel’ or ‘layered-layered-spinel’ structures.
- Use complementary theoretical approaches to further the understanding of the structural and electrochemical properties of lithiated Li-Co-Ni-O spinel electrodes and protective surface layers.

Background:

Li-Co-Ni-O spinels

- Li-Co-Ni-O spinels are not commonly known.
- In 1992, Thackeray et al. reported that $LiCo_{1-x}Ni_xO_2$ compounds with "spinel-like" character could be prepared at moderately low temperatures (LT, ~400 °C)
- Lithiated $LiCo_{1-x}Ni_xO_2$ spinels offer:
  - attractive 3.6 V plateau compared to 3.0 V plateau of Mn-spinel
  - less propensity for Co-migration
- Systematic studies are required to understand the complex interplay between synthesis, structure, and electrochemistry of lithiated spinels, LT-$LiCo_{1-x}Ni_xO_2$

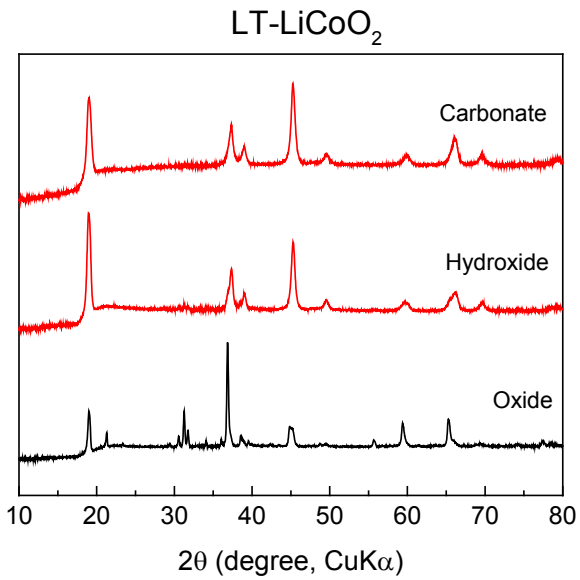
	h-layered	*c*-layered	lithiated spinel
temperature	HT form	LT form	LT form
Lattice frame	hexagonal	Cubic	Cubic
Li/Co ordering	Layered	Layered	Spinel
			



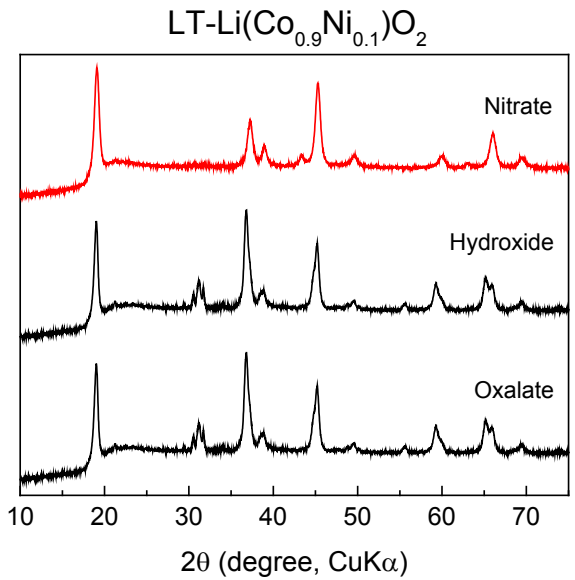
Various $LiCoO_2$ structures and ambiguity in structure determination (h = hexagonal; c = cubic)

Solid-State Synthesis Optimization

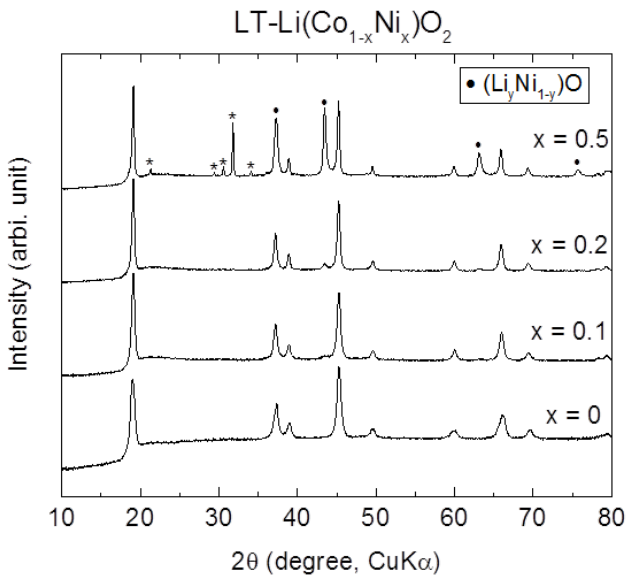
- Co_3O_4, Li_2CO_3, $Li_xNi_{1-x}O$ impurities are observed after a prolonged firing time (~1 week).
- Lithium carbonate, cobalt carbonate, and nickel nitrate precursors are used.
- Small degree of Ni substitution (LT-$LiCo_{1-x}Ni_xO_2$) is possible.



Effect of Co precursors for LT-$LiCoO_2$



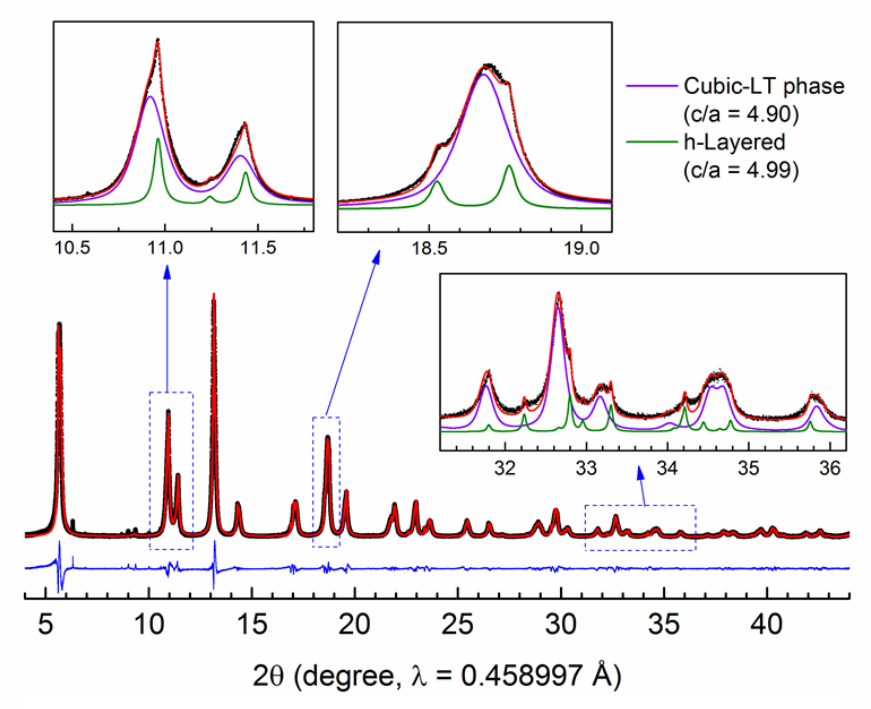
Effect of Ni precursors for LT-$LiCo_{0.9}Ni_{0.1}O_2$



XRD patterns of $LiCo_{1-x}Ni_xO_2$ prepared at 400 °C for 6d in air

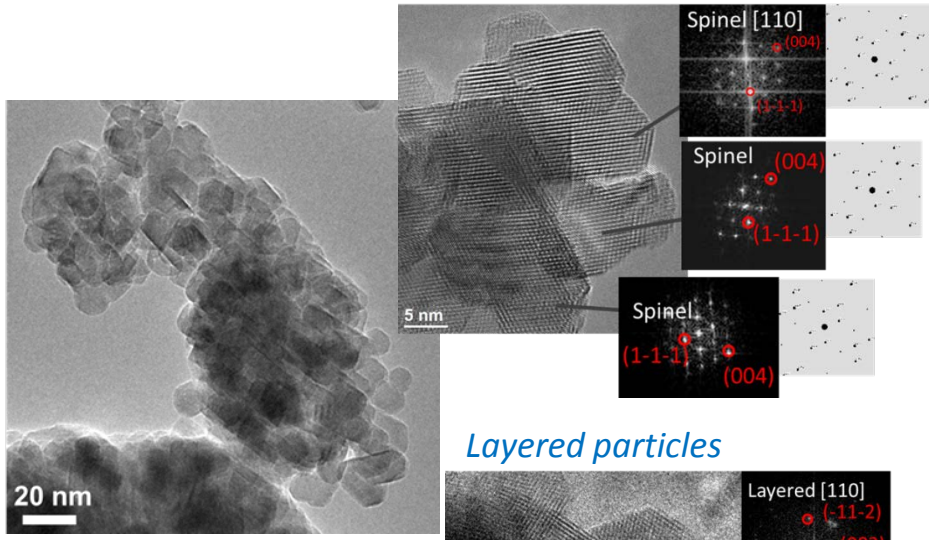
LT-$LiCoO_2$ – Synchrotron HR-XRD and HR-TEM phase analysis

- Synchrotron HR-XRD and HR-TEM analyses reveal that LT-$LiCoO_2$ consists of nanoparticles with both *h*-layered and c-spinel structures.



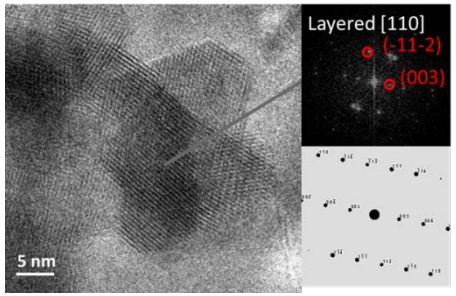
Synchrotron HR-XRD pattern of as-prepared LT-$LiCoO_2$

Spinel particles



Crystalline flakes, ~20 nm in size, aggregated together

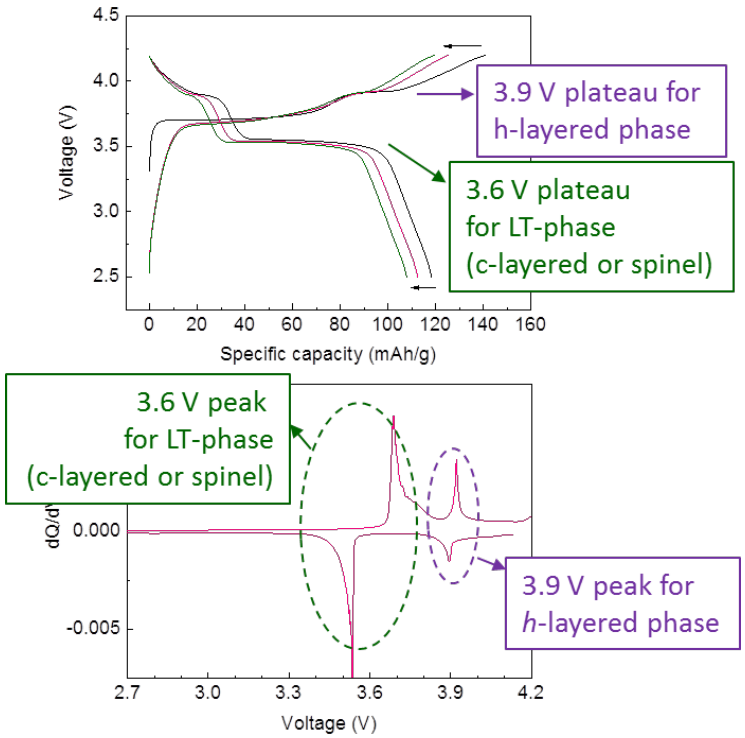
Layered particles



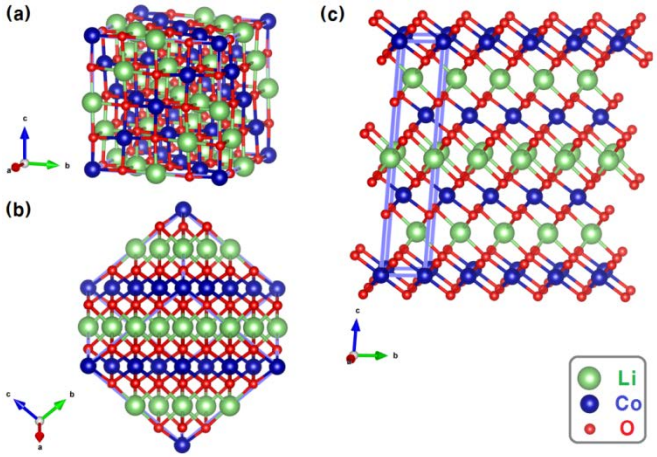
HR-TEM images of as-prepared LT-$LiCoO_2$ particles

LT-$LiCoO_2$ –Electrochemistry and DFT energy calculation

- Two voltage plateaus correspond to the two phase components (*h*-layered and cubic phase) in LT-$LiCoO_2$.
- Theoretical modeling shows negligible energy difference between the *h*-layered, '*c*-layered', and '*c*-lithiated spinel' structures suggesting that all three phases could co-exist, depending on synthesis conditions used.



Voltage profile and dQ/dV curve of LT-$LiCoO_2$

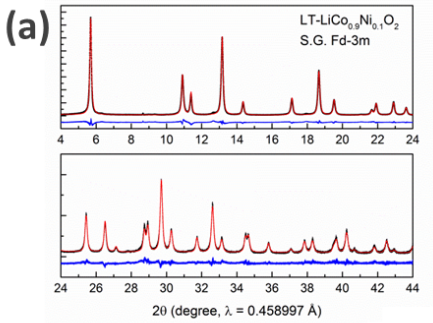


Structures	space group	DFT energies [meV/atom]
h-layered $LiCoO_2$	$R\bar{3}m$	-5.687
c-layered $LiCoO_2$	$R\bar{3}m$	-5.687
Lithiated spinel	$Fd\bar{3}m$	-5.685

DFT energy calculations for (a) lithiated spinel, (b) c-layered, and (c) h-layered $LiCoO_2$ models

LT-$LiCo_{0.9}Ni_{0.1}O_2$ – Phase analysis

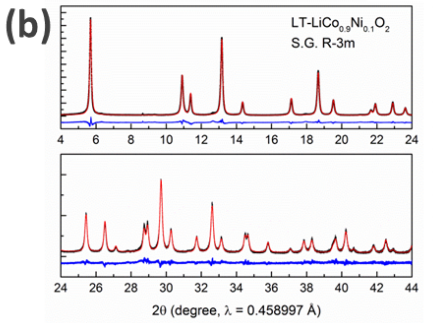
- 10% Ni substitution eliminates *h*-layered component: LT-$LiCo_{0.9}Ni_{0.1}O_2$ XRD data can be fitted to either a *c*-lithiated spinel (*Fd-3m*) or a *c*-layered ("*R-3m*", c/a = 4.90, ideal ccp) structure.
- Electron microscopy analysis reveal the presence of both spinel and *c*-layered crystallites in LT-$LiCo_{0.9}Ni_{0.1}O_2$ samples.



Space group	Fd-3m
Lattice constants (Å)	a = 8.007(4)
R_p / R_{wp} / R_{exp} (%)	6.85 / 9.28 / 4.81
Goodness-of-fit	1.93

Atom	Site	x	y	z	Occ.	B_{eq}
Li1	16c	0	0	0	0.97(6)†	0.38(6)‡
Li2	16d	0.5	0.5	0.5	0.02(4)†	0.38(6)‡
Co1	16d	0.5	0.5	0.5	0.97(6)†	0.38(6)‡
Co2	16c	0	0	0	0.02(4)†	0.38(6)‡
O	32e	0.259	0.259	0.259	1	0.47(3)

†Occupancies of Li and Co were refined with a constraint that would satisfy the anti-site exchange condition.
‡B_{eq} of Li and Co was constrained to have the same value.

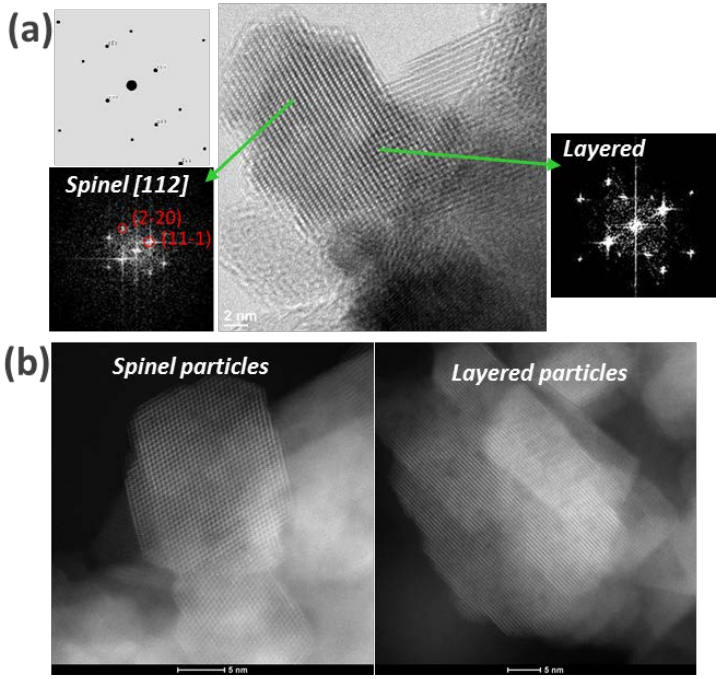


Space group	R-3m
Lattice constants (Å)	a = 2.830(7), c = 13.872(3), c/a = 4.90
R_p / R_{wp} / R_{exp} (%)	6.83 / 9.11 / 4.81
Goodness-of-fit	1.89

Atom	Site	x	y	z	Occ.	B_{eq}
Li1	3a	0	0	0	0.98(3)†	0.33(1)‡
Li2	3b	0	0	0.5	0.01(7)†	0.33(1)‡
Co1	3b	0	0	0.5	0.98(3)†	0.33(1)‡
Co2	3a	0	0	0	0.01(7)†	0.33(1)‡
O	6c	0	0	0.240(3)	1	0.37(7)

†Occupancies of Li and Co were refined with a constraint that would satisfy the anti-site exchange condition.
‡B_{eq} of Li and Co was constrained to have the same value.

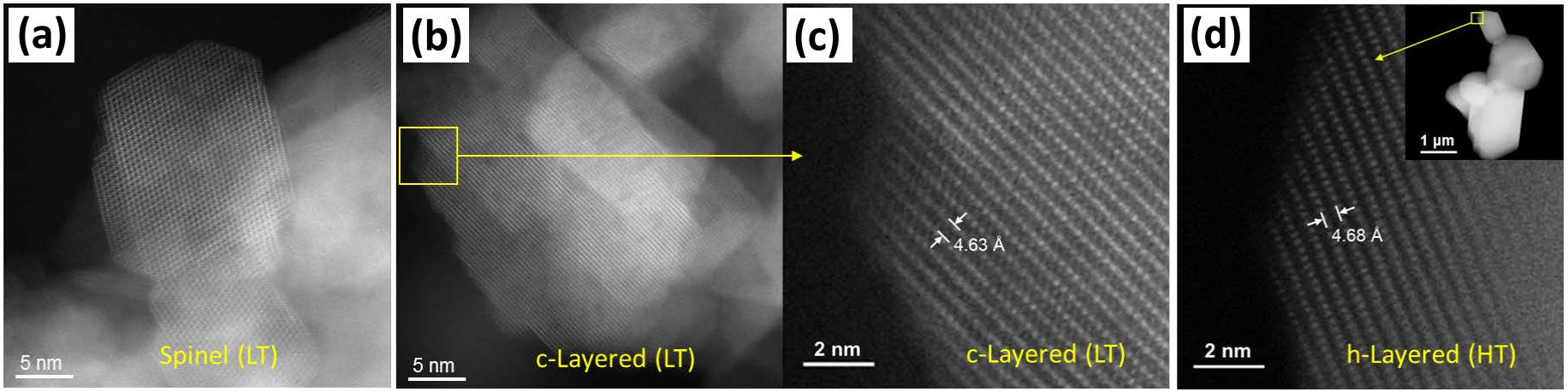
Rietveld refinement of synchrotron XRD patterns of LT-$LiCo_{0.9}Ni_{0.1}O_2$ using (a) c-lithiated spinel, or (b) c-layered structure model



(a) HR-TEM and (b) STEM-HAADF images of spinel and layered particles in a LT-$LiCo_{0.9}Ni_{0.1}O_2$ sample

Structure of LT-phase

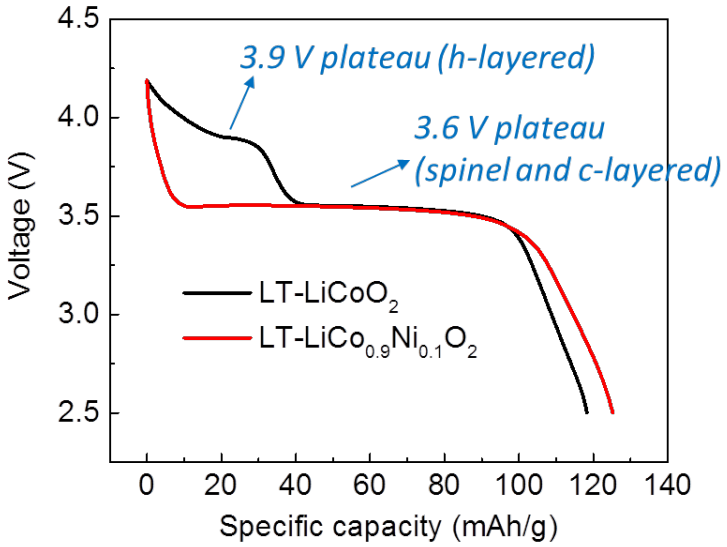
- The overall structure of LT-$LiCo_{1-x}Ni_xO_2$ samples can be considered to be composed of a lithiated spinel component and a *c*-layered structure, the latter having cation configurations intermediate between pure lithiated spinel and h-layered structures.



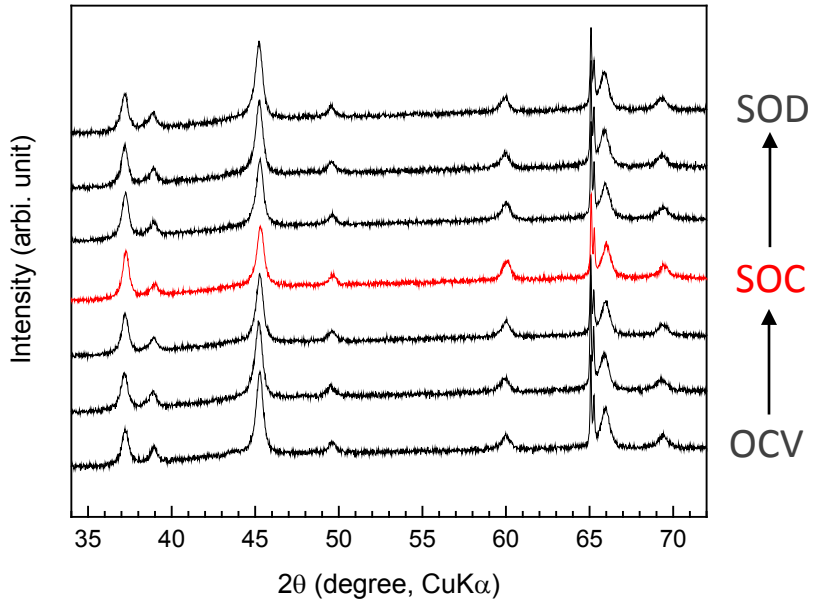
STEM-HAADF images of the (a-c) LT-$LiCo_{0.9}Ni_{0.1}O_2$ and (d) HT-$LiCo_{0.9}Ni_{0.1}O_2$ samples. Compared to the perfectly ordered Li/TM layers shown in the clear lattice images of HT-$LiCo_{0.9}Ni_{0.1}O_2$ in (d), the high magnification lattice image of the c-layered particle in (c) shows some atomic contrasts in between the transition metal layers indicating a structural configuration intermediate between lithiated spinel and h-layered structures.

LT-$LiCo_{0.9}Ni_{0.1}O_2$ – Electrochemistry

- 10% Ni substitution eliminates the h-layered phase and 3.9 V voltage plateau.
- LT-$LiCo_{0.9}Ni_{0.1}O_2$ electrode (c-lithiated spinel and c-layered structure) is stable during the initial charge-discharge
- Use LT-$LiCo_{1-x}Ni_xO_2$ component to stabilize "layered-layered" composite structures.



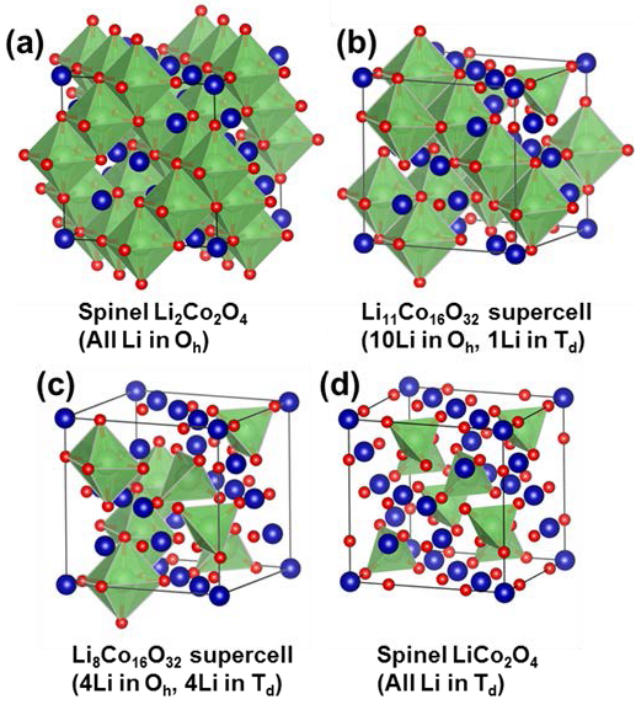
Sample	Phase	c/a	Echem profile
LT-$LiCoO_2$	h-Layered	4.99	3.9 V plateau
	LT-phase	4.90	3.6 V plateau
LT-$LiCo_{0.9}Ni_{0.1}O_2$	LT-phase	4.90	3.6 V plateau



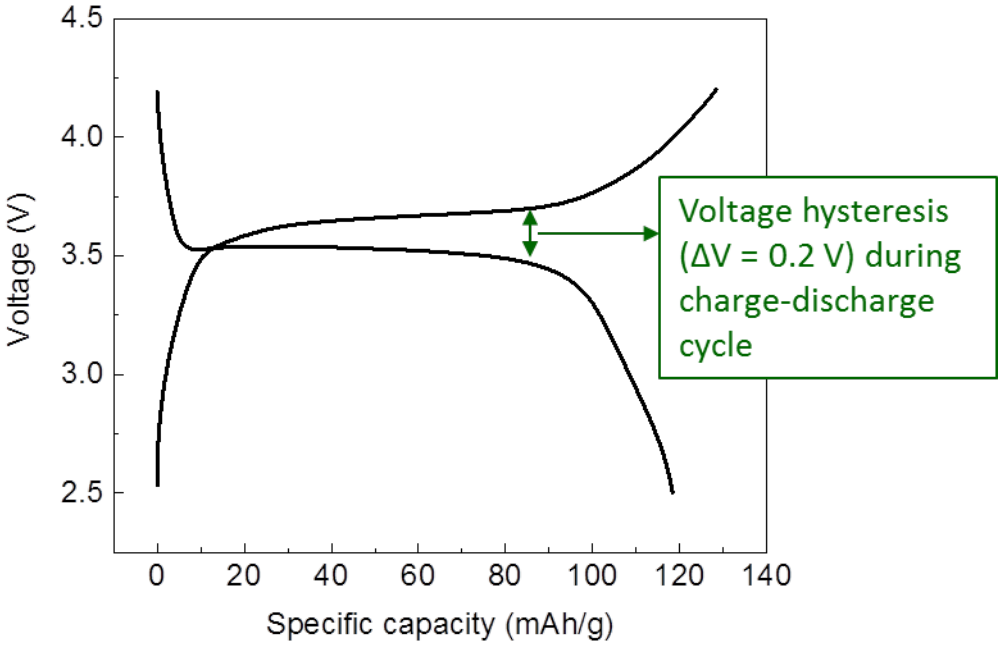
Ex-situ XRD during charge-discharge of LT-$LiCo_{0.9}Ni_{0.1}O_2$

LT-$LiCo_{0.9}Ni_{0.1}O_2$ – Charge/discharge mechanism

- Ex-situ XRD and DFT calculations suggest movement of Li ions between octahedral and tetrahedral sites during charge-discharge cycle of LT-$LiCo_{0.9}Ni_{0.1}O_2$
- Modeling provides explanation on the voltage hysteresis during cycling.



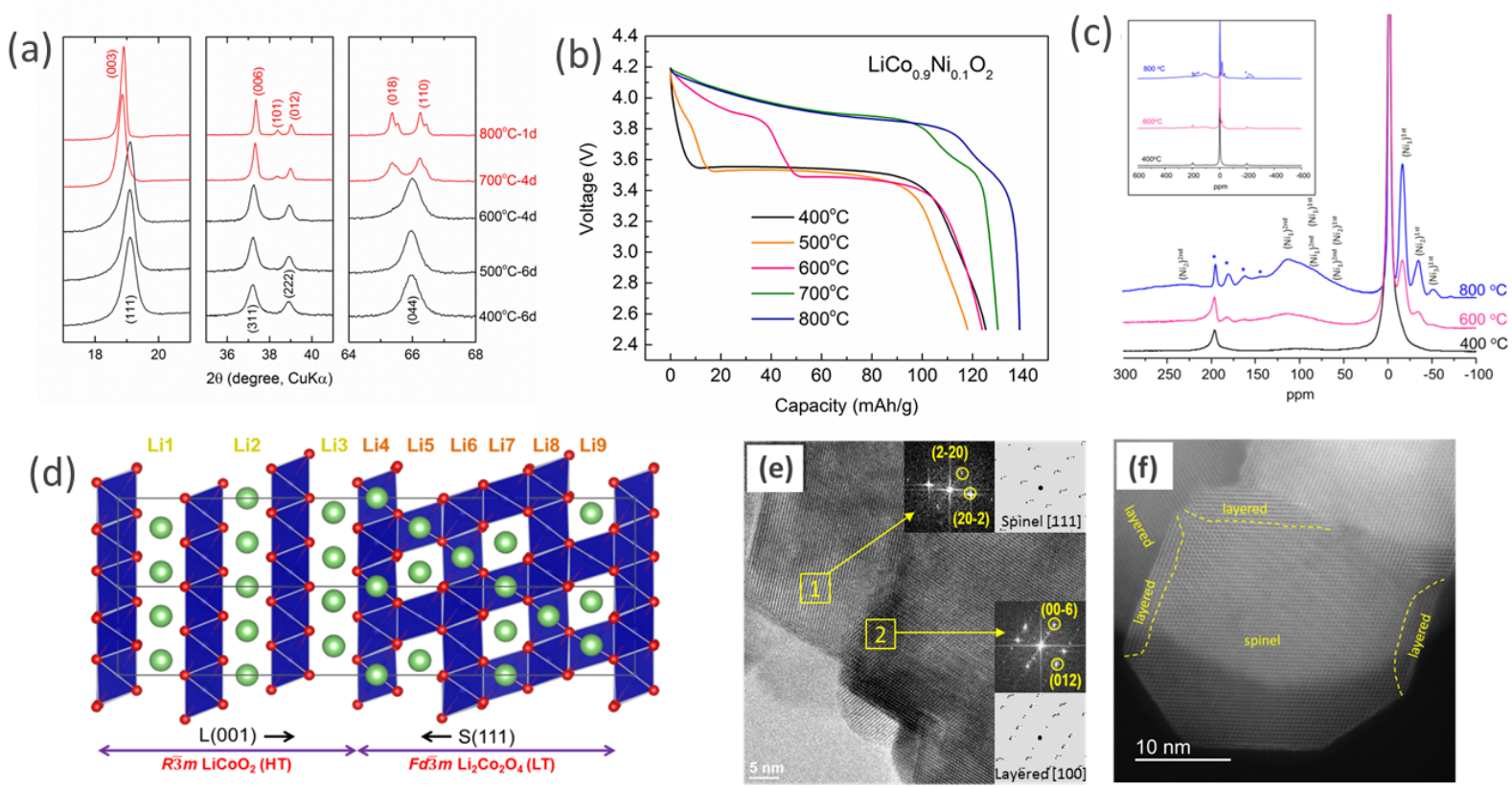
Atomic structure models used for DFT calculation during charge-discharge cycle of lithiated spinel structure



Voltage profile of LT-$LiCo_{0.9}Ni_{0.1}O_2$ showing voltage hysteresis during charge-discharge of the LT-phase.

Formation of layered-spinel composite $LiCo_{1-x}Ni_xO_2$

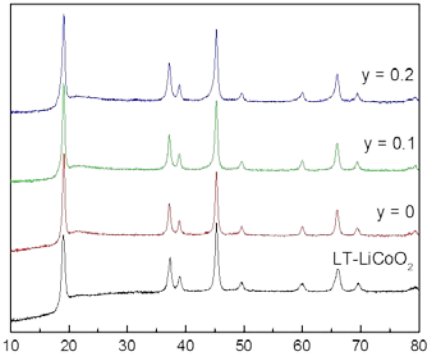
- At intermediate temperatures (e.g., ~600 °C), LT-spinel and layered components integrate to yield structures with increasing h-layered character

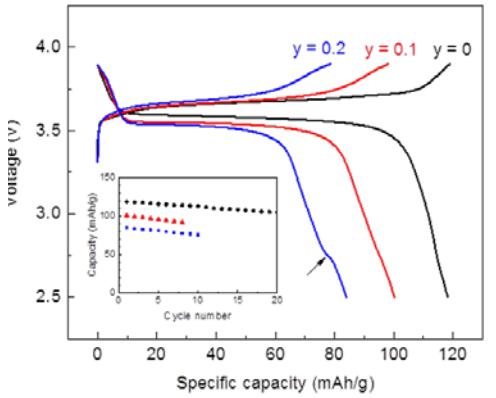


(a) XRD patterns, (b) voltage profiles, and (c) ^{7}Li-MAS NMR peaks of $LiCo_{0.9}Ni_{0.1}O_2$ synthesized at different temperatures; (d) DFT interface model between h-layered in (001) direction and lithiated spinel in (111) direction; (e) HR-TEM and (f) STEM-HAADF images of layered-spinel composite particles in a $LiCo_{0.9}Ni_{0.1}O_2$ sample prepared at 600 °C.

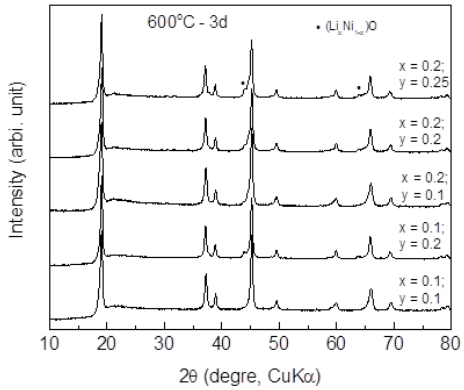
Exploration of Co-based spinel phase in composite structures

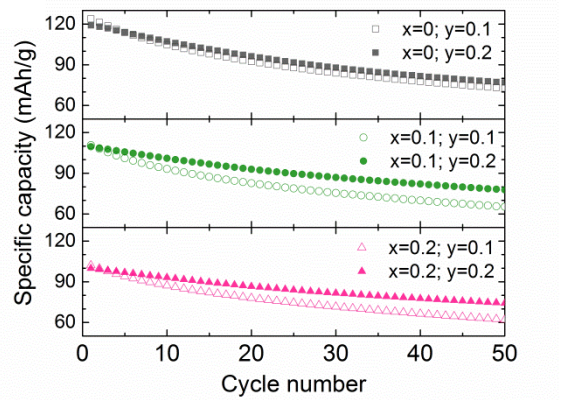
- Synthesis efforts to explore novel composite materials with Co-based spinel and layered structures are on going.



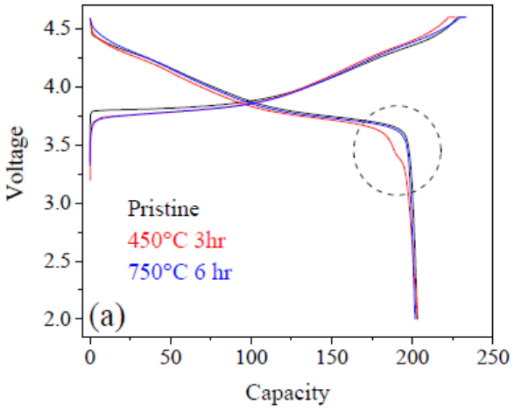


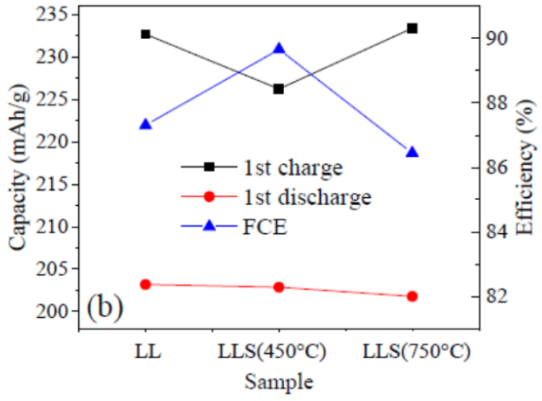
$Li(Co,Ni,Mn)O_2$ spinel





Li_2MnO_3•$Li(Co,Ni)O_2$ L-S composite





Li_2MnO_3•$Li(NMC)O_2$ L-L-S composite

Future Work – FY2016/FY2017

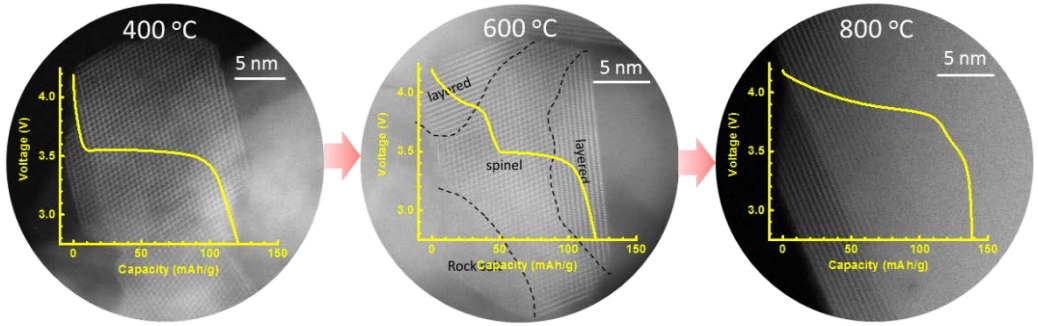
- Structure and electrochemical characteristics of various low-temperature $Li(Co_{1-x}Ni_x)O_2$ and $Li(Co_{1-x-y}Ni_xMn_y)O_2$ materials have been screened. For the remainder of FY2016 and in FY2017, synthesis efforts will focus on incorporating $Li(Co_{1-x}Ni_x)O_2$ spinel components into 'layered-spinel' and 'layered-layered-spinel' composite cathodes.

- Characterization and analysis of cycled materials will be conducted to understand capacity fading mechanisms of structurally-stable spinel $Li(Co_{1-x}Ni_x)O_2$ and $Li(Co_{1-x-y}Ni_xMn_y)O_2$ compositions and materials.

- Theoretical modeling will be expanded to composite electrode structures containing Co-based spinel components.

Summary

- Systematic synthesis and advanced characterization have revealed the complex structural nature of $Li(Co_{1-x-y}Ni_xMn_y)O_2$ spinel-related materials synthesized at moderately low, intermediate and high temperatures.
- The structures and electrochemical properties of lithiated spinel $Li(Co_{1-x}Ni_x)O_2$ have been confirmed and new information gathered.
- Efforts to incorporate Co-based spinels to stabilize high-capacity 'layered-layered' cathodes are ongoing.



Spinel | *Spinel – Layered composite* | *Layered*

Acknowledgments

Support for this work from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong, David Howell