SAND2024-10364C

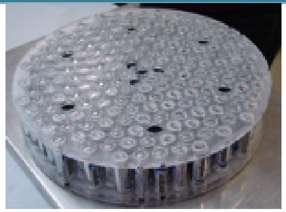
Sandia National Laboratories

POWER SOURCES TECHNOLOGY GROUP 7540

Investigating Safety In High Nickel NMC||LTO Batteries

Component Science, Engineering, & Production — CENTER 7500




Noah B. Schorr,

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Thanks to the Current BTMS Team:
Andrew Meintz, Brian Perdue, Eric Dufek, Jack Deppe, Andrew Jansen, John Farrell, Kandler Smith, Kevin Gering, Matthew Keyser, Steve Trask, **Drew Pereira**, Donald Karner, Sergiy Sazhin, Alastair Thurlbeck, Vaibhav Pawaskar, Alison R Dunlop, Matthew Shirk, Paul Gasper, Richard Carlson, John Kisacikoglu, Ed Watt, Ryan Tancin, Kae Fink, Bertrand Tremolet de Villers, Noah Schorr, Fernando Salcedo, Katie Harrison, Anthony Burrell

Denver X-ray Conference
August 9th 2024

U.S. DEPARTMENT OF ENERGY NNSA

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Behind The Meter Storage

Energy demand at commercial retailers is growing with electric vehicle charging ubiquity
BTMS consortium investigates battery storage to offset new energy demands
EV and BTMS battery considerations are not equivalent

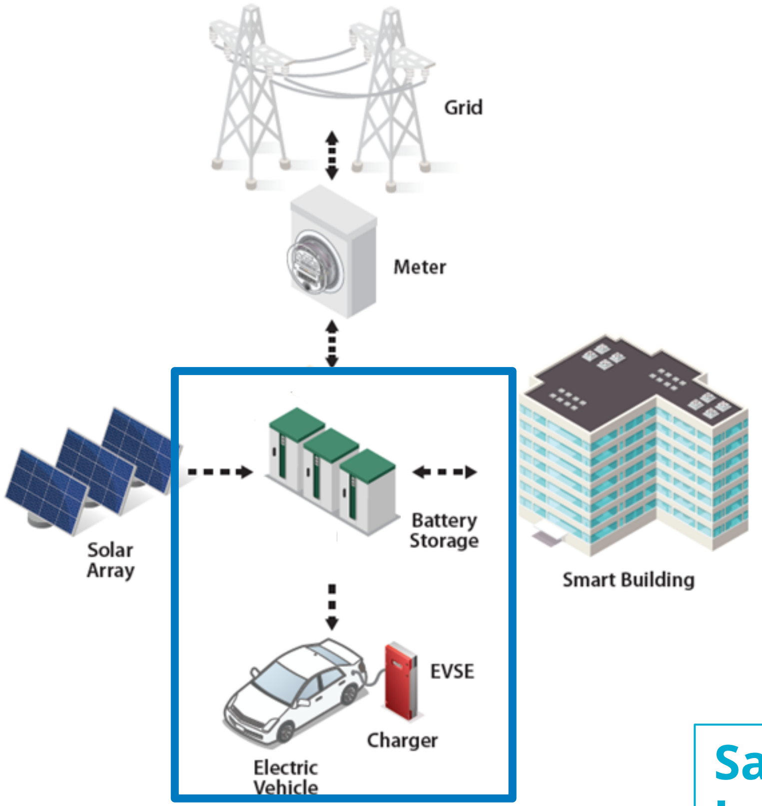
Sandia National Laboratories

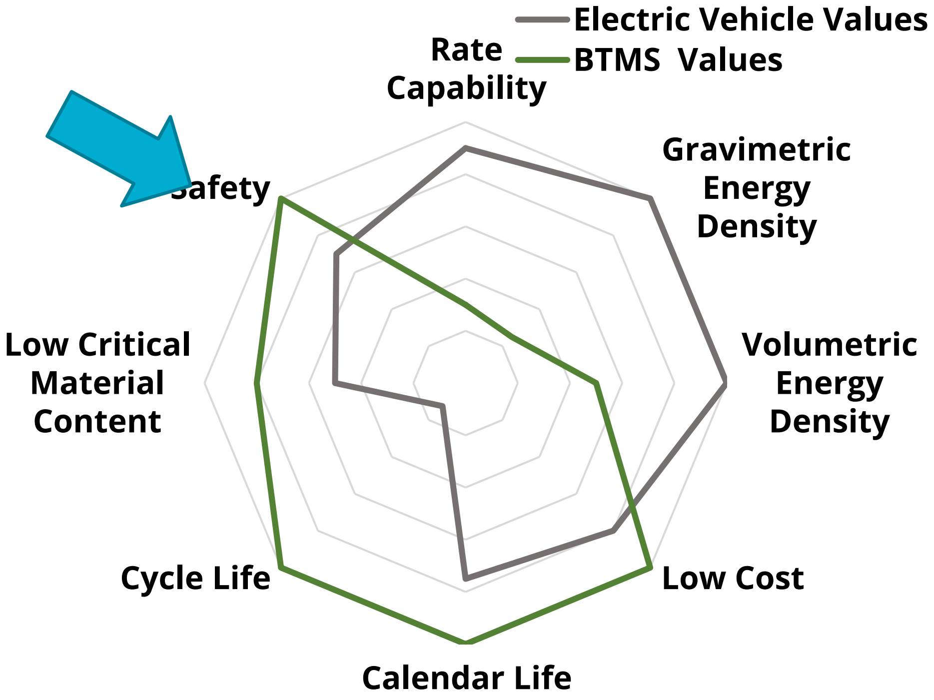
NREL Transforming ENERGY

INL Idaho National Laboratory

Argonne NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY





Safety is very important for large BTMS batteries located near buildings → need to select safe materials

Burrell, A., 2020. *Department of Energy Annual Merit Review presentation, bat442.*
Data courtesy of Jason Woods and the BTMS team.

Safety Background

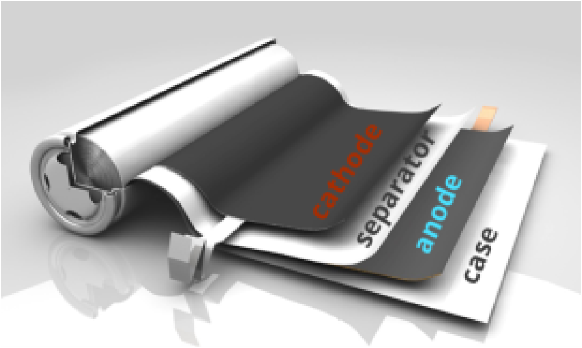
What does it mean for a battery to be safe?
Thermal runaway is the largest threat to whole system failure and danger to surroundings
No stopping cascading exothermic reactions of thermal once started

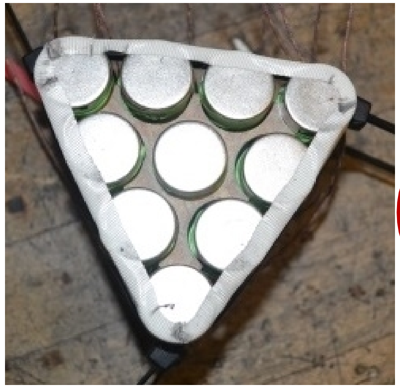
The Issues

- Energetic thermal runaway
  - Anode and cathode decomposition reactions
- Electrolyte flammability
  - Low flashpoint electrolyte solvents
  - Vent gas management
  - Fuel-air deflagrations
  - Wide flammability range of decomposition products
- Thermal stability of materials
  - Separators, electrolyte salts, active materials
- Failure propagation from cell-to-cell
  - Single point failures that spread throughout an entire battery system

Need to understand

- Battery failure mechanisms
- Fundamentals causes of failure
- Impact of failure:
  - Heat release
  - Gas emission
  - Pressure generation
  - Burn time
  - Waste generation
- Direct comparisons with like battery chemistries/sizes
- Information to help aid in safer batteries:
  - Materials choice
  - Design
  - Engineering controls

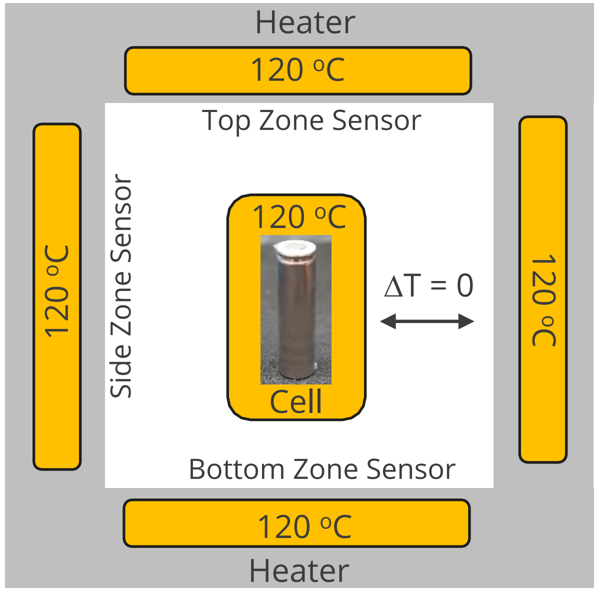


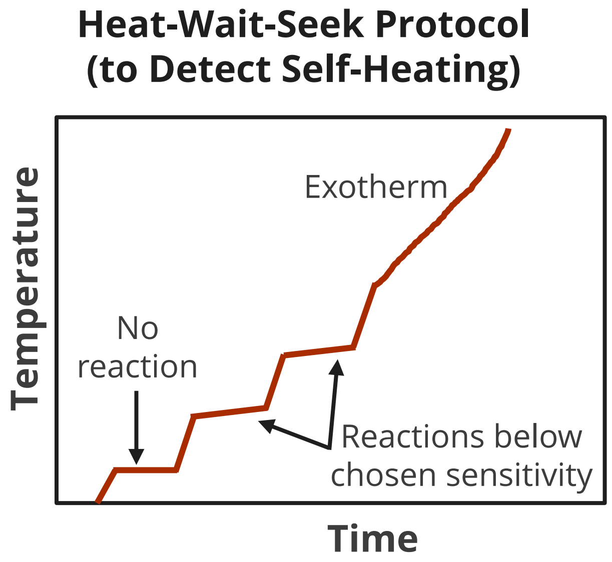


Measuring Cell Failure Properties

Accelerated rate calorimetry (ARC) operated under adiabatic conditions to measurer exothermic reactions that lead to self heating events at a given temperature

- Gives info about total energy released by cell failure and heating of thermal runaway events

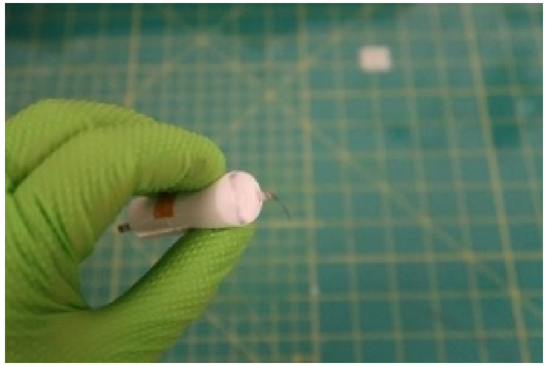





Thermal Hazard Technologies Extended Volume ARC

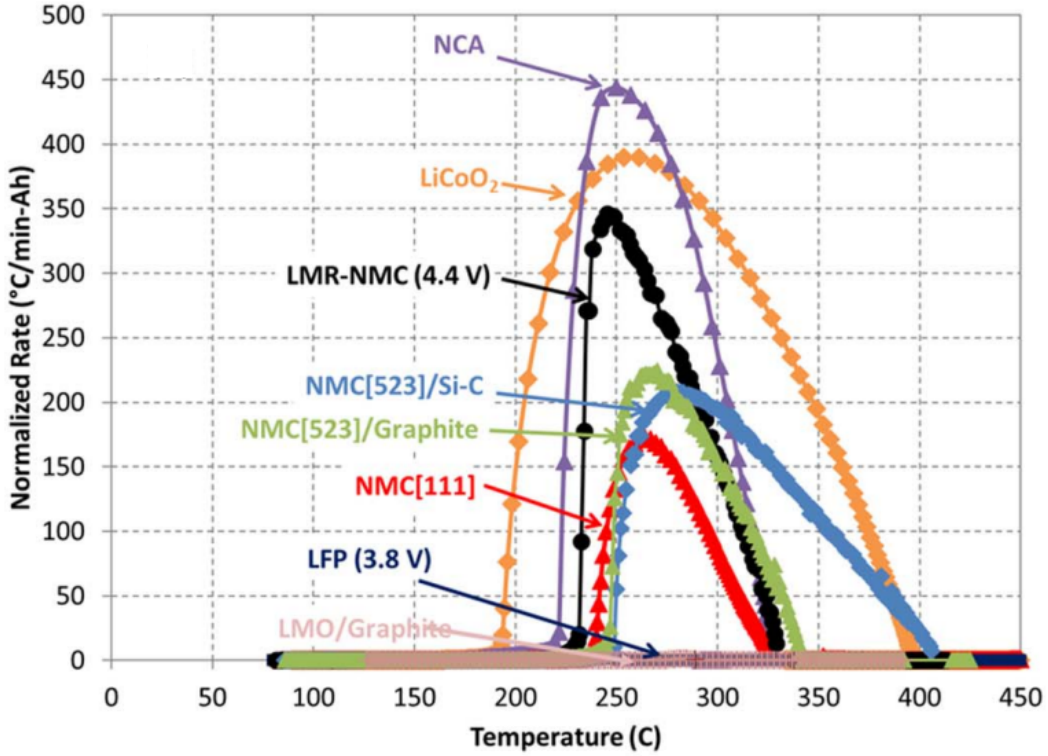
18650 cell format gives scalable idea of heat release during failure (coin cells too much non-active mass)

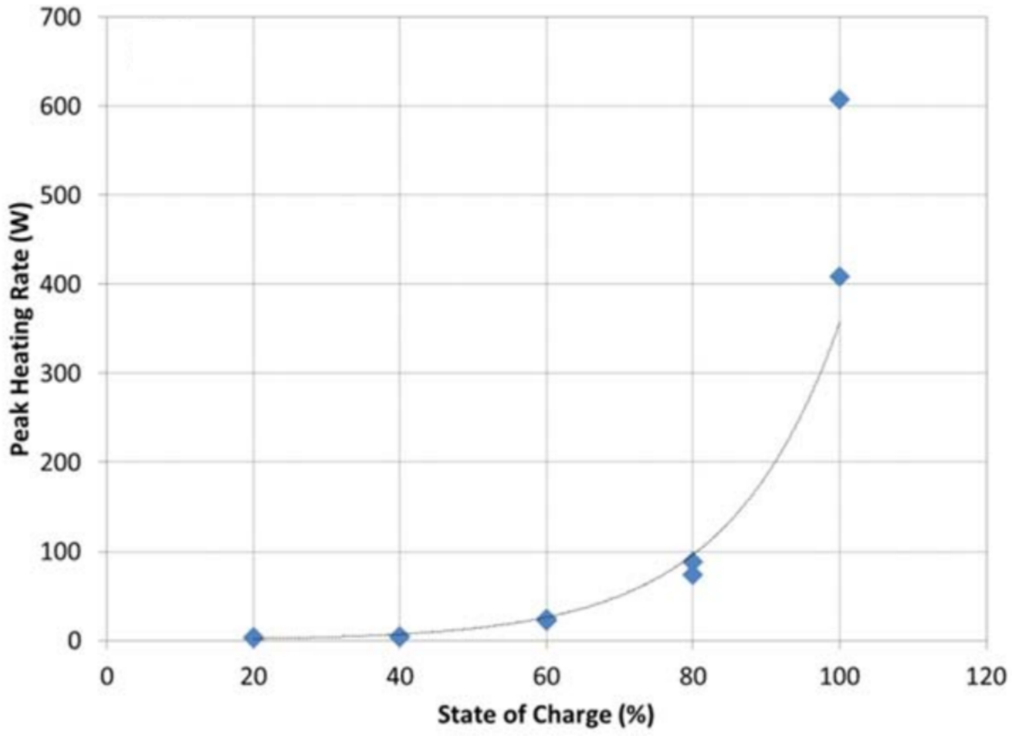





Safety of Common Battery Chemistries

Amount of heat and how fast it is released from a battery is dependent on the electrode identity and state of charge





Lamb, J., Torres-Castro, L., Hewson, J.C., Shurtz, R.C. and Preger, Y., 2021. *Journal of The Electrochemical Society*, *168*(6), p.060516.

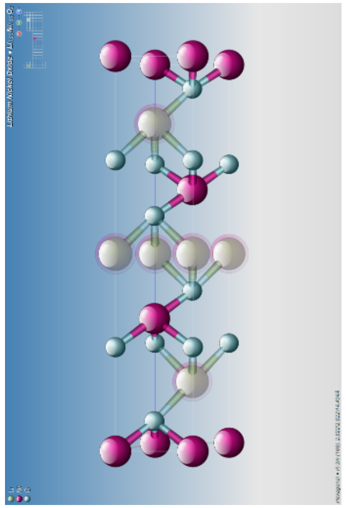
- **Cell chemistry that can make a safer cell that still meets energy density requirements?**
- **Cycling conditions that can make a safer cell that sill meets energy density requirements?**

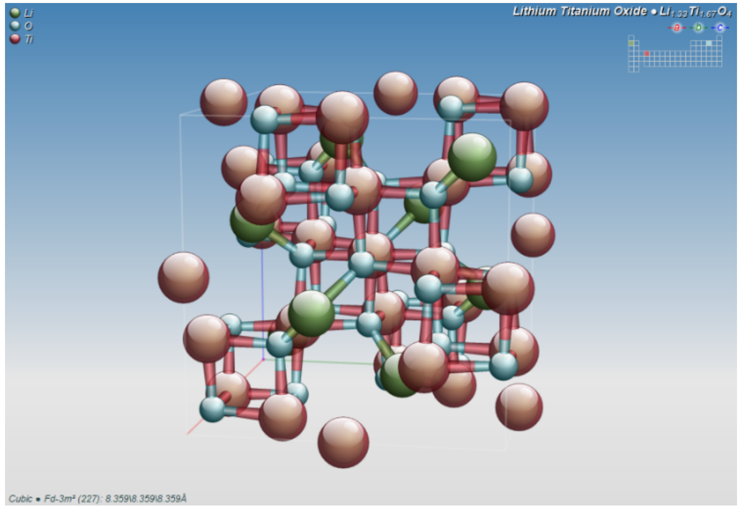
90-5-5 NMC || LTO Voltage Dependance

A nickel manganese cobalt oxide (NMC) cathode with a high percent of Ni and lower amounts of Co paired with a lithium titanate (LTO) anode is a good candidate for BTMS needs

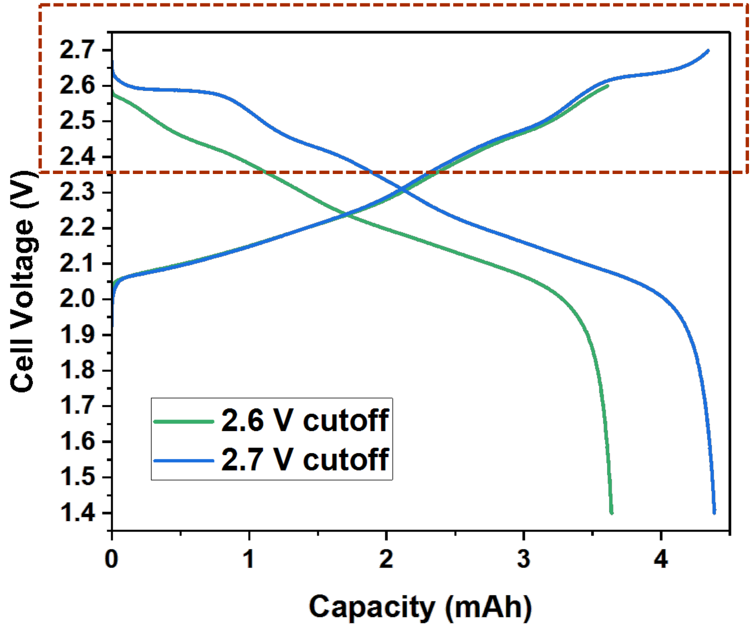
- **Lower cost / critical material**
  - Less Co content decreases material cost ($Ni_{0.5}Mn_{0.3}Co_{0.2}$ common in commercial cells)
- **Cycle Life**
  - LTO (compared to graphite) enables long life batteries
- **Energy Density**
  - Increasing Ni content improves cathode capacity, somewhat making up for LTO's higher V
- **But does a NMC||LTO battery meet safety requirements?**

$Ni_{0.9}Mn_{0.05}Co_{0.05}$ (90-5-5 NMC)||$Li_4Ti_5O_{12}$ (LTO)



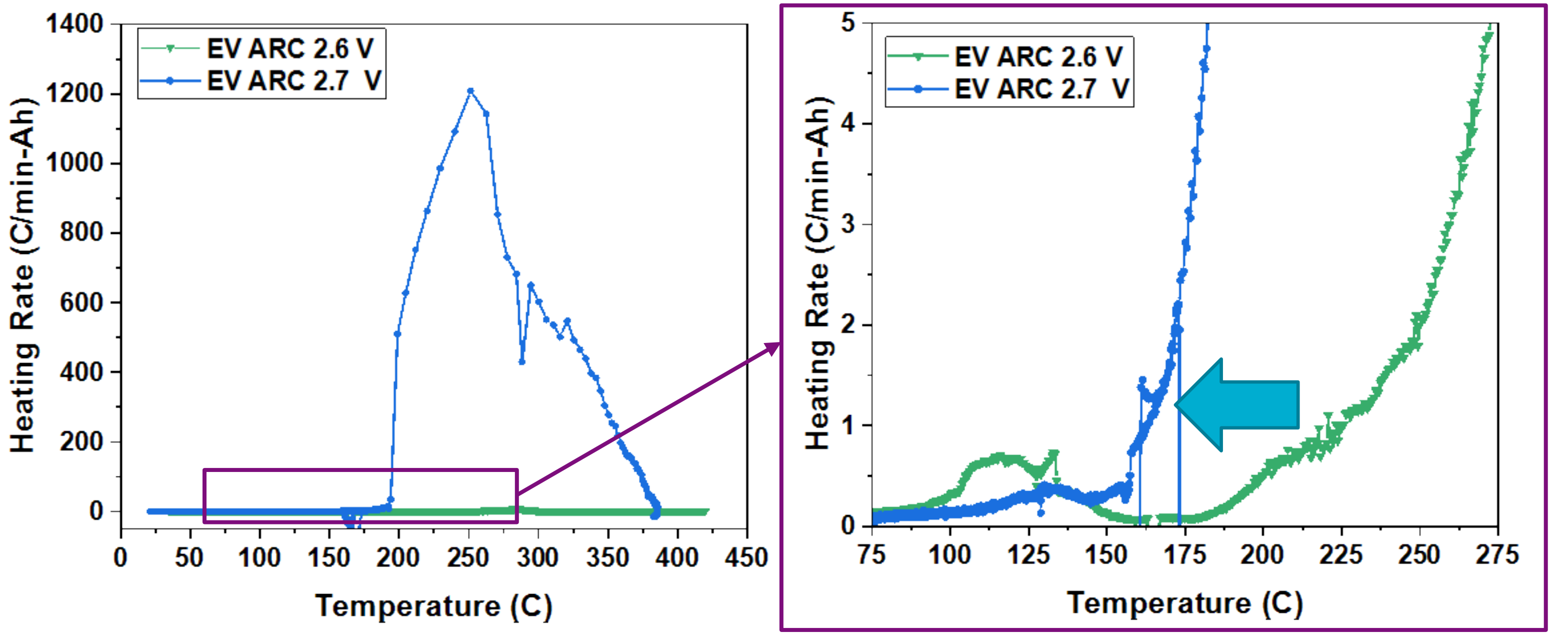


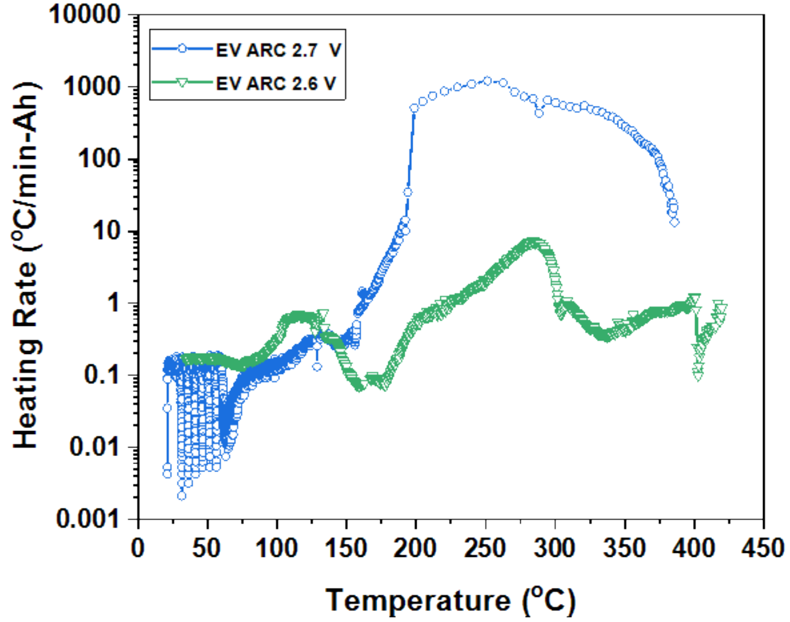
Need to study safety of chemistry and cycling conditions



90-5-5 NMC || LTO Voltage Dependance

Onset of thermal runaway higher and the max heat rate lower for cells cycled to 2.6 V limit



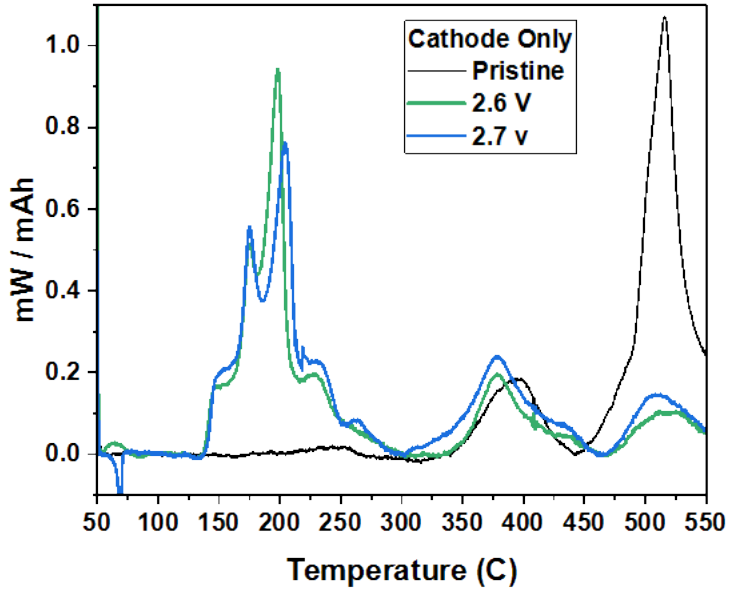


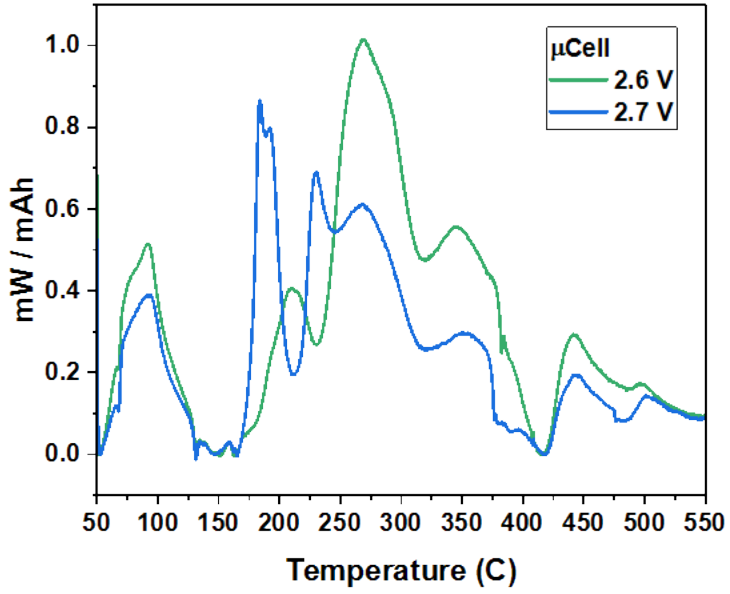
Voltage Limit	Onset Self Heating (°C/min > 0.2 °C/min)	Onset Thermal Runaway (TR) (°C)	Temperature at Max Rate (°C)	Max Rate (°C/minAh)	Peak Heating Rate (W)	Enthalpy (kJ)	Max T (excluding chamber heating)	Time TR to Max Rate (h)	Time TR to Max Temp (h)
2.7 V	62	**156**	251	**1209**	604	7.4	386	0.568	0.580
2.6 V	35	**188**	284	**7**	2.9	7.3	419 (403)	1.583	3.842

2.6 V limited cells are safer than 2.7 V!

Differential Scanning Calorimetry of 90-5-5 NMC

DSC measures the heat flow associated of a sample as a function of temperature





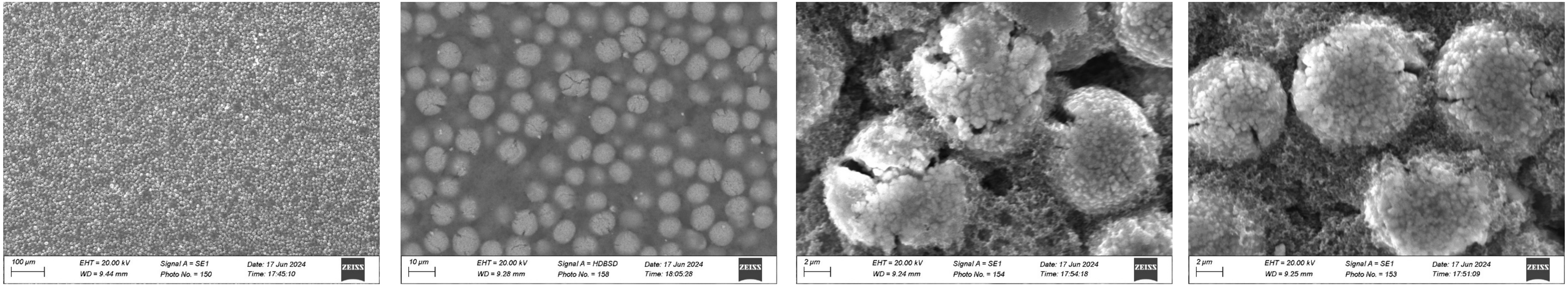
Cathodes charged to 2.6 and 2.7 V showed more minor differences with voltage limit but much larger exotherms than the pristine (uncharged) cathode

Microcell tests shows that maximum exotherms and self heating rates occur at lower temperature in cells cycled to 2.7 V relative to those cycled to 2.6 V (agrees with ARC)

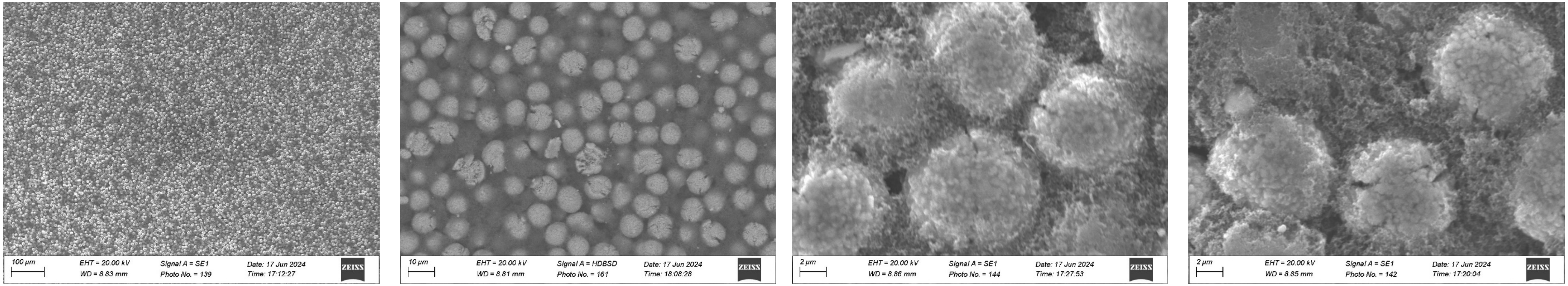
Imaging of Electrodes

Scanning electron microscopy of cathodes from cells cycled 1000 times

Charged to 2.7 V



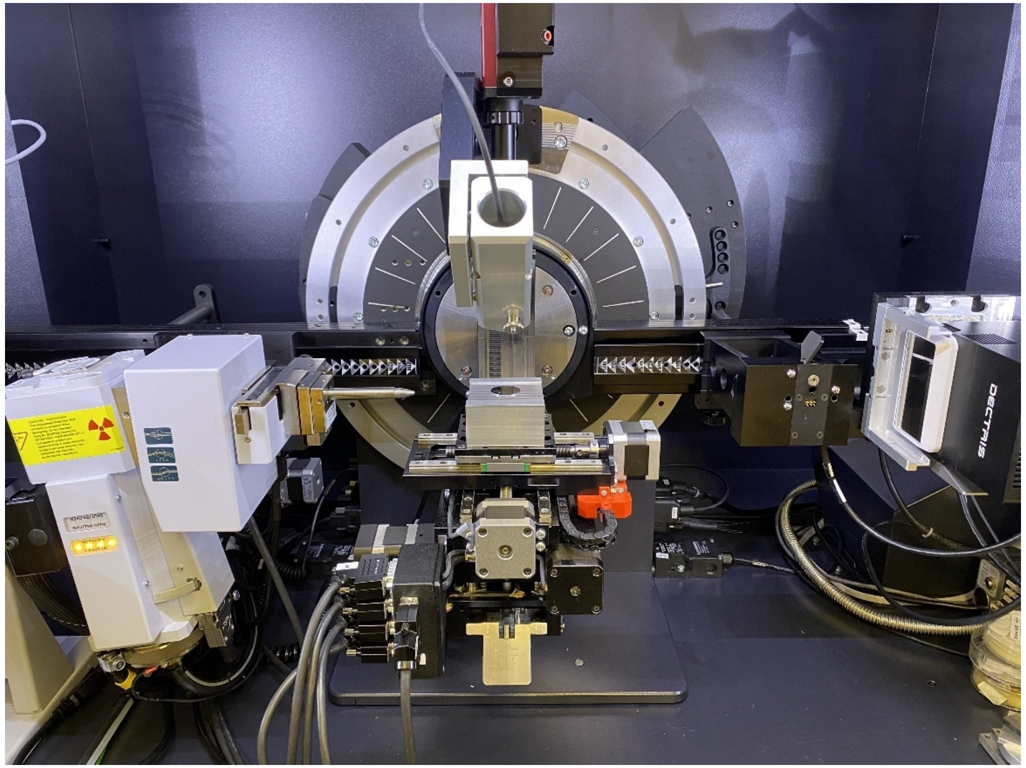
Charged to 2.6 V

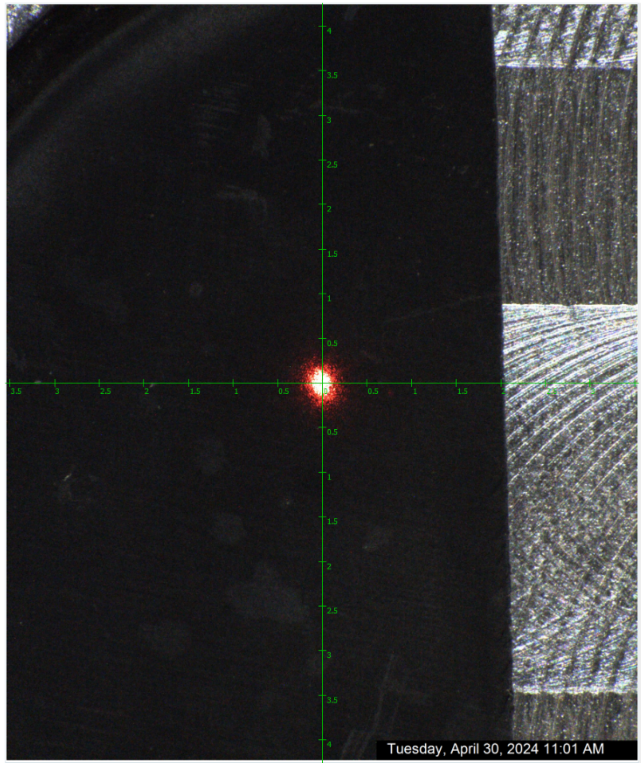


No obvious difference in particle morphology after cycling

X-ray Diffraction of Electrodes

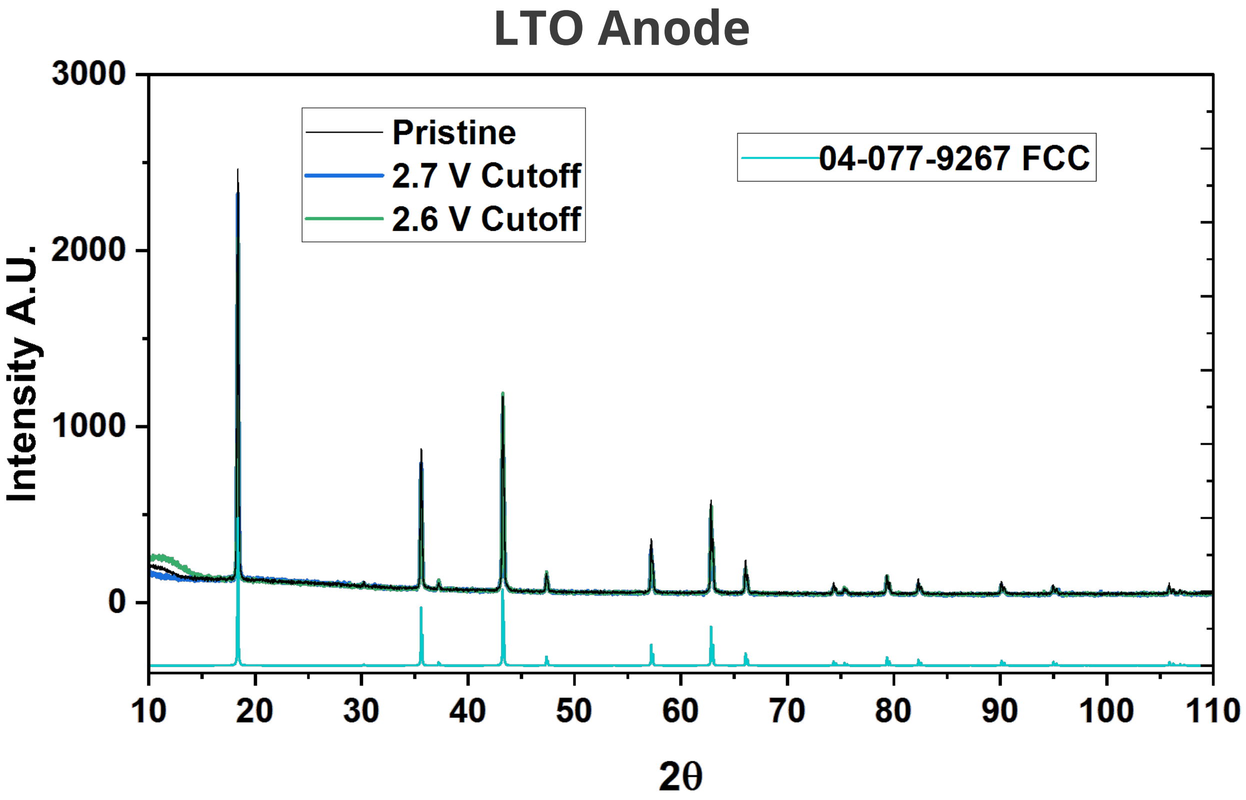
Powder X-ray diffraction data was collected on a Bruker Trio system equipped with a sealed tube X-ray source (Cu Ka radiation), Dectris CMOS area detector, and Eulerian texture cradle with an XYZ translation stage. Power settings for X-ray generation were 40 kV and 40 mA. The scan range was 5-110° 2θ with a step size of 0.02° 2θ and a dwell time of 0.15 seconds. Microdiffraction was performed on small solid samples using a 1 mm collimator and Göbel focusing mirror in 2D detector mode.

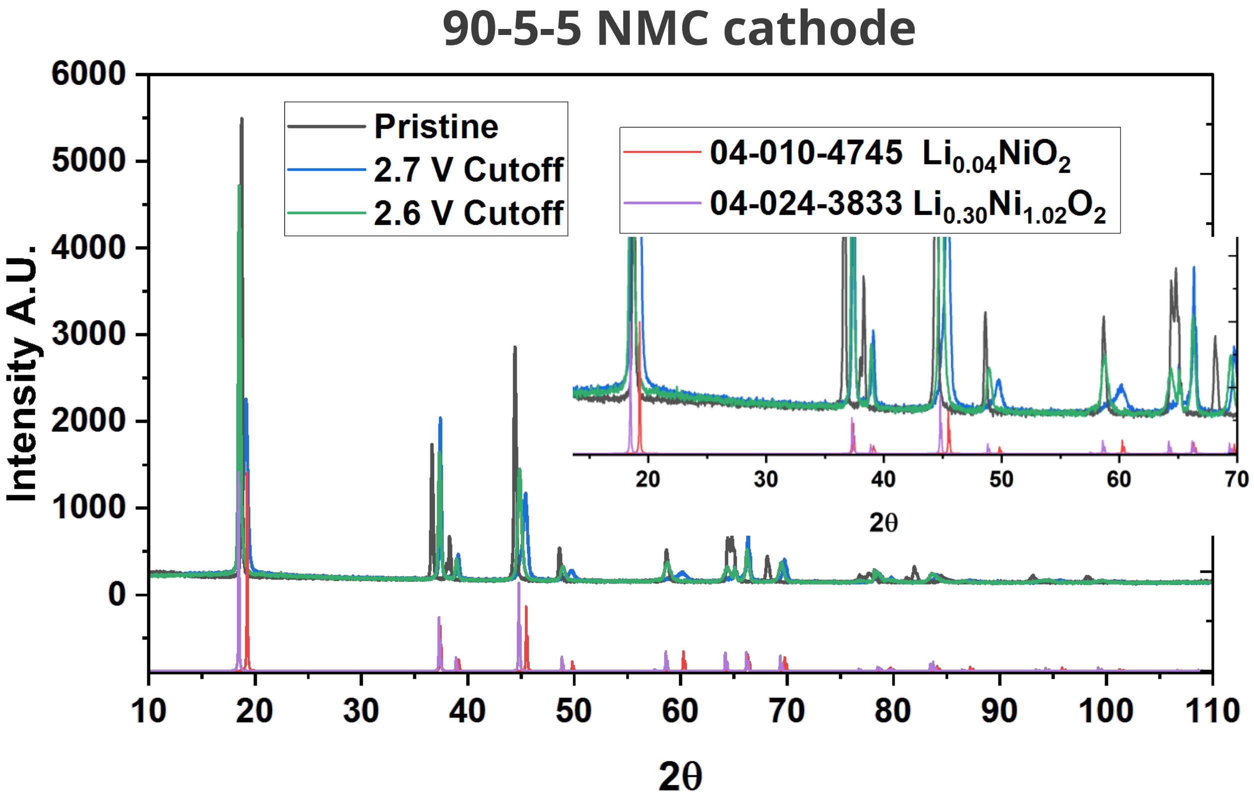




X-ray Diffraction of Electrodes **after 10 cycles**

Electrodes harvested from coin cells, dried but not washed before analysis





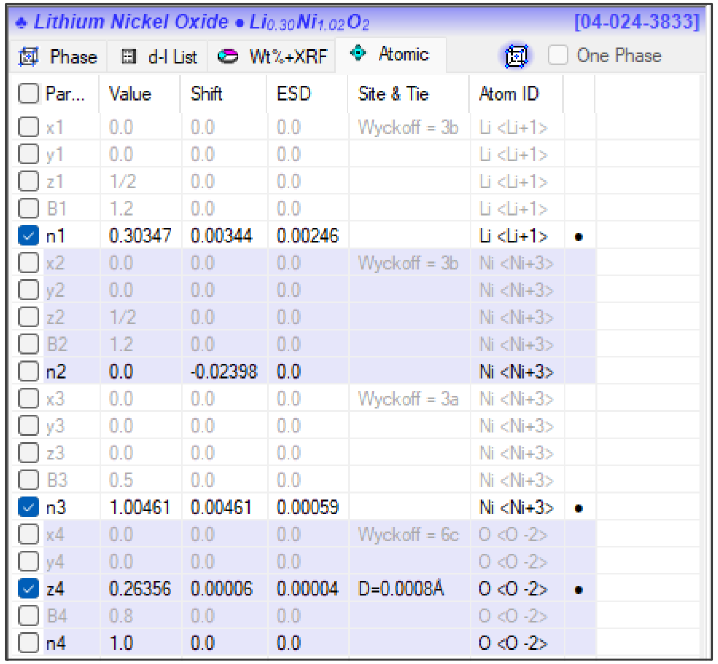
LTO anode shows no structure change with cycling

90-5-5 NMC cathode has voltage dependent structure

X-ray Diffraction of Cathode 2.6 V Limit

The phases used as phase ID are analogues, not exactly the chemistry of the samples

$Li_{0.3}Ni_{1.02}O_2$ phase is used to represent a possible lithiated Ni-Mn-Co oxide phase



X-ray Diffraction of Cathode 2.7 V Limit

The phases used as phase ID are analogues, not exactly the chemistry of the samples
$Li_{0.3}Ni_{1.02}O_2$ and $Li_{0.04}NiO_2$ phase is used to represent a possible lithiated Ni-Mn-Co oxide phase

Scan Parameters: 5.0°/110.0°/0.02°/94.95(s), I(p)=2257.9/121.9, Cu(40kV,40mA), Tuesday, December 19, 2023, 11:29 AM

☑ Zero Offset = -0.087 (0.0036) ☐ Displacement = 0.0 ☐ Distance Slack = 0.0
☑ Kα2 Peaks Present ☐ Kα2/Kα1 Ratio = 0.5 ☐ X-Ray Polarization = 1.0

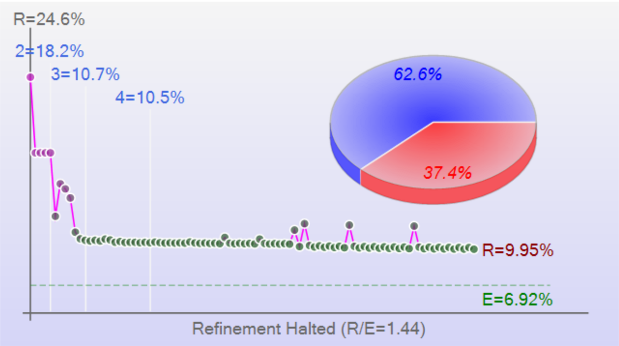
Geometry: Diffractometer Lp Fitted-Range: 15.0° - 105.0° BG-Model: Polynomial (3) λ: 1.54059Å (Cu)

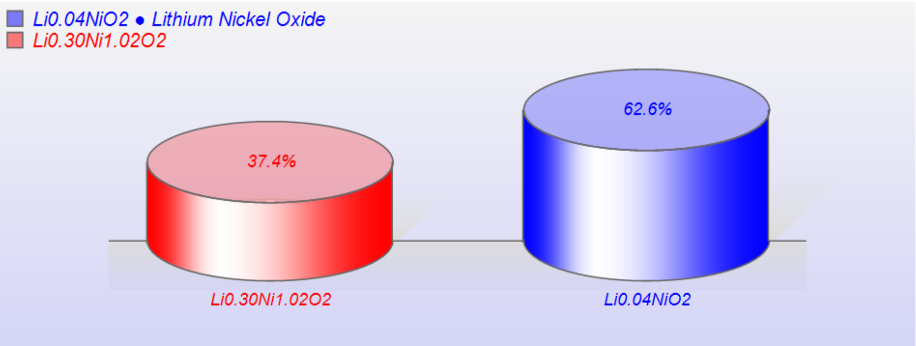
PSF: pseudo-Voigt Broadening: Crystallite Size & Strain Instrument: LaB6 Trio 2D uXRD 1mm

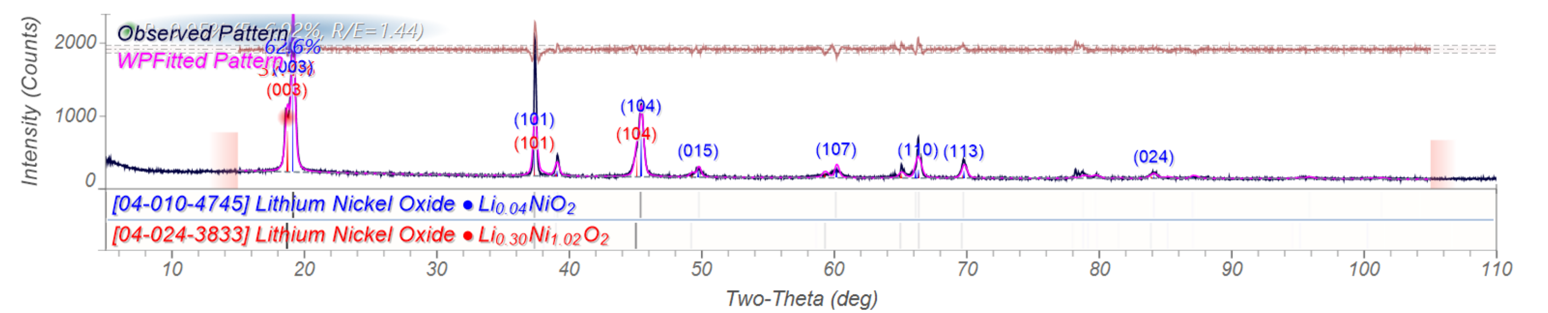
Phase ID (2)	Chemical Formula	PDF-#	Wt% (σ)	XS(Å)	ST(%)	a (σ)	b (σ)	c (σ)	Volume (σ)
Lithium Nickel Oxide (?)	$Li_{0.04}NiO_2$	04-010-4745	62.6 (4.2)	317 (17)	0.0 (0.0)	2.81245 (23)	2.81245 (23)	13.83900 (214)	94.799 (18)
Lithium Nickel Oxide	$Li_{0.30}Ni_{1.02}O_2$	04-024-3833	37.4 (3.8)	204 (16)	0.0 (0.0)	2.81077 (48)	2.81077 (48)	14.15710 (314)	96.863 (32)

XRF(Wt%): NiO=81.3%, Li2O=3.6%

Refinement Halted (R/E=1.44), ♣ Round=4, Iter=12, P=24, R=9.95% (E=6.92%, EPS=0.5)







♣ Lithium Nickel Oxide • $Li_{0.30}Ni_{1.02}O_2$ [04-024-3833]

Phase | d-I List | Wt%+XRF | Atomic | ☐ One Phase

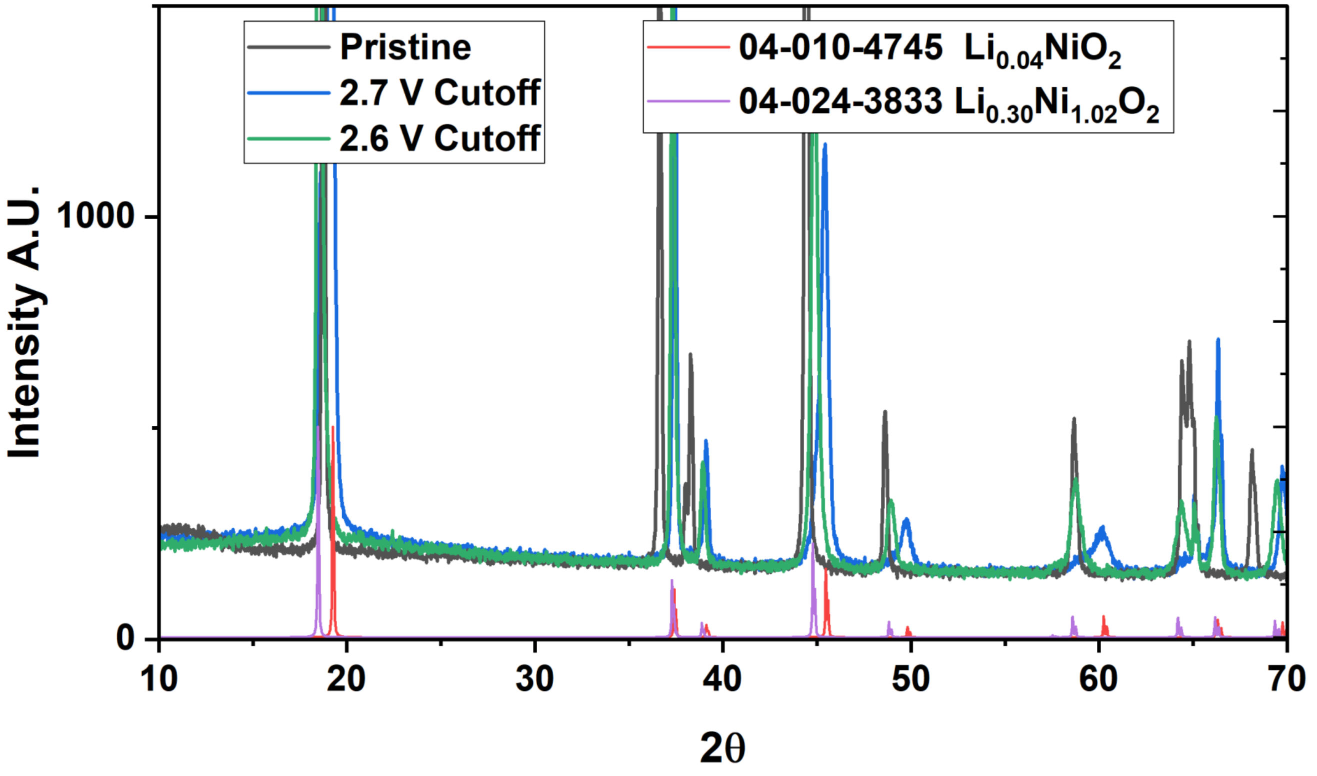
Par...	Value	Shift	ESD	Site & Tie	Atom ID	
☐ x1	0.0	0.0	0.0	Wyckoff = 3b	Li <Li+1>	
☐ y1	0.0	0.0	0.0		Li <Li+1>	
☐ z1	1/2	0.0	0.0		Li <Li+1>	
☐ B1	1.2	0.0	0.0		Li <Li+1>	
☑ n1	0.3369	0.03688	0.35089		Li <Li+1>	•
☐ x2	0.0	0.0	0.0	Wyckoff = 3b	Ni <Ni+3>	
☐ y2	0.0	0.0	0.0		Ni <Ni+3>	
☐ z2	1/2	0.0	0.0		Ni <Ni+3>	
☐ B2	1.2	0.0	0.0		Ni <Ni+3>	
☑ n2	0.02498	0.001	0.03349		Ni <Ni+3>	•
☐ x3	0.0	0.0	0.0	Wyckoff = 3a	Ni <Ni+3>	
☐ y3	0.0	0.0	0.0		Ni <Ni+3>	
☐ z3	0.0	0.0	0.0		Ni <Ni+3>	
☐ B3	0.5	0.0	0.0		Ni <Ni+3>	
☑ n3	0.98268	-0.01732	0.00378		Ni <Ni+3>	•
☐ x4	0.0	0.0	0.0	Wyckoff = 6c	O <O -2>	
☐ y4	0.0	0.0	0.0		O <O -2>	
☑ z4	0.26351	0.00001	0.00016	D=0.0002Å	O <O -2>	•
☐ B4	0.8	0.0	0.0		O <O -2>	
☐ n4	1.0	0.0	0.0		O <O -2>	

♣ Lithium Nickel Oxide (?) • $Li_{0.04}NiO_2$ [04-010-4745]

Phase | d-I List | Wt%+XRF | Atomic | ☐ One Phase

Par...	Value	Shift	ESD	Site & Tie	Atom ID	
☐ x1	0.0	0.0	0.0	Wyckoff = 3b	Li <Li+1>	
☐ y1	0.0	0.0	0.0		Li <Li+1>	
☐ z1	1/2	0.0	0.0		Li <Li+1>	
☐ B1	0.5	0.0	0.0		Li <Li+1>	
☑ n1	0.15504	0.11504	0.0063		Li <Li+1>	•
☐ x2	0.0	0.0	0.0	Wyckoff = 3a	Ni <Ni+3>	
☐ y2	0.0	0.0	0.0		Ni <Ni+3>	
☐ z2	0.0	0.0	0.0		Ni <Ni+3>	
☐ B2	0.5	0.0	0.0		Ni <Ni+3>	
☑ n2	1.01365	0.01365	0.00209		Ni <Ni+3>	•
☐ x3	0.0	0.0	0.0	Wyckoff = 6c	O <O -2>	
☐ y3	0.0	0.0	0.0		O <O -2>	
☑ z3	0.26395	-0.00605	0.0001	D=0.0838Å	O <O -2>	•
☐ B3	0.5	0.0	0.0		O <O -2>	
☐ n3	1.0	0.0	0.0		O <O -2>	

X-ray Diffraction of Electrodes **after 10 cycles**



90-5-5 NMC cathode

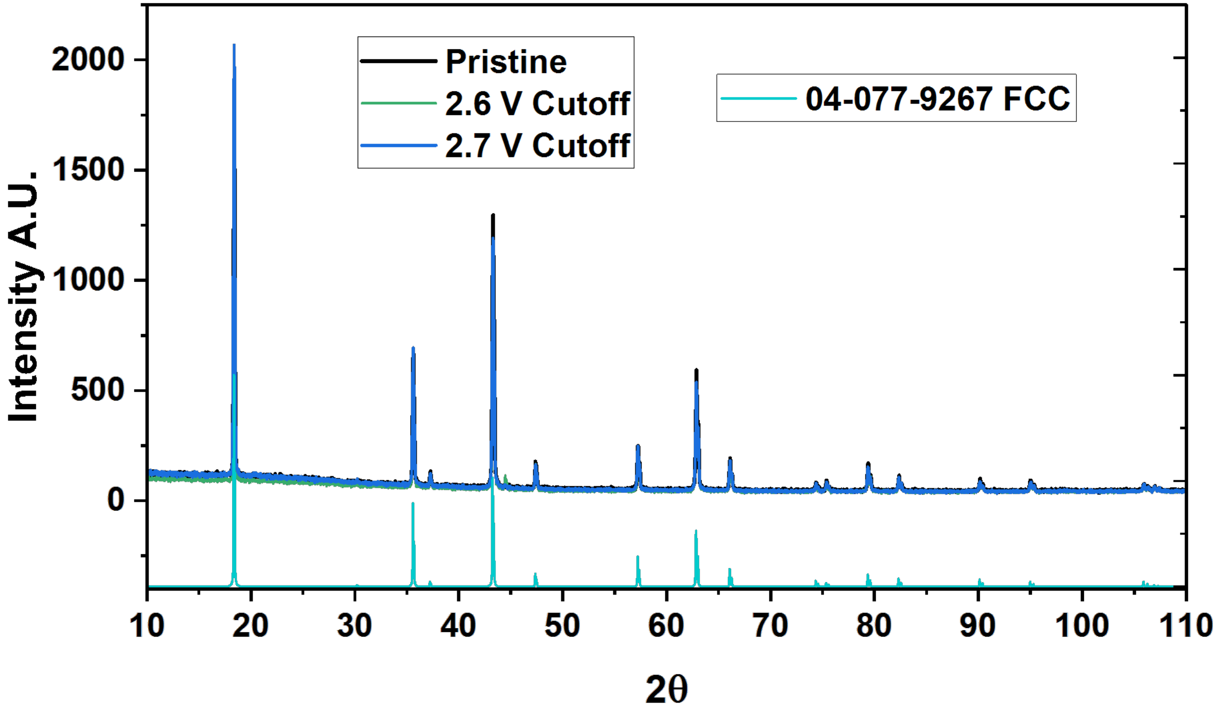
NMC Cathode	Hexagonal ($Li_xNi_yO_2$ analogue #1) 04-012-0511			Hexagonal ($Li_xNi_yO_2$ analogue) 04-024-3833			Hexagonal ($Li_xNi_yO_2$ analogue #2) 04-010-4745			Lithium content
	a=b	c	Volume	a=b	c	Volume	a=b	c	Volume	
Pristine	2.875	14.201	101.7							fully lithiated
2.6 V CCCV				2.820	14.361	98.9				reduced lithium
2.7 V CCCV				2.811	14.157	96.9	2.812	13.839	94.8	reduced lithium

LTO anodes show no structure change with cycling → same FCC $Li_4Ti_5O_{12}$ structure

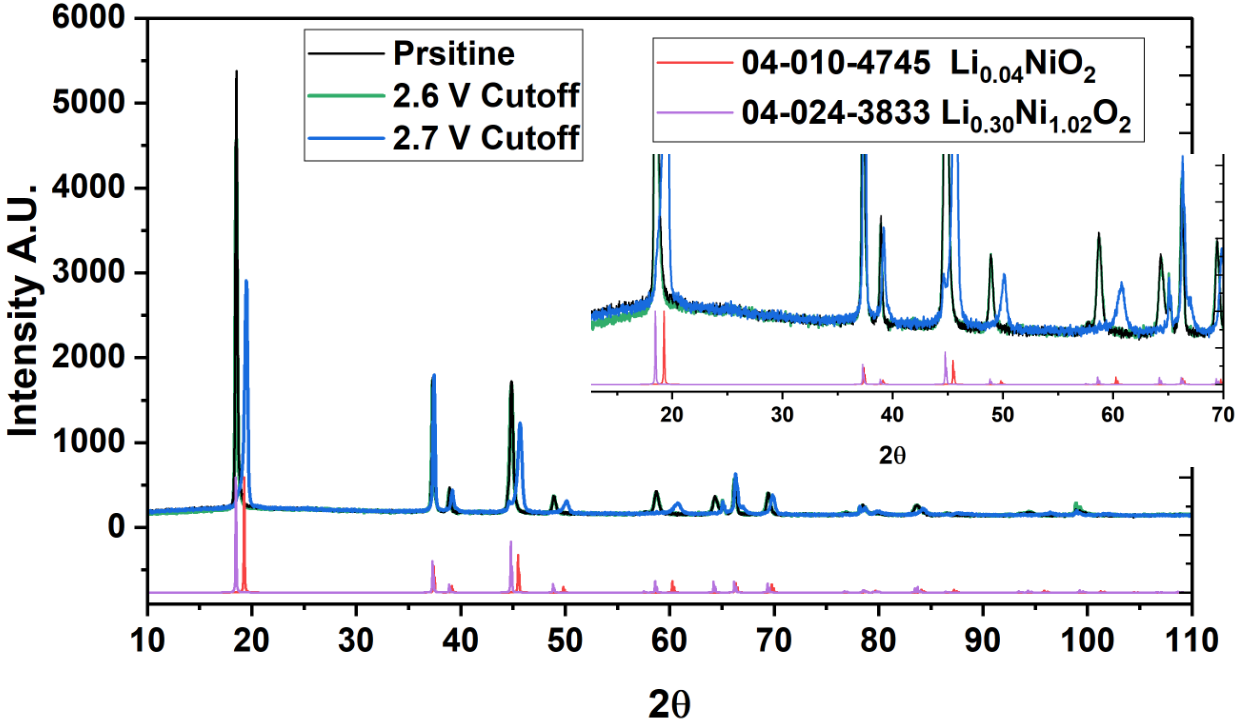
90-5-5 NMC cathode has voltage dependent phase → Li drastically changes unit cell volume

X-ray Diffraction of Electrodes **after 1,000 cycles**

LTO Anode



90-5-5 NMC cathode



	Hexagonal (LixNiyO2 analogue) 04-024-3833			Hexagonal (LixNyO2 analogue #2) 04-010-4745				
90-5-5 NMC	a=b	c	Volume	a=b	c	Volume	Lithium Content	Structure
2.6 V	2.822 ±0.002	14.36 ± 0.01	99.0 ± 0.2				reduced lithium	layered
2.7 V	2.820 ± 0.004	14.25 ± 0.3	98.1	2.8163 ± 0.0006	13.672 ± 0.008	93.93 ± 0.06	reduced lithium	layered

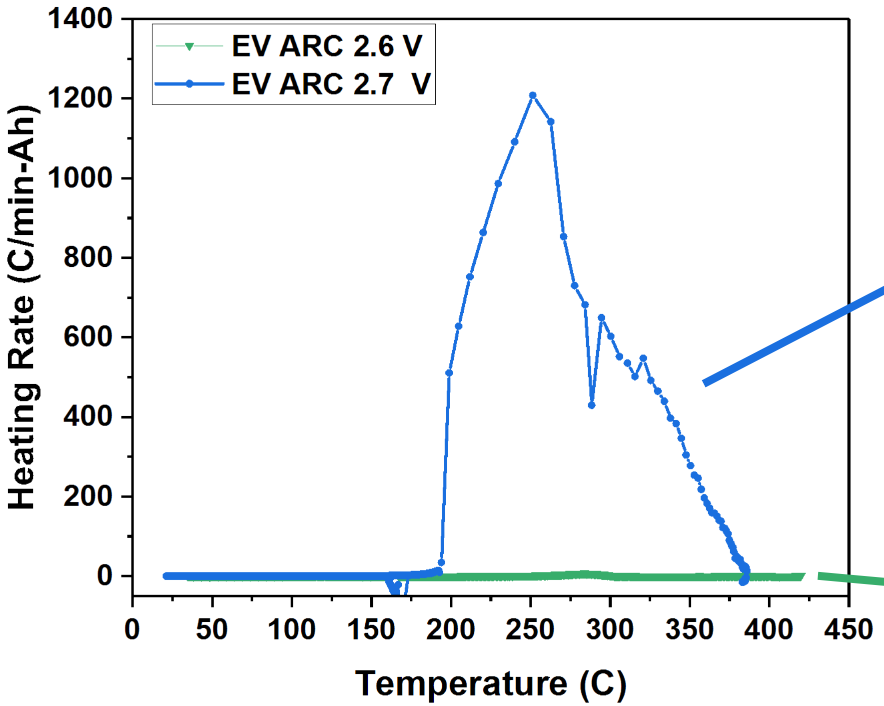
LTO anodes still show no structure change with cycling

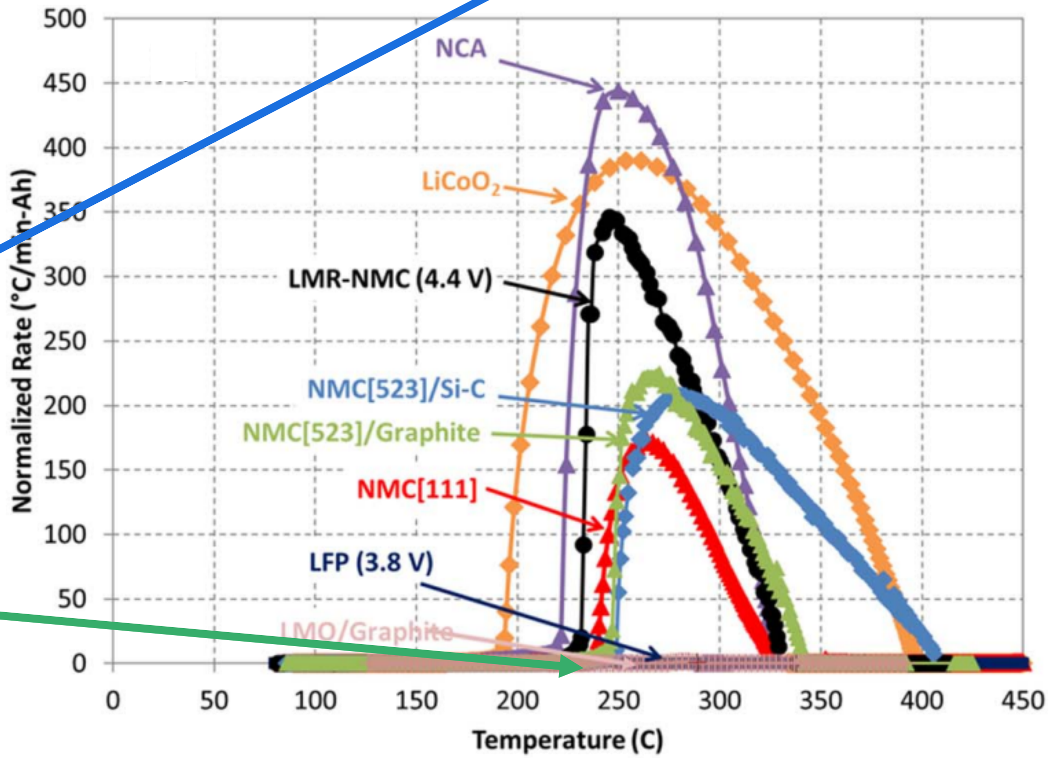
90-5-5 NMC cathode has voltage dependent phase → Li drastically changes unit cell volume

Conclusions

$Ni_{0.9}Mn_{0.05}Co_{0.05}$ (90-5-5 NMC)||$Li_4Ti_5O_{12}$ (LTO) is a safer Li-ion chemistry → if proper voltage controls are in place

Even with LTO anode a fully charged 90-5-5 NMC||LTO cell will heat rapidly → LTO does not inherently impart safety!



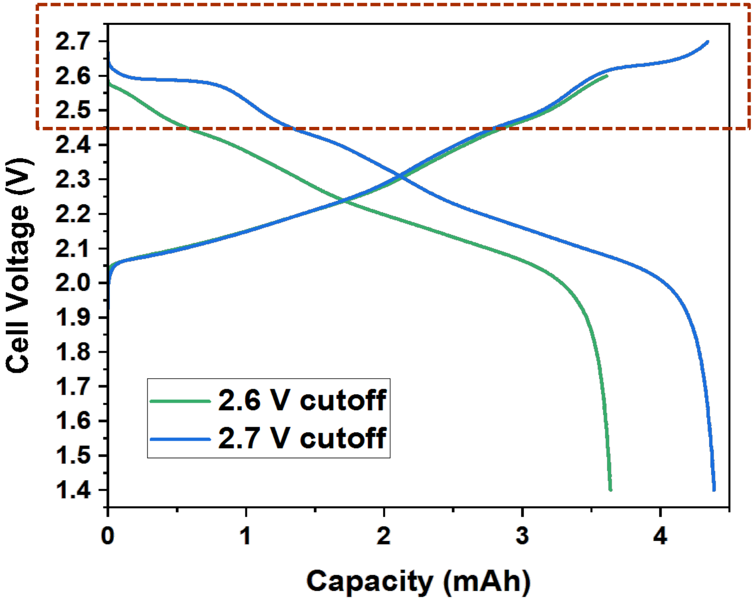


~20% loss of capacity tradeoff for immensely improved safety

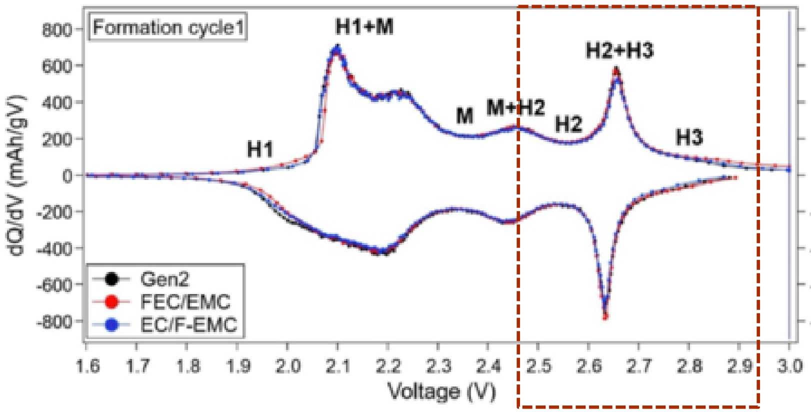
Conclusions

XRD was able to show the voltage dependance changes in the 90-5-5 cathode

2.6 V cutoff is enough to stop H2 → H3 transition (Even after 1000 cycles)
Delithiated, constricted c-axis H3 phase a danger for high Ni cathodes even with LTO anode



H3 ~ 2.6 – 2.7 V in LTO/NMC90-10-0 cell



Zhang, Y., Teeter, G., Dutta, N.S., Frisco, S. and Han, S.D., 2023. Chemical Engineering Journal, 460, p.141239.

Acknowledgements

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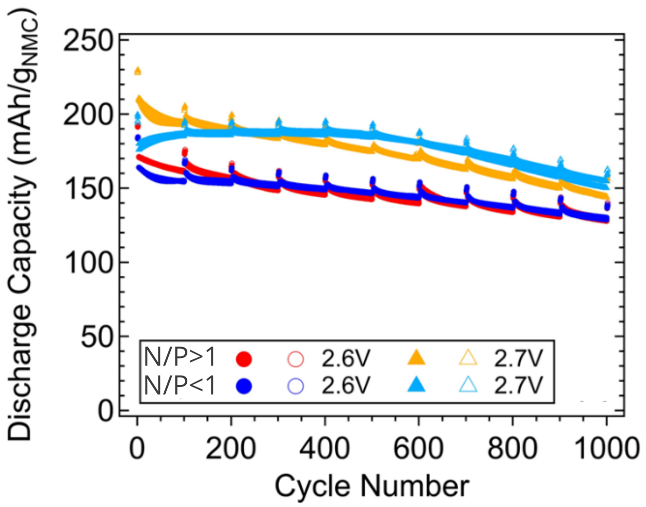
SNL Abuse team:
Lucas Gray, Jill Langendorf, Loraine Torres-Castro, Alex Bates

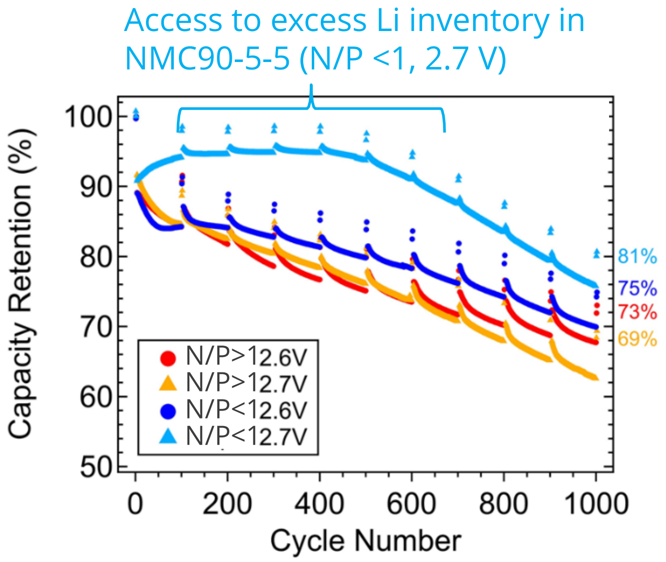
Thank You!

Questions?

Choosing the right Anode and Cathode

Need long cycle life without sacrificing too much energy density





Similar mAh/g_{NMC} if cycle to 2.6 V → initially N/P>1 and N/P<1 µm are NMC limited at 2.6 V

N/P>1 & N/P<1 cycled to 2.6 V similar fade → H3 plateau unavailable at 2.6 V even if N/P<1

In early cycles N/P<1 cycled to 2.7 V similar to N/P>1 & N/P<1 cycled to 2.6 V but capacity increases

N/P>1 & N/P<1 cycled to 2.7 V → higher capacity than N/P>1 and N/P<1 cycled to 2.6 V in later cycles

N/P<1 cycled to 2.7 V no fade until excess cathode Li depleted → then similar fade as N/P>1 to 2.7 V

Parts of a Battery

A *cell* is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction.

The *anode* is the negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit.

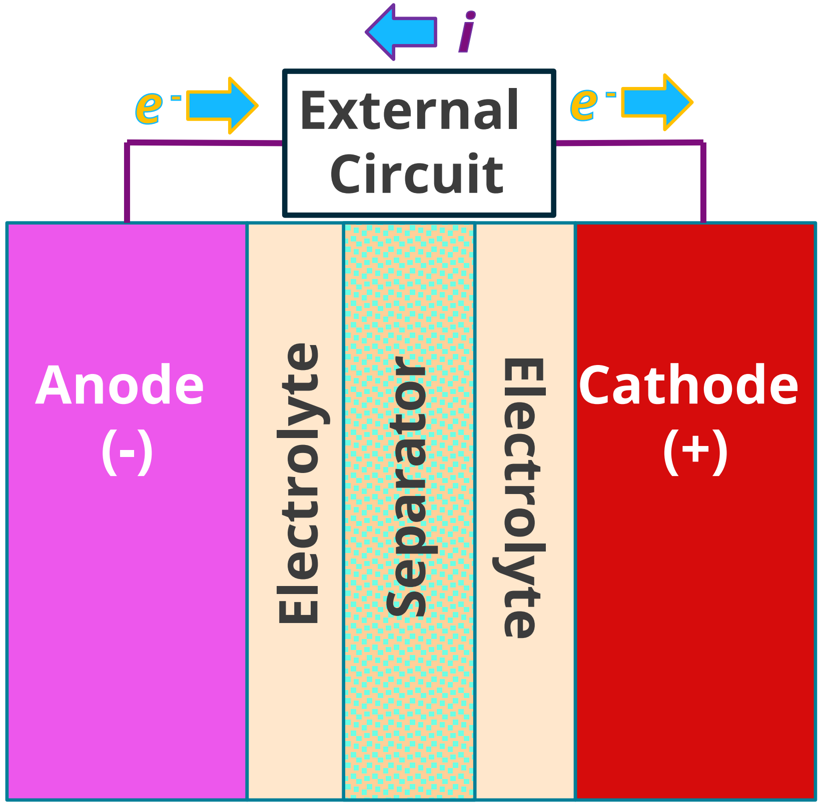
The *cathode* is the positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit.

An *electrolyte* is a material that provides pure ionic conductivity between the positive and negative electrodes of a cell.

A *separator* is a physical barrier between the positive and negative electrodes that must be ionically conductive and electrically insulating.

A *current collector* is an inert member of high electrical conductivity used to conduct current from or to an electrode during discharge or charge.

The *casing* is the material that encapsulates the all other components of a battery.



Current → large = fast ; small = slow *Voltage* → large = more force ; small = less force

A *battery* consists of one or more *cell(s) in parallel and/or series.*

Battery Terminology

Discharge: An operation in which a battery delivers electrical energy to an external load.
Charge: An operation in which the battery is restored to its original charged condition by reversal of the current flow.

Capacity: The total number of Ampere-hours (**Ah**) that can be withdrawn from a fully charged cell or battery under specified conditions of discharge
Specific Capacity: The ratio of the capacity delivered by a cell or battery to its weight (Ah/kg or **mAh/g**).

State Of Charge (SOC): Remaining capacity in cell or battery, usually given as (**%**)

Depth of Discharge (DOD): Amount of capacity used for given discharge as a ratio of total capacity (**%**)

Gravimetric Energy Density: The ratio of the energy output of a cell or battery to its weight (Wh/kg).
Volummetric Energy Density: The ratio of the energy available from a battery to its volume (Wh/L).

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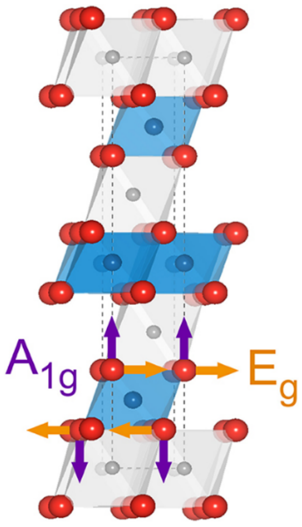
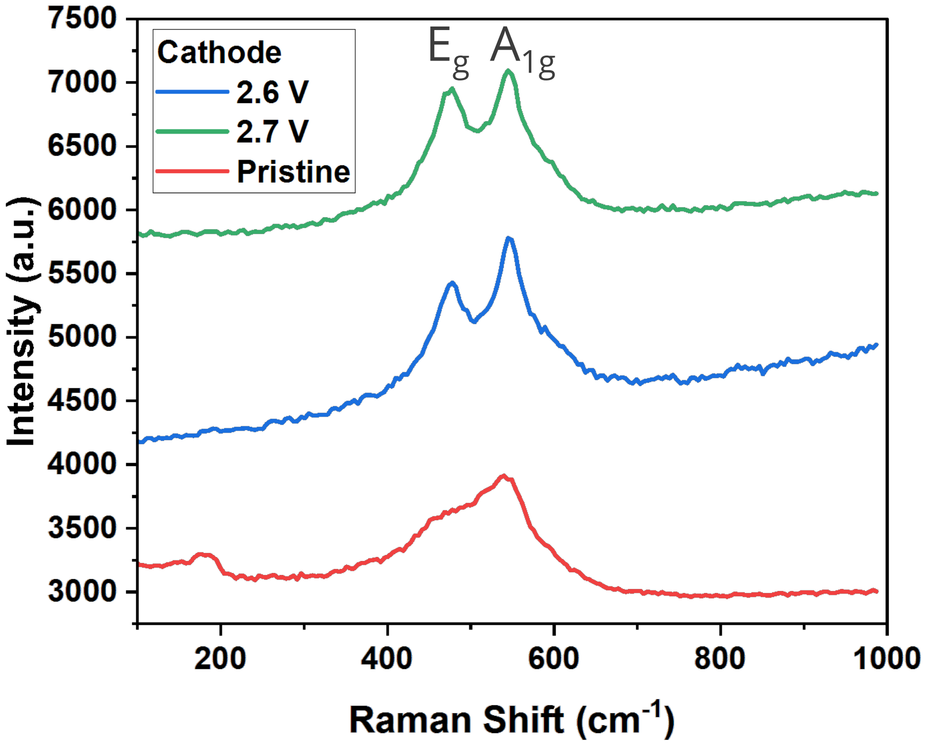
Efficiency: The ratio (**%**) of the output of a secondary cell or battery on discharge to the input required to restore it to the initial state of charge under specified conditions.

C-Rate: It is the rate of charge or discharge of a cell or battery. Generally, it is expressed by n C.

Example: 0.1 C means the full charge or discharge time is 1/0.1 h (10 h); 10 C is 1/60 h (6 min).

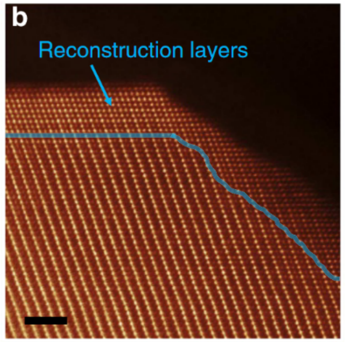
Trying to see if there are major structural changes in cathode with charging voltage





See more prominent peaks and more intense E_g mode, but not qualifiable differences between 2.6 and 2.7 V

LiNi 0.4Mn 0.4Co 0.18 Ti 0.02 O2



reconstruction layer consists primarily of an Fm3m rock-salt structure (Fig. 5c,d), with a few atomic layers of spinel structure as a 'bridge' between the layered structure (containing Ni 2+, Mn4 + and Co 3 +) and **rock-salt** structure (containing Ni 2 + , Mn2 + and Co 2+).

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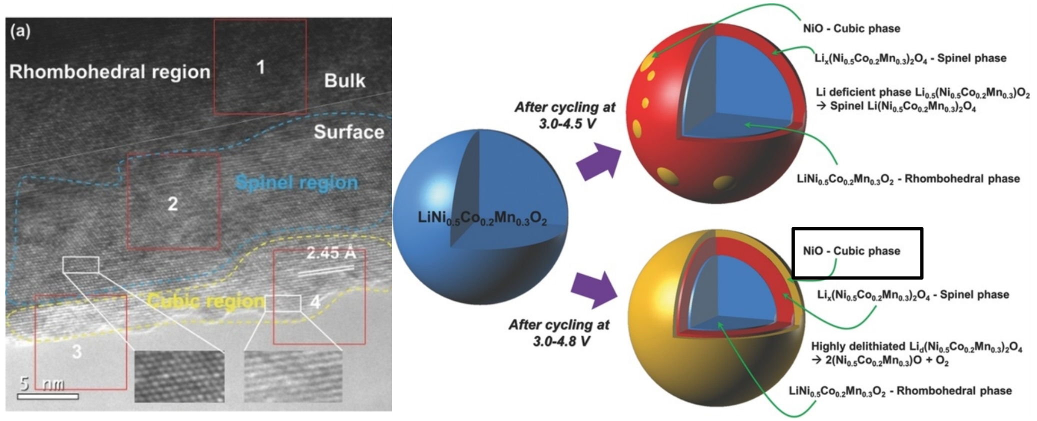
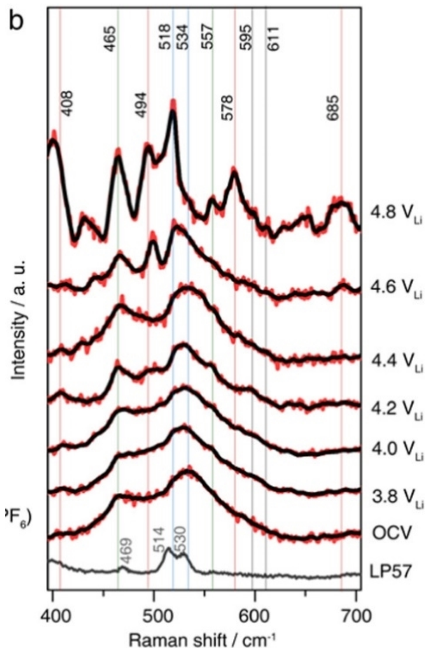
DOI: 10.1038/ncomms4529 |

$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$



Adv. Energy Mater. 2014, 4, 1300787
DOI: 10.1002/aenm.201300787

$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$



The peak around 498 cm^{-1} became prominent at 4.6 V_{Li} and further grew to 4.8 V_{Li}, which could be assigned to the one-phonon longitudinal optic mode (1LO) of **NiO**

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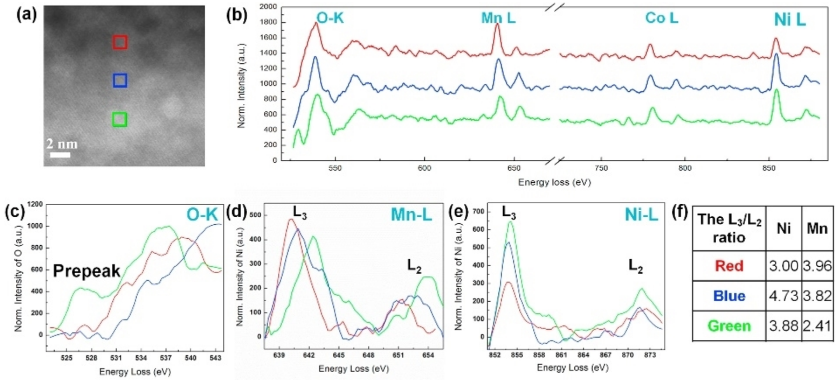
https://doi.org/10.1021/acs.jpcc.9b11677

$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$



The L_3/L_2 ratio	Ni	Mn
Red	3.00	3.96
Blue	4.73	3.82
Green	3.88	2.41

N.Y. Kim et al. / Journal of Power Sources 307 (2016) 641e648
http://dx.doi.org/10.1016/j.jpowsour.2016.01.023

The structural instability is caused by a migration of TM ions, especially Ni ions to Li sites. This migration can trigger phase transformation from layered (R-3m) to spinel (Fd-3m) and **rock-salt** (Fm-3m) phase [2], [3], [4], [5]. ... This phase transformation accompanies a lattice distortion, volume shrinkage and oxygen loss from the structure [4], [6].