PURIFICATION OF LITHIUM-ION BATTERY BLACK MASS THROUGH TAILORED ALKALINE CORROSION

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National Renewable Energy Laboratory

K. Fink et al., "Optimized purification methods for metallic contaminant removal from directly recycled Li-ion battery cathodes" (under review)

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Direct Recycling of Li-Ion Batteries

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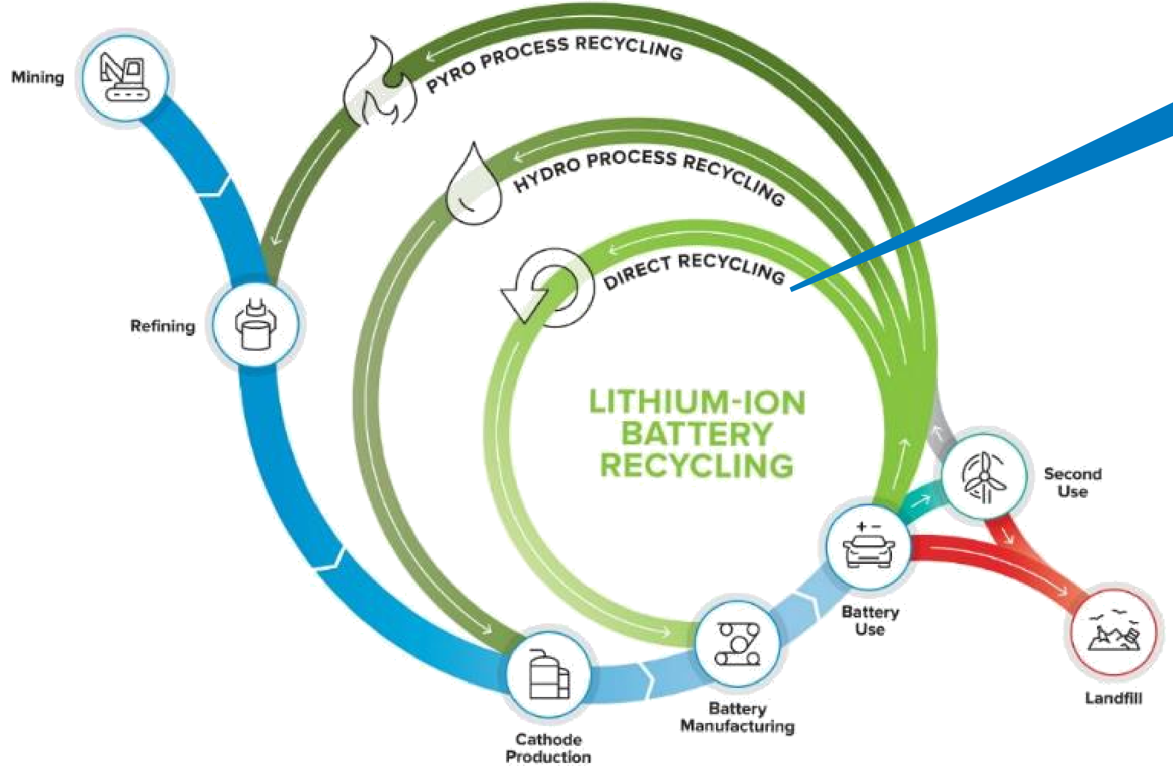
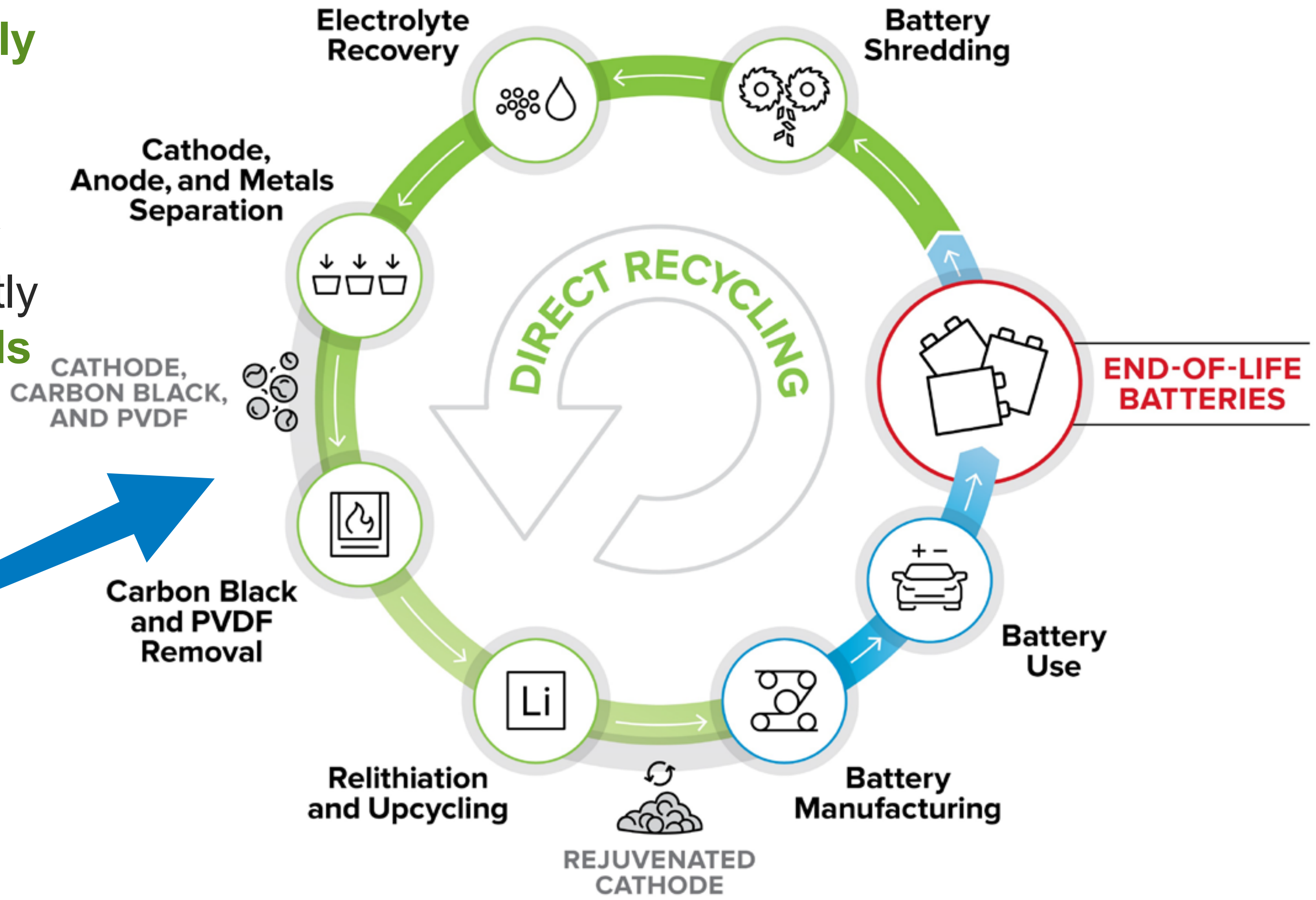
- Burgeoning demand for Li-ion batteries induces **supply chain instability** and raises concerns regarding **end-of-life disposal**.
- <u>DOE goal:</u> “Reduce the cost of electric vehicle battery packs to <$150/kWh with technologies that significantly reduce or eliminate **dependency on critical materials** and utilize **recycled material feedstocks**”

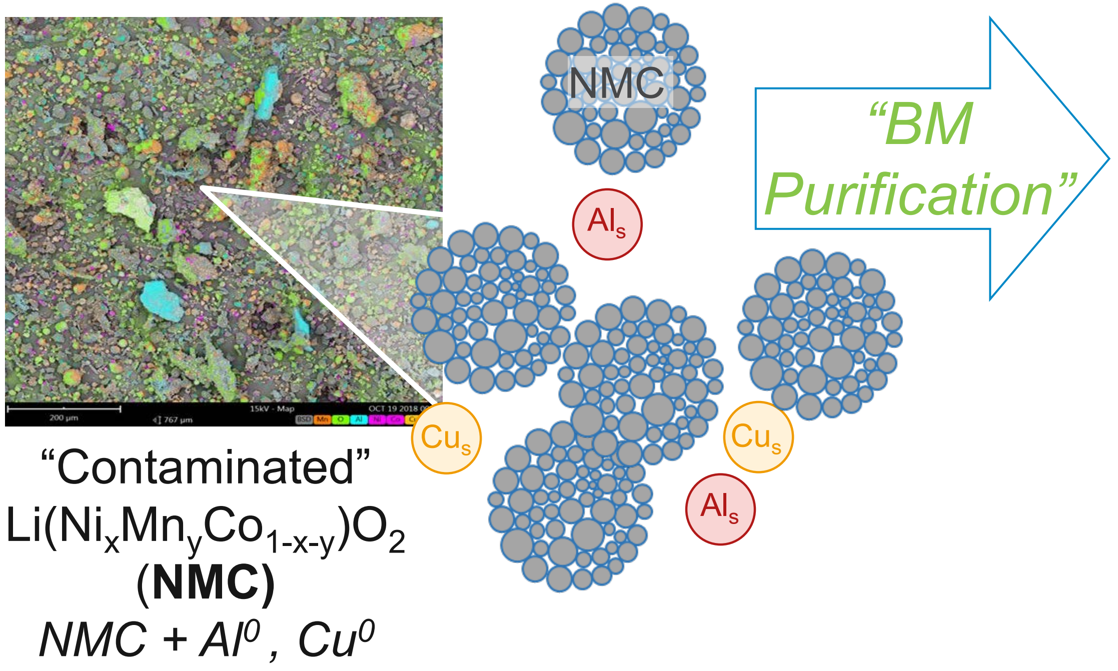


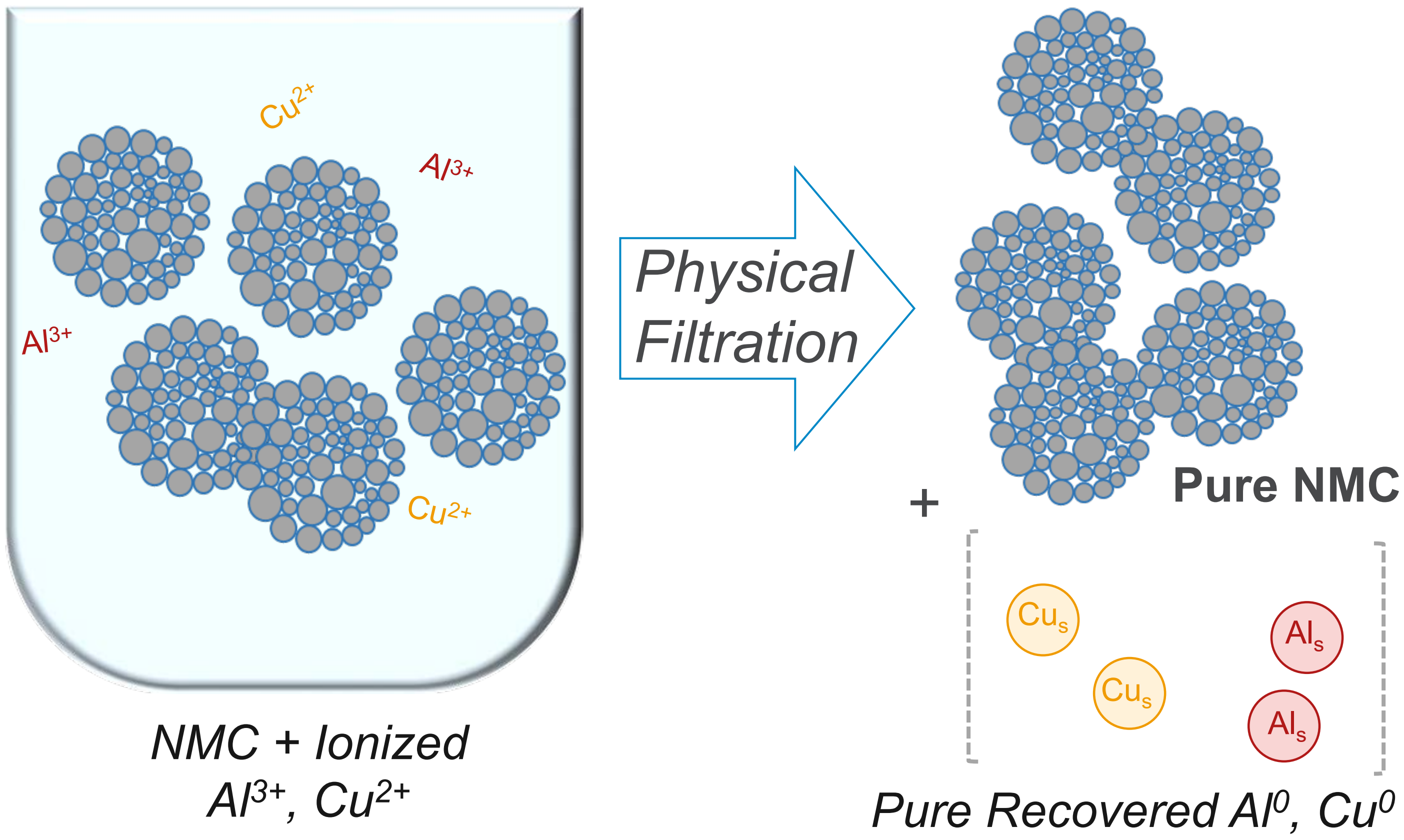


Direct recycling retains the engineered value of battery materials and minimizes processing steps.

Black Mass Purification: Process Overview

Shredded black mass contains trace Al & Cu from current collectors that may **inhibit cell performance** and impacts **purity** of recycled product.





Goal: **Identify** and **optimize** BM purification process to enable complete and rapid dissolution of solid contaminants (Al^0, Cu^0) without adversely impacting structure or electrochemical performance of NMC.

Approach: "Kinetically & thermodynamically assisted" alkaline aqueous corrosion

Overview of Project Workflow

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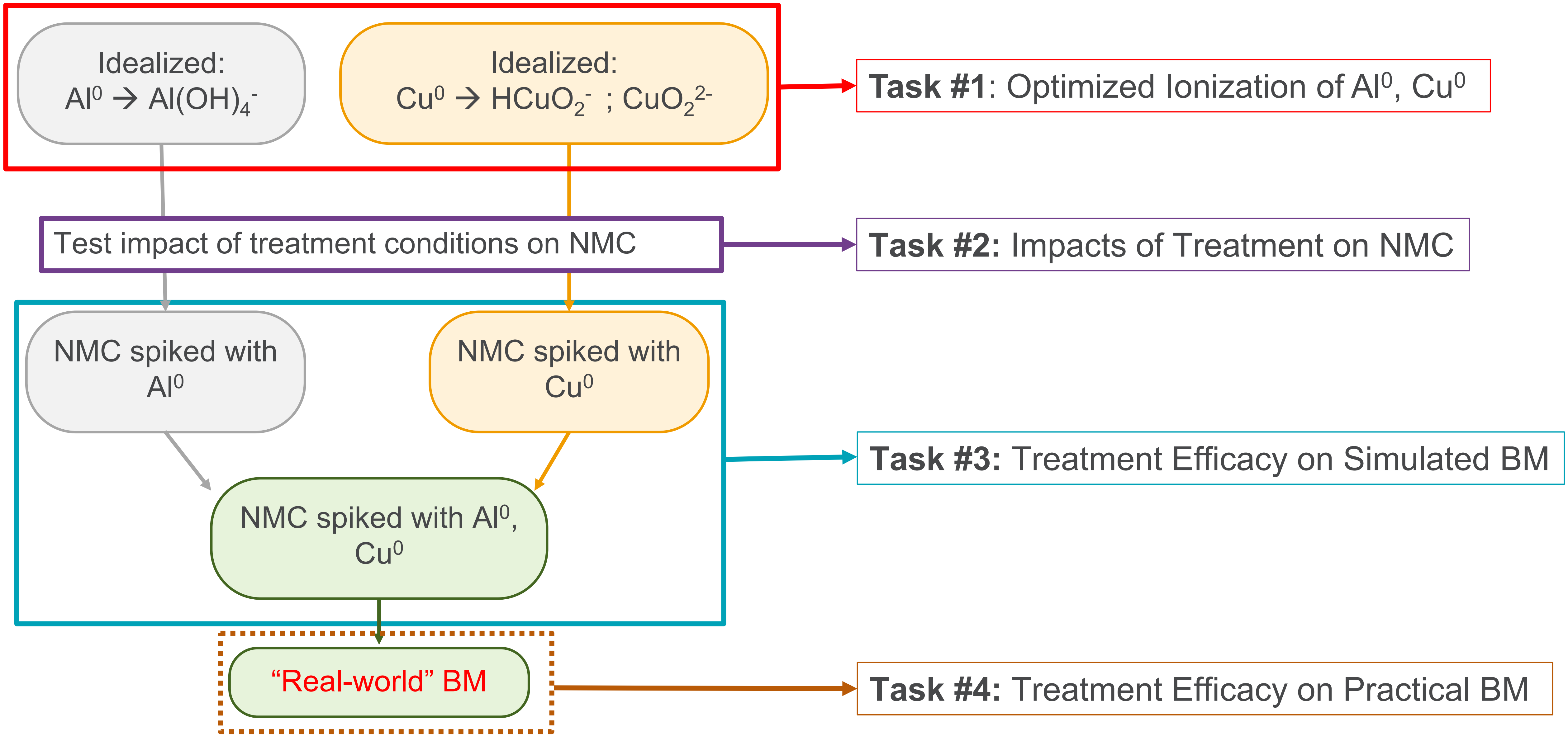

Task #1: Optimized Ionization of Al_0, Cu_0

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Idealized:
$Al_0 \rightarrow Al(OH)_4^-$

Idealized:
$Cu_0 \rightarrow HCuO_2^-$; CuO_2^{2-}

Al^0 or Cu^0 *(~1/3 of RT solubility)*

DI H_2O

OH^- *(conc.; "carbonate-free")*

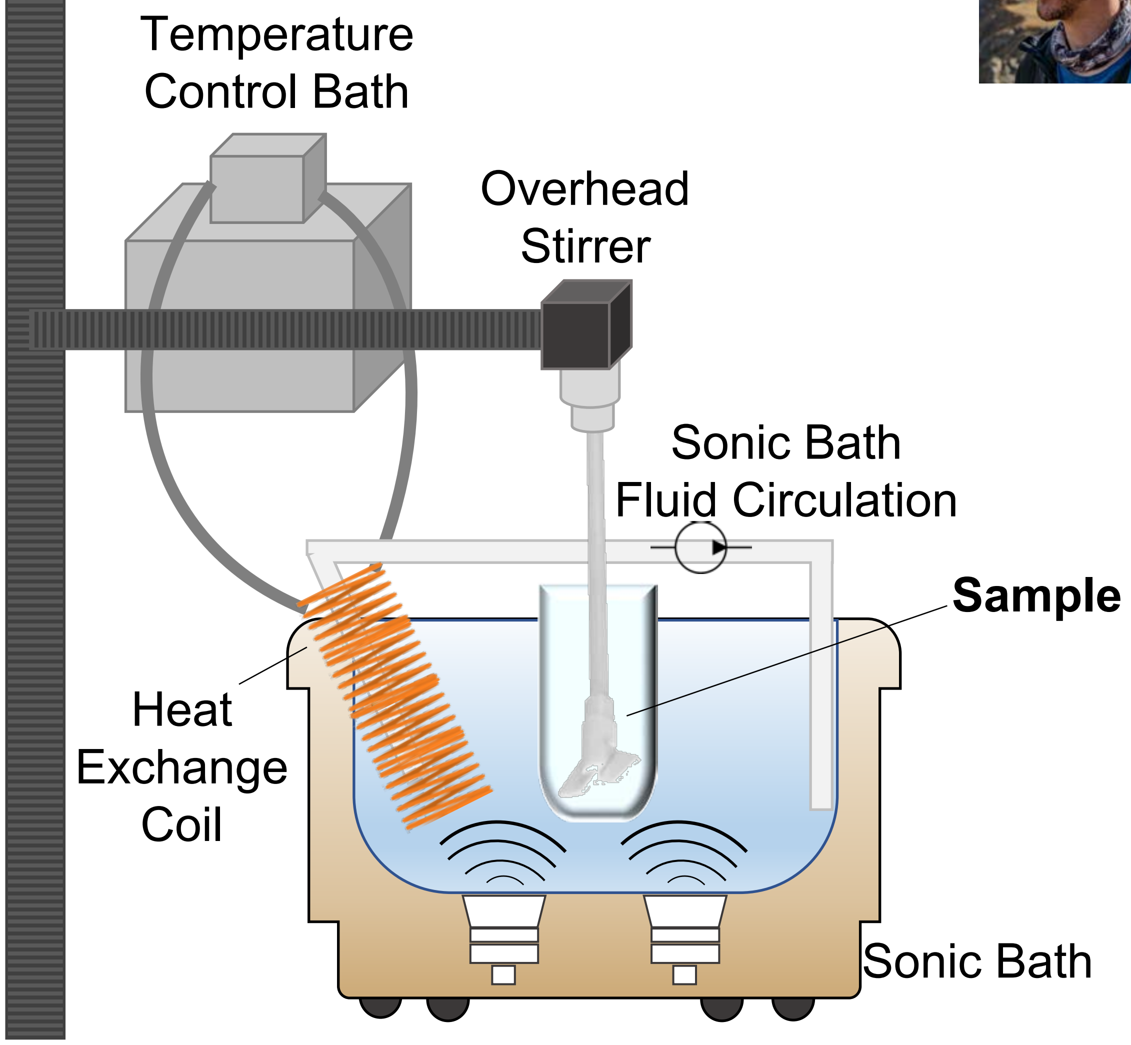
Cl^- *(saturated; ~4.5 M)*

DTPA *(2x molar equivalent)*

"Bench-scale" testing:
- 40-45 mL solution
- 10 mg contaminant

Modular overhead sonic-stirrer

Designed and built support: Joshua Major (NREL)



Al^0 & Cu^0 Corrosion: Theoretical Foundations

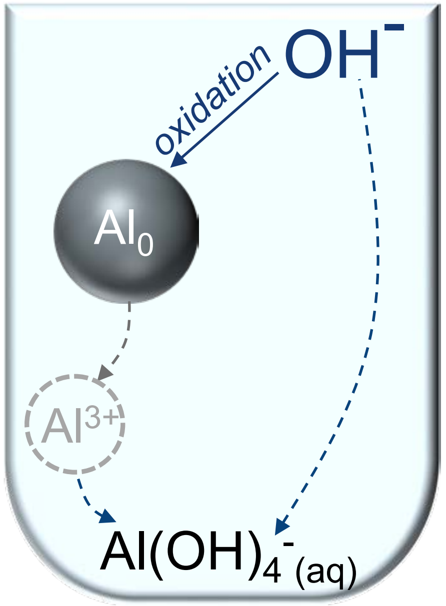
Al^0 Corrosion:

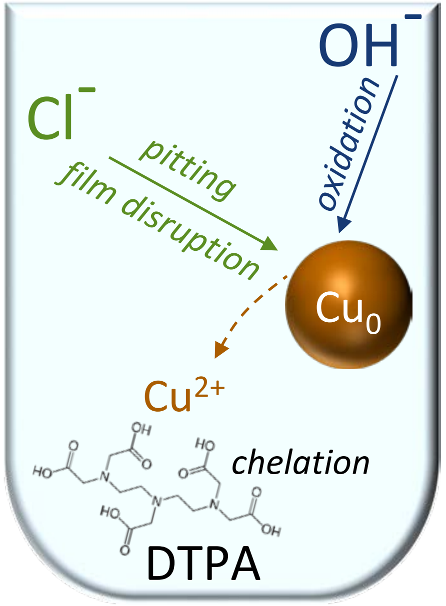
-Rapid, strongly pH-dependent reaction under ambient oxidative conditions

$Al_{(s)} \rightarrow Al^{3+} + 3e^-$ (anodic)
$2H_2O + 2e^- \rightarrow 2OH^- + H_{2(g)}$ (cathodic)

$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)}$
$Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow Al(OH)_4^-{}_{(aq)}$

$\mathbf{Al_{(s)} + OH^- + 3H_2O \rightarrow Al(OH)_4^-{}_{(aq)} + 3/2\ H_2}$



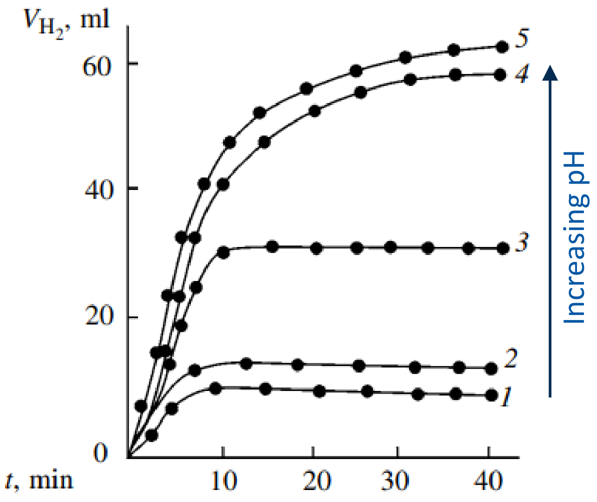


Cu^0 Corrosion:

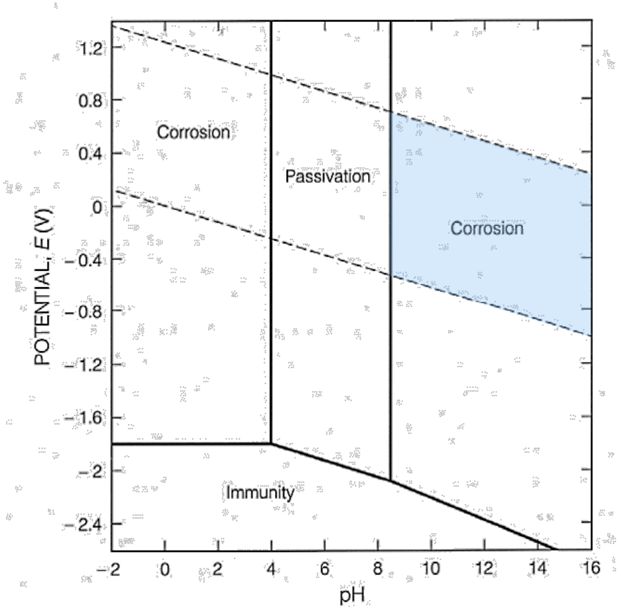
-Kinetically slow and thermodynamically unfavorable

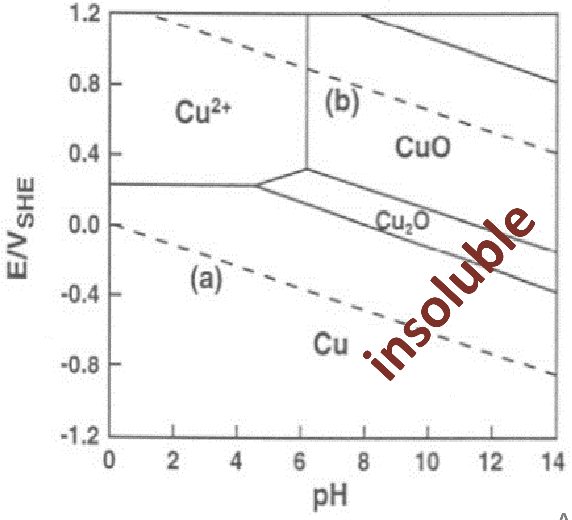
-Low solubility of Cu^{2+} species and formation of passivating surface films

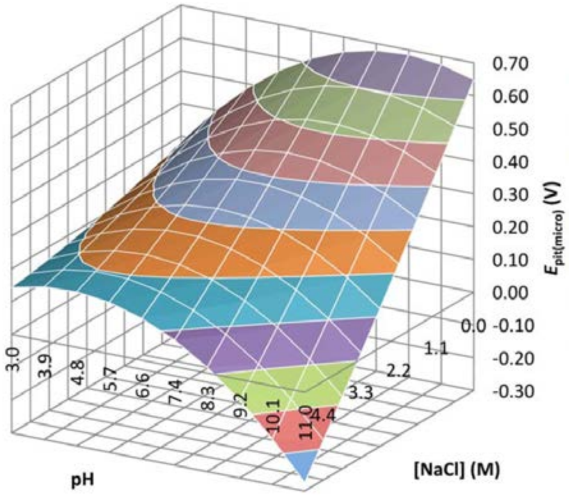
-**Chloride** reportedly enhances corrosion in alkaline media through pitting and surface film disruption



Alexsandrov et al., Russian J. Gen. Chem. 73, 5 (2003), 689-694.







Arjmand and Adriaens, Materials 2012, 5, 2439-2464

Al^0 Corrosion: Bench-Scale Optimization

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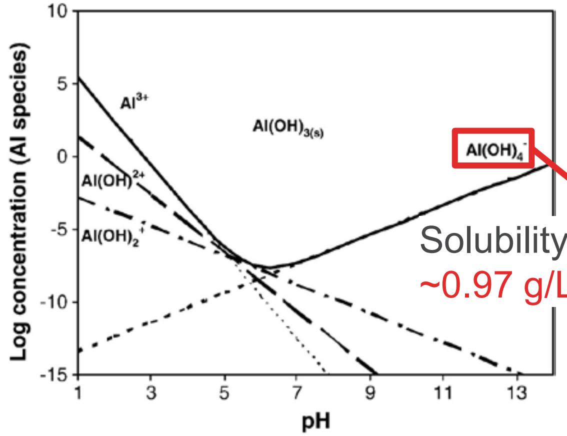
Approach: pH monitoring (*unbuffered system*)

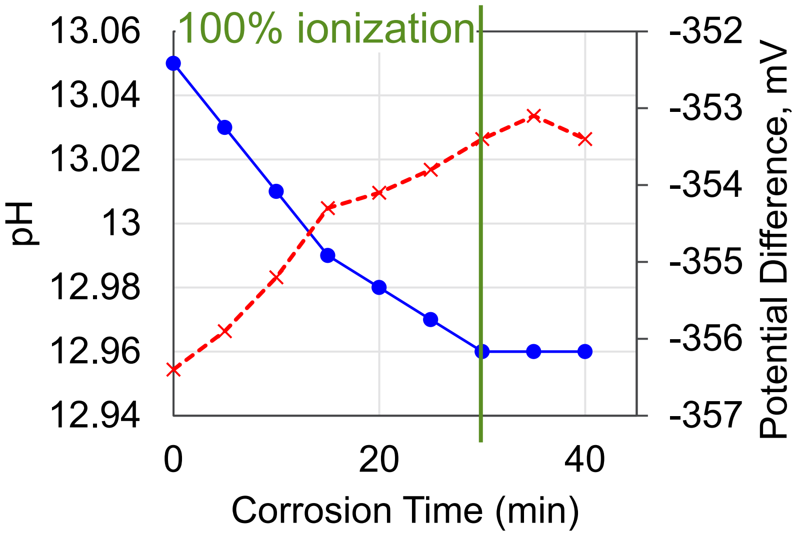
$Al_{(s)} + OH^- + 3H_2O \rightarrow Al(OH)_4^-{}_{(aq)} + 3/2\ H_2$	log K_f $[Al(OH)_4^-]$ = 33.0 (25 °C)
Each extent of reaction consumes Al_0 and OH^- on a 1:1 molar basis	*Al^{3+} preferentially and strongly binds OH^- in alkaline solution to form soluble $Al(OH_4)^-$.*
Reaction kinetics and extent may be quantified by **tracking solution pH**	***Thermodynamically favorable*** *reaction; room for* ***kinetic tuning****.*



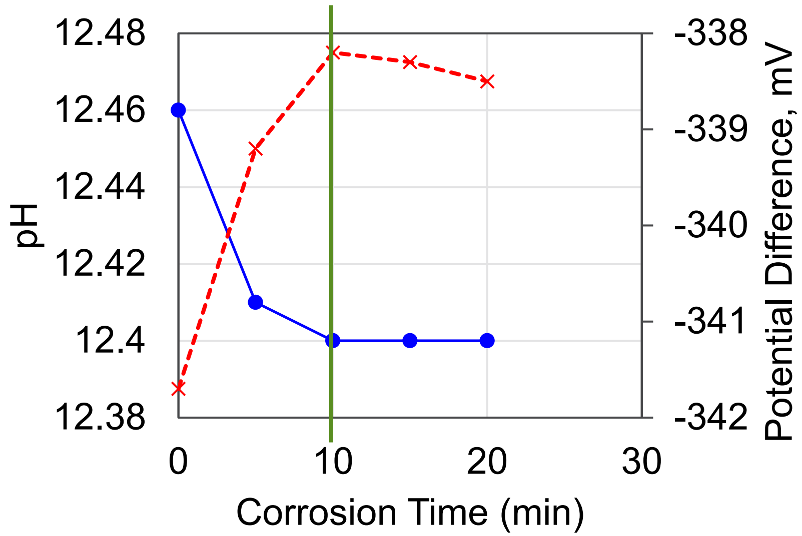
Emamjomeh et al, *Desalination* 275, 1-3 (2011), 102-106.

Solubility of $Al(OH)_4^-$: ~0.97 g/L at pH 13; 25 °C

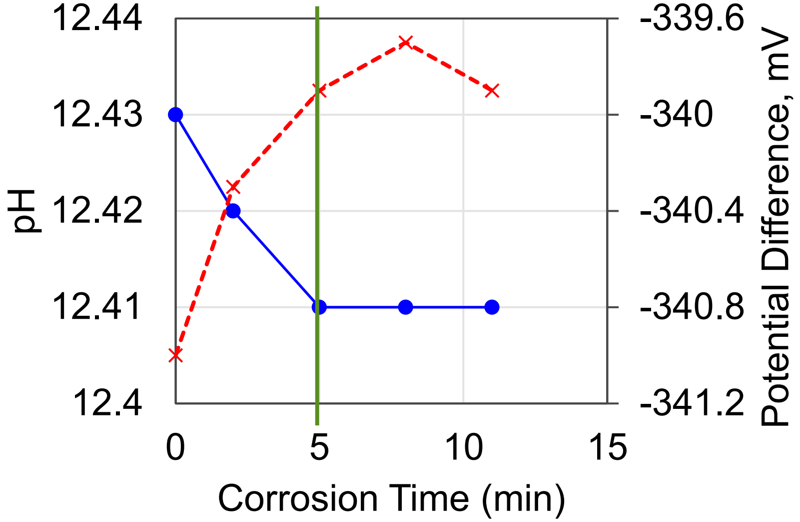
RT, no T control *(20–22 °C)*



40 °C, No Sonics



40 °C, With Sonics



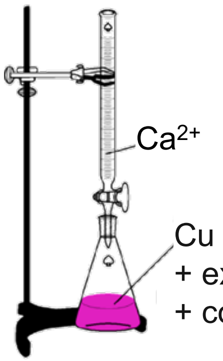
All samples were prepared at pH 13 at calibrated room temperature (~22 °C)

Mildly elevated temperature and sonication increase corrosion rate for Al^0.

Full corrosion achieved in **5 min** (*40 °C with sonication; 10 mg Al^0 at pH 13*)

Cu^0 Corrosion: Bench-Scale Optimization

All samples shown were prepared at pH 13 (*measured at RT*)



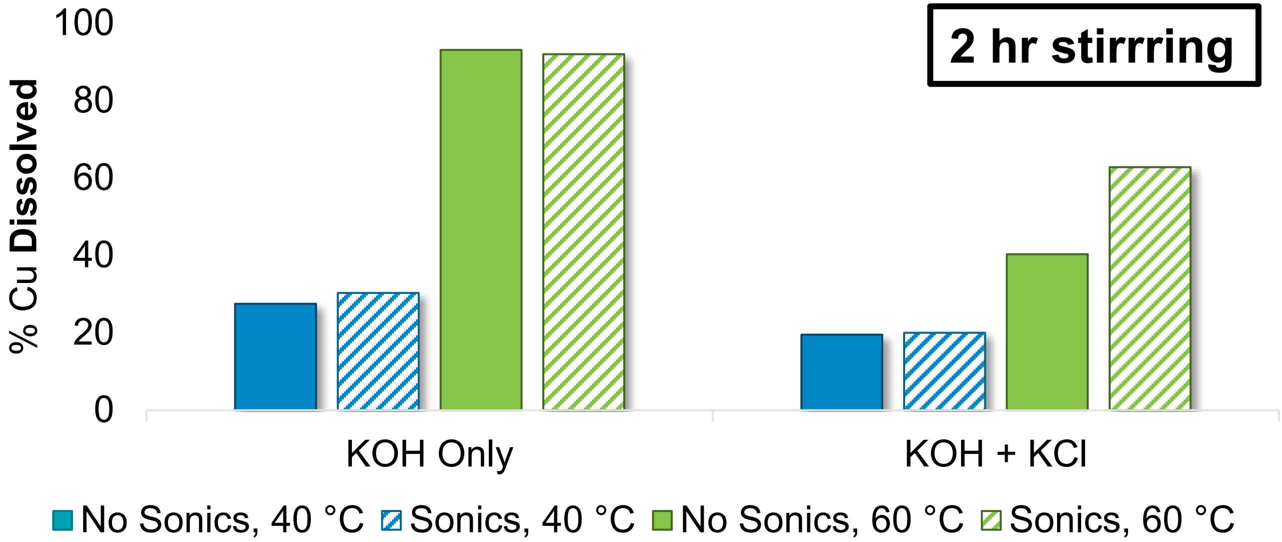
Approach: colorimetric titration
(± *1-2 wt % Cu*)

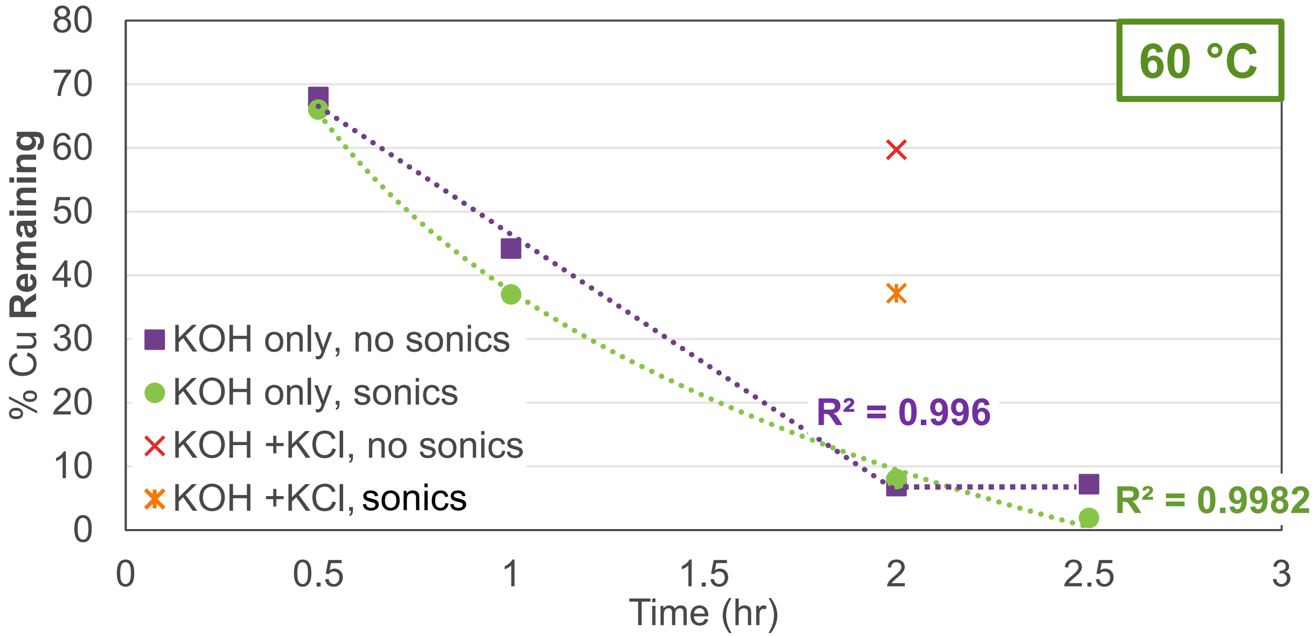
Cu + DTPA (complexed)
+ excess DTPA
+ colorimetric indicator

"Base" solution w/ dissolved Cu
Blue color: Cu-DTPA

Solution + P-R dye

Solution titrated to eq. pt. with $Ca(NO_3)_2$





- Cl^- *inhibits* Cu^0 corrosion at moderate temperatures.
- Sonication improves extent of ionization for Cl^--treated samples, but does not sufficiently compensate for passivating effects.

Without Sonication:
- **Linear (0^{th} order)** kinetics until ~93% ionization
- Thermodynamic maximum <100% ionization

With Sonication:
- **Logarithmic (1^{st} order)** kinetics (conc. dependence on ionized product)
- ~100% corrosion achieved after **2.5 hr** (*within error*)

Task #2: Impacts of Treatment on NMC

Idealized: $Al_0 \rightarrow Al(OH)_4^-$

Idealized: $Cu_0 \rightarrow HCuO_2^-$; CuO_2^{2-}

Test impact of treatment conditions on NMC

NMC spiked with Al^0

NMC spiked with Cu^0

NMC spiked with Al^0, Cu^0

"Real-world" BM

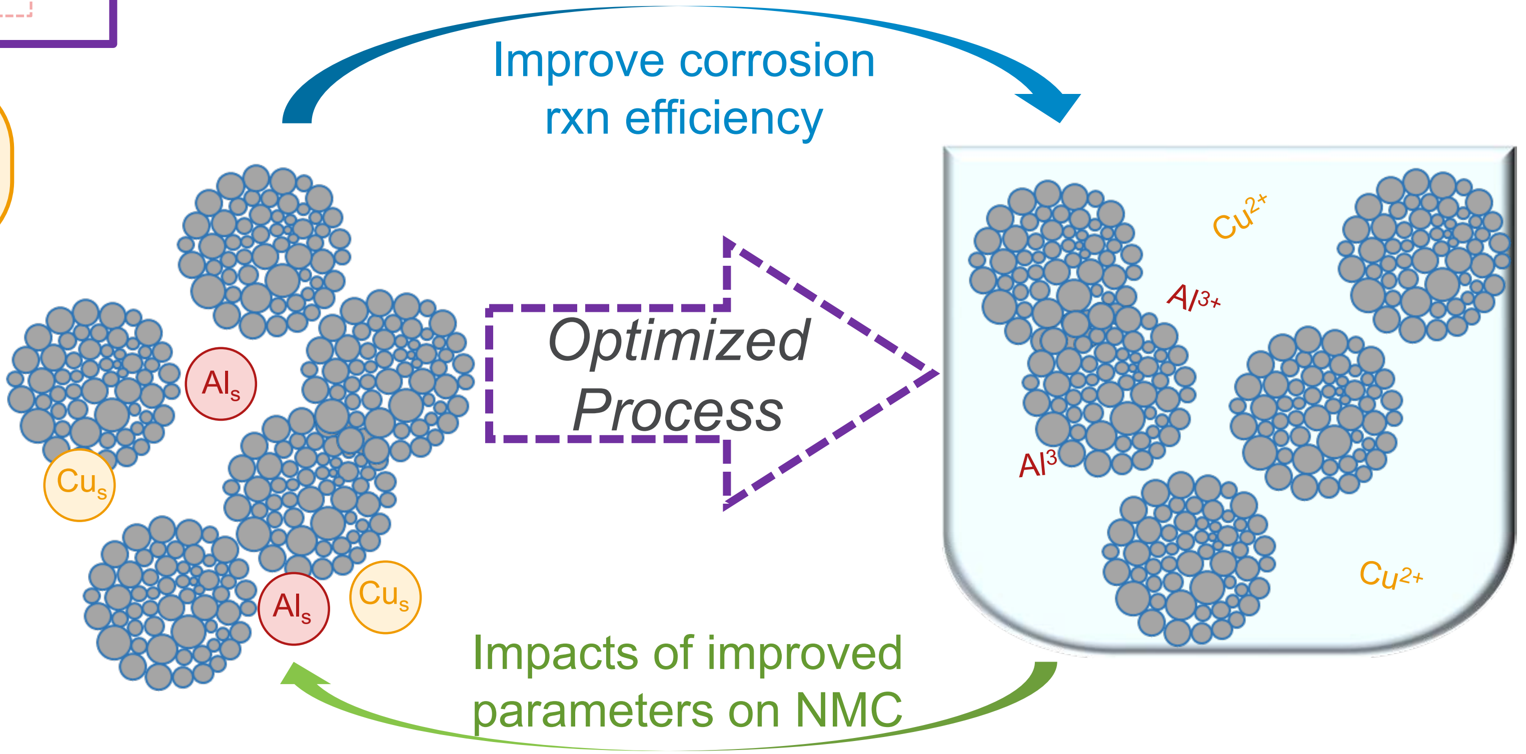
Electrochemical Performance

Structural/Morphological Changes

- -XRD
- -SEM

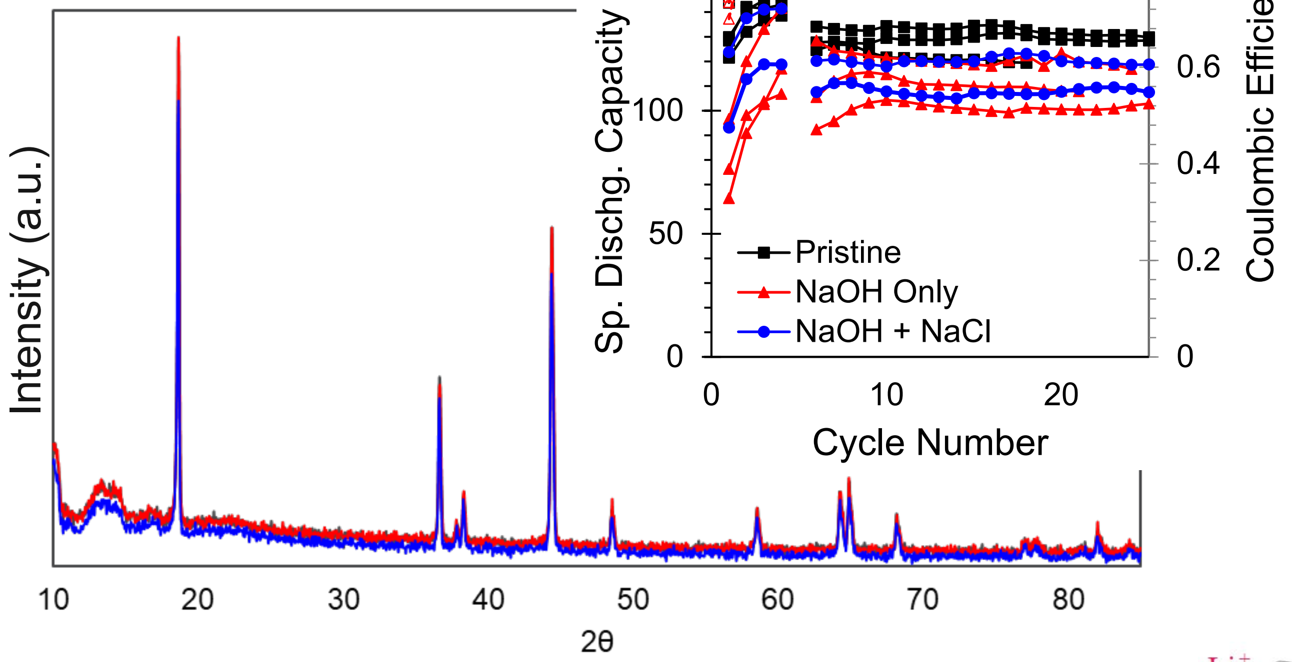
Chemical Changes

- -ICP (*pending*)

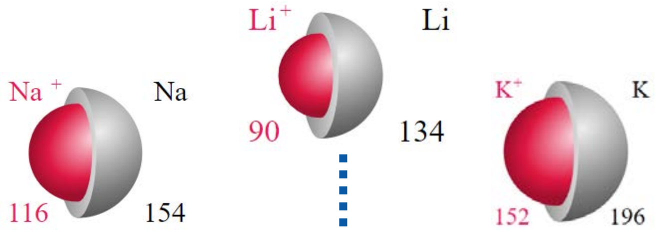


Iterative Process Optimization

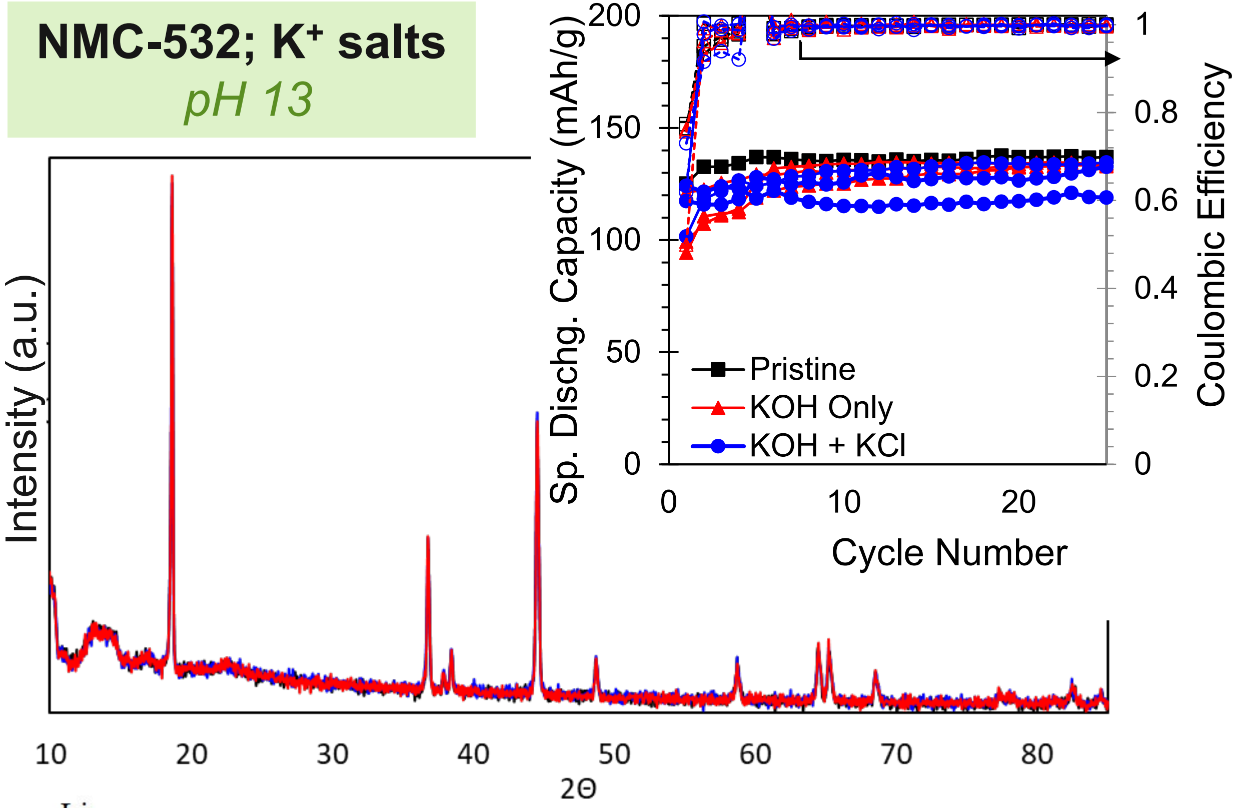
NMC-532; Na^+ salts
pH 11



Condition	% Co_3O_4 ± SE	*a*	*c*	*I(003)/I(104)*
Pristine	1.0 ± 0.7	0.288	1.426	1.03
NaOH	1.5 ± 0.9	0.289	1.425	1.06
NaOH/NaCl	1.1 ± 0.5	0.288	1.426	1.12



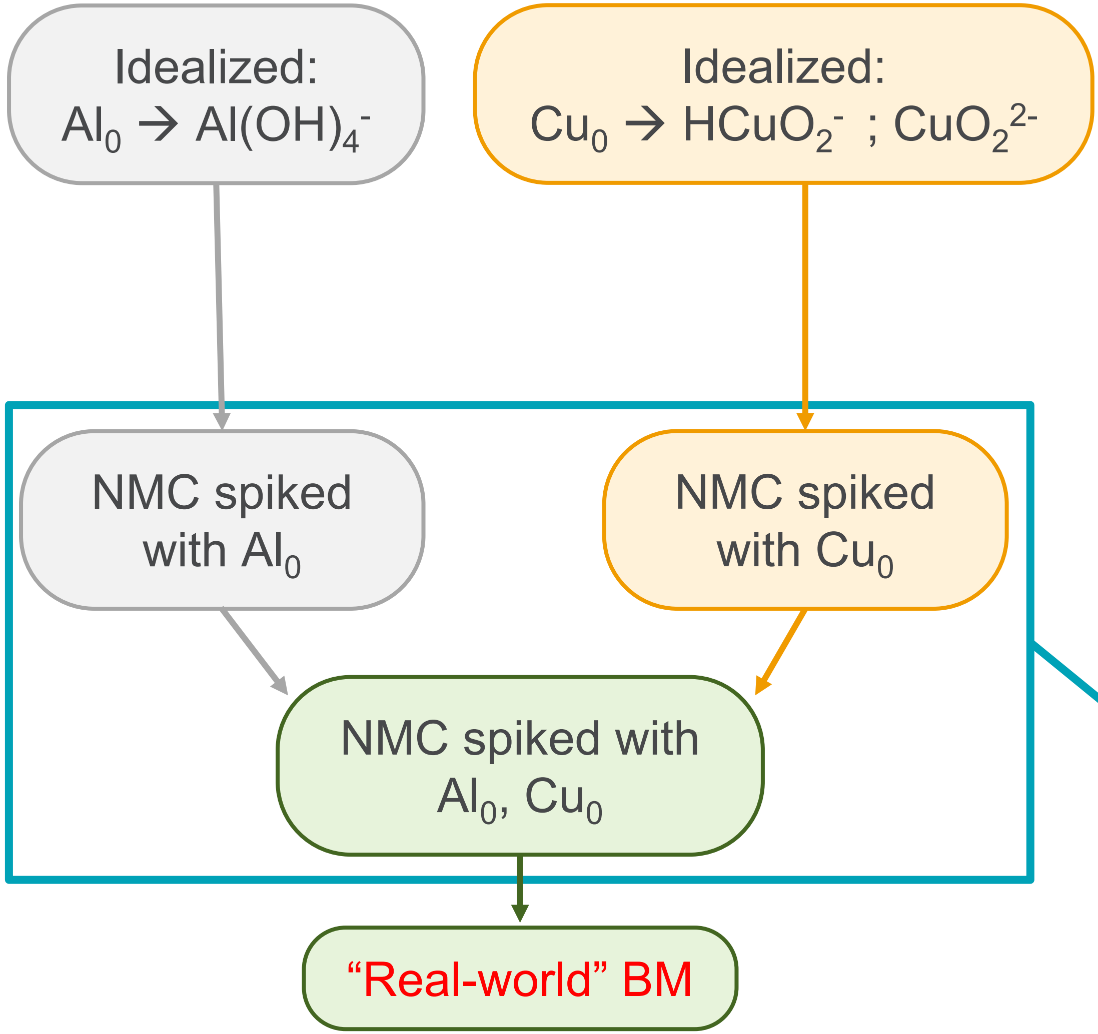
NMC-532; K^+ salts
pH 13

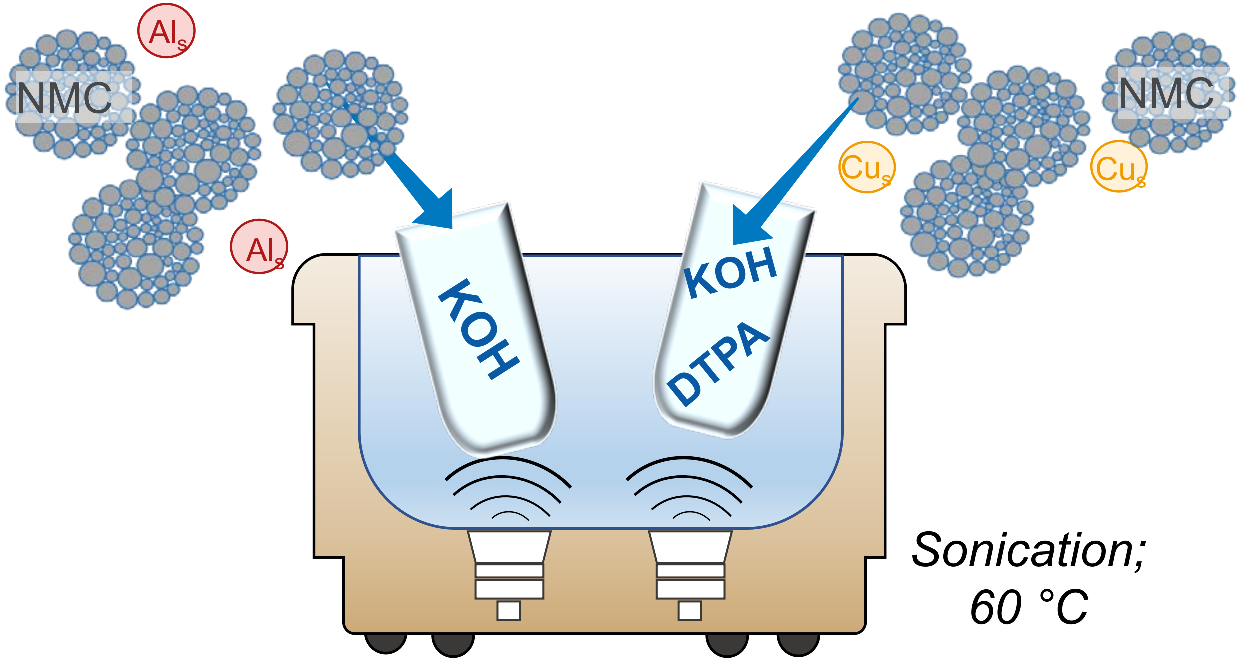


Condition	% Co_3O_4 ± SE	a	c	I(003)/I(104)
Pristine	0.05 ± 0.01	0.286	1.423	1.05
KOH	0.04 ± 0.01	0.286	1.423	1.08
KOH/KCl	0.05 ± 0.01	0.286	1.422	1.09

Evidence of cation mixing and bulk structural rearrangement with Na^+ salts prompted shift to K^+ salts.

Task #3: Treatment Efficacy on Simulated BM

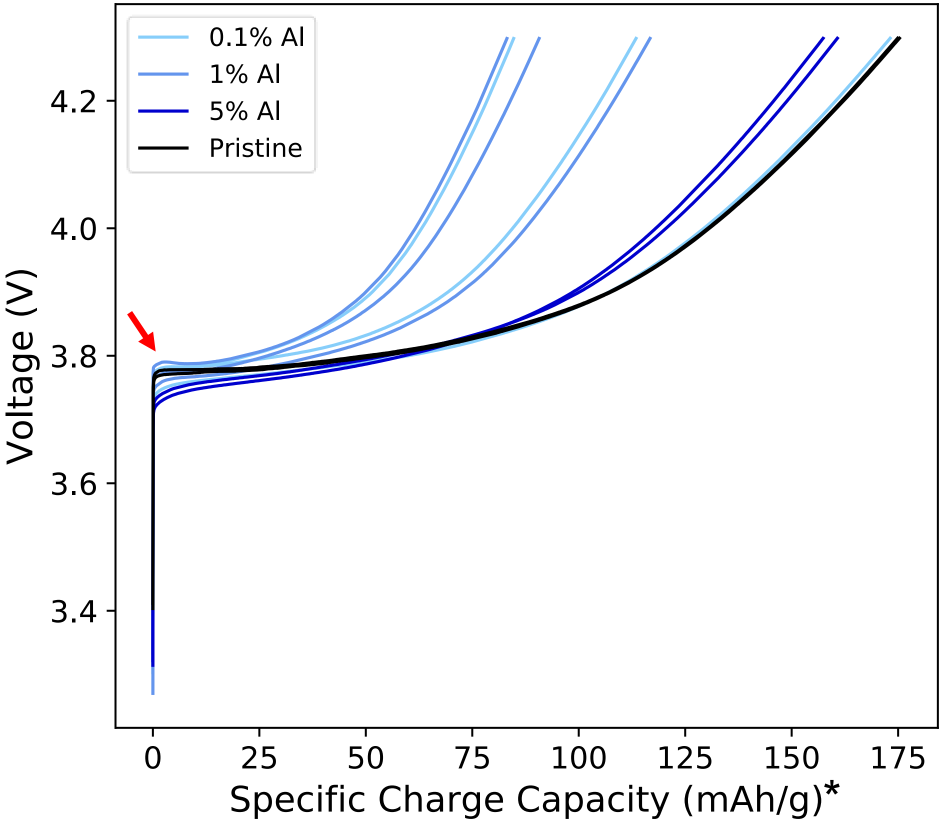


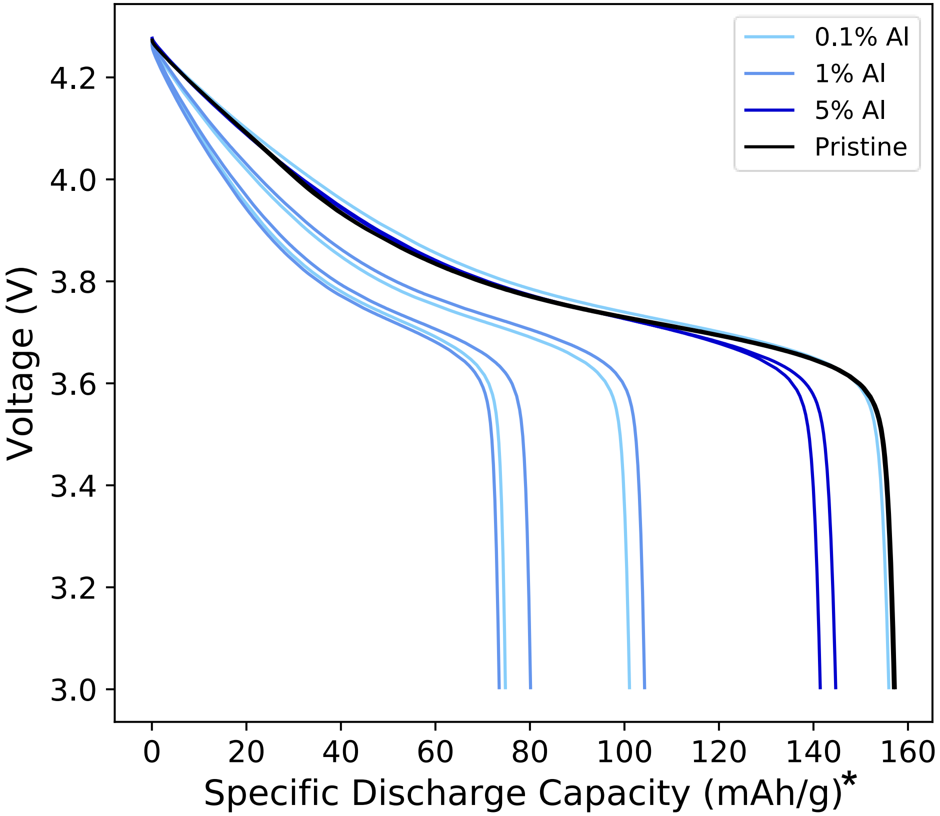


Prepare batches of NMC spiked with relevant contaminant loadings (0.1 – 5 wt%)

Electrochemical & structural testing on spiked NMC **before and after BMP treatment**

Pre-Treatment Baselining: Al^0-Contaminated NMC



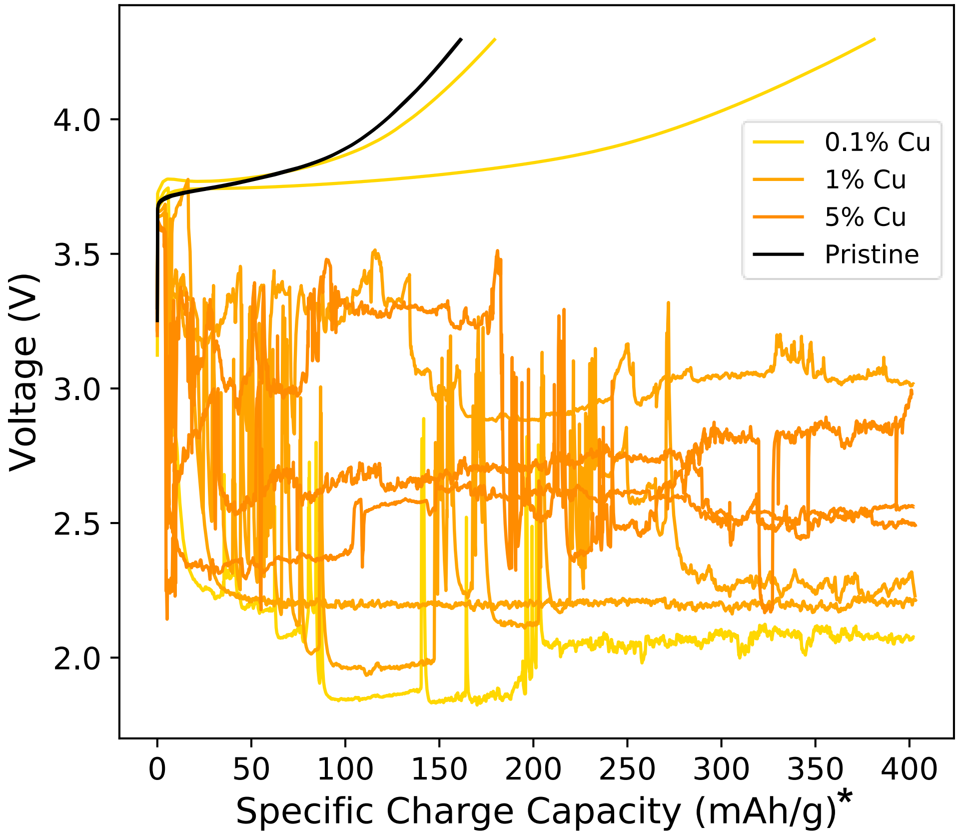


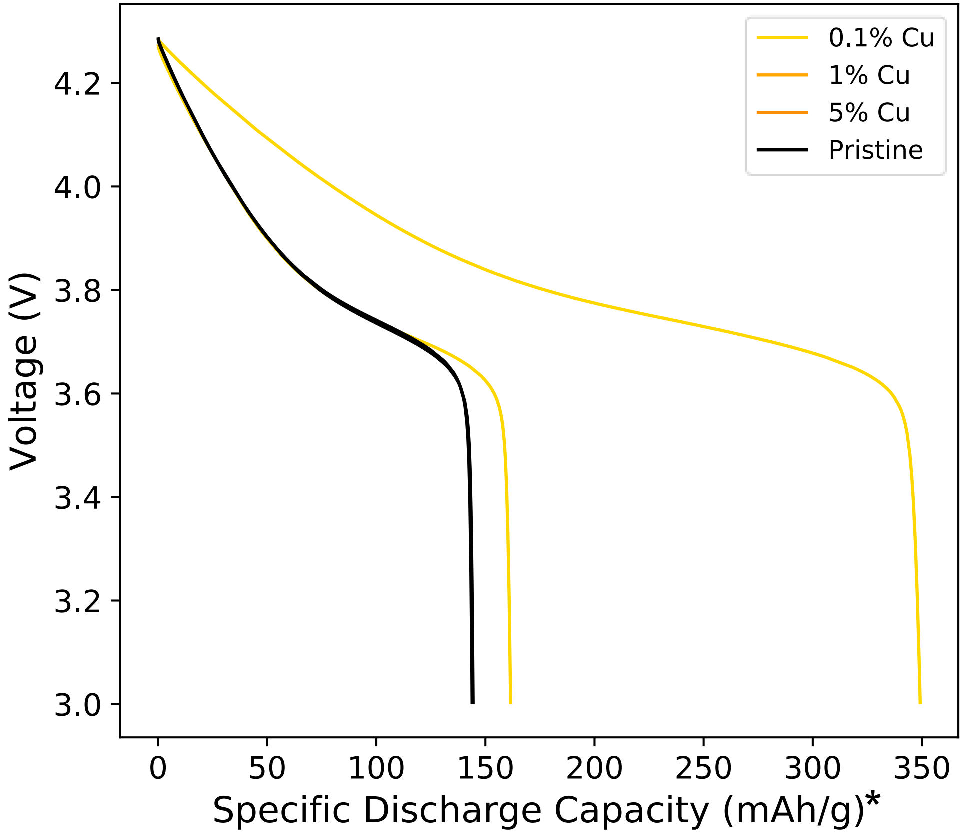
**Specific capacity normalized with respect to mass of NMC (contaminant mass excluded)*

- Al^0 contamination may function as a conductive dopant (reduces initial charge resistance), particularly at higher impurity concentrations,[1] but negatively impacts overall cell capacity (higher overpotential)
- Interestingly, the worst impact on performance is seen between 0.1% - 1% Al^0…i.e., the practically relevant contamination level for shredded black mass

[1]Fink, K. et al., Influence of Metallic Contaminants on the Electrochemical and Thermal Behavior of Li-Ion Electrodes (*submitted*)

Pre-Treatment Baselining: Cu^0-Contaminated NMC





**Specific capacity normalized with respect to mass of NMC (contaminant mass excluded)*

- Practically relevant level of Cu^0 concentration in black mass (~1%) is detrimental to performance (consistent with previous findings)[1]
- Apparent increase in capacity for some 0.1% Cu^0 replicates attributed to irregular and continued reactivity

[1]Fink, K. et al., Influence of Metallic Contaminants on the Electrochemical and Thermal Behavior of Li-Ion Electrodes (*submitted*)

Treatment of Al^0 and Cu^0-Contaminated NMC

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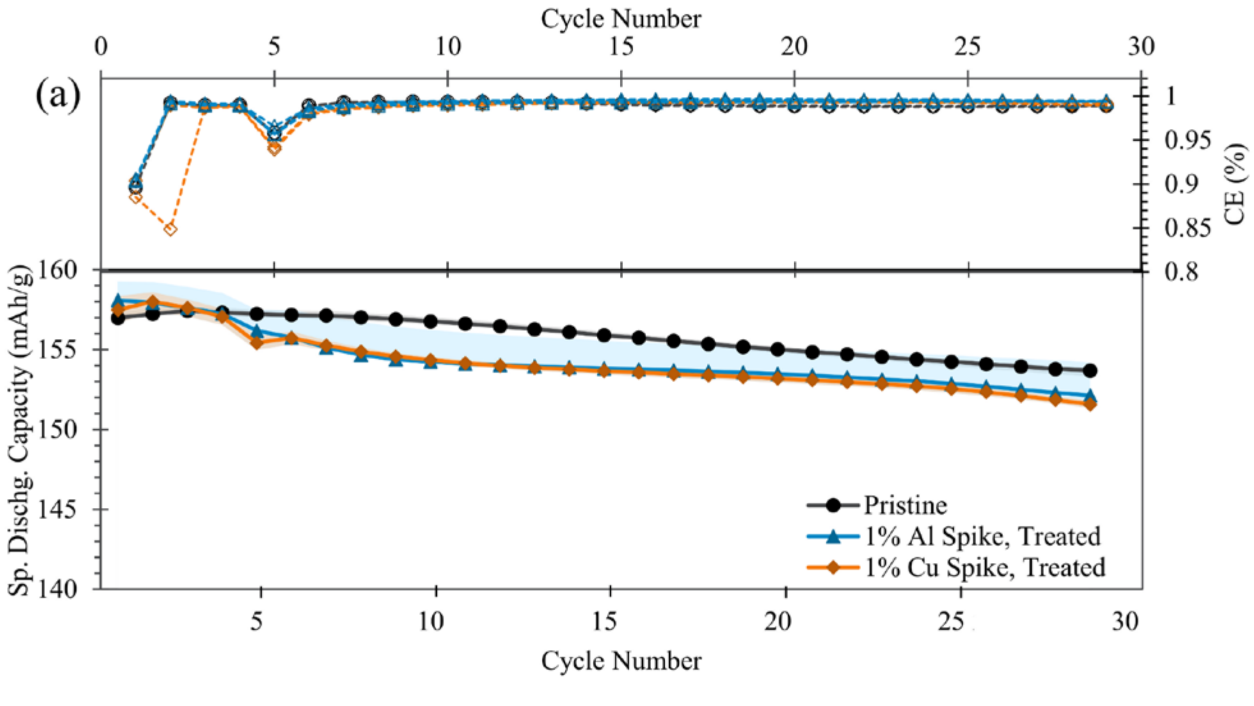

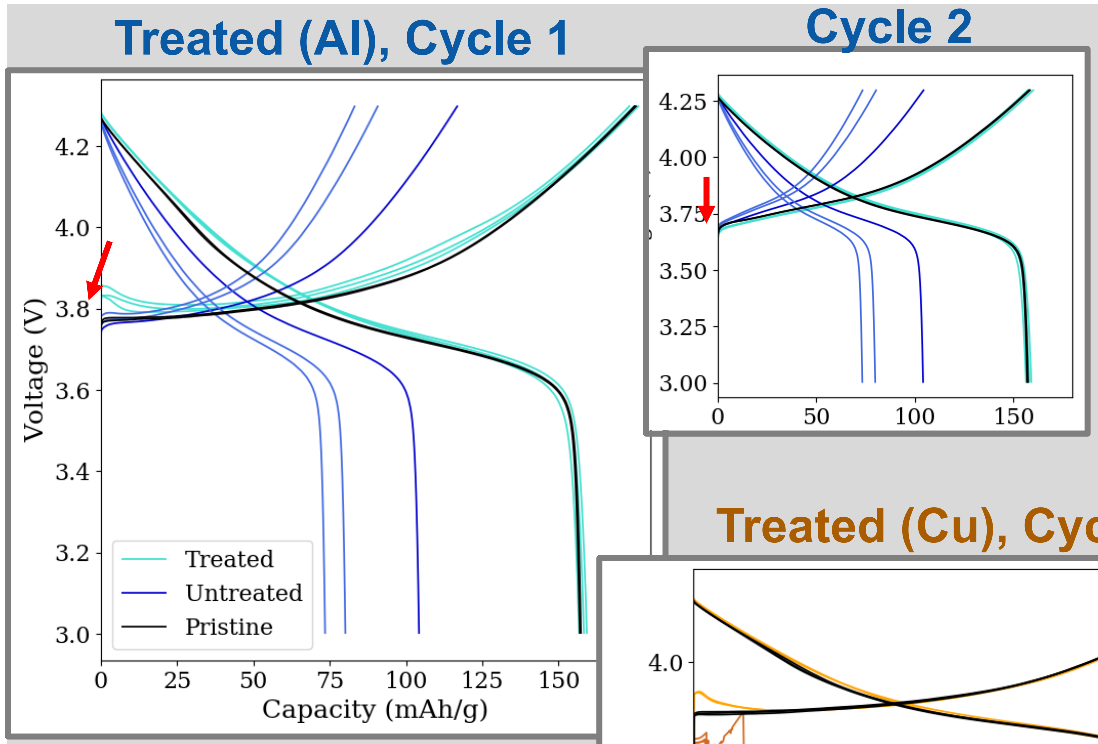

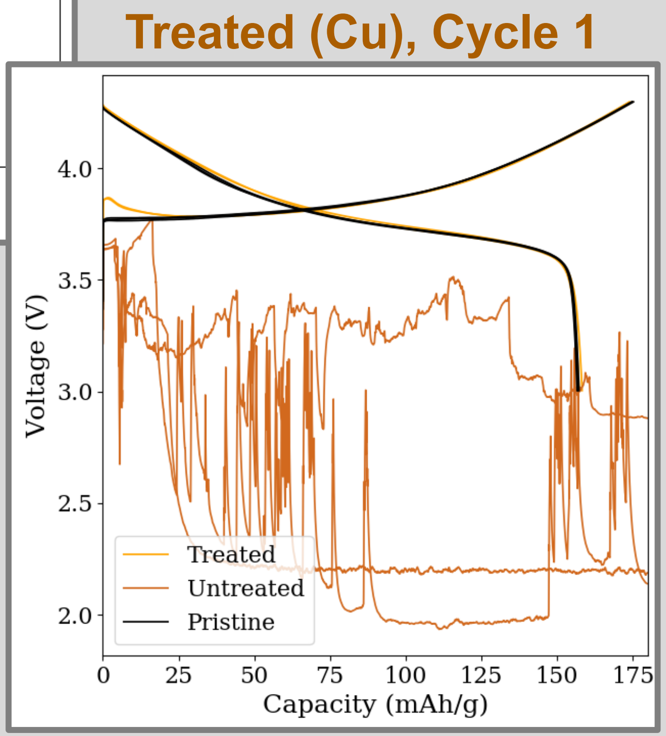

- Half-cell capacity is nearly identical to pristine material, suggesting a **successful purification process** that **does not adversely impact bulk NMC performance**.
- Irregular high resistance observed at beginning of first cycle; pristine behavior recovered on cycle 2 and beyond.
- This suggests the presence of a reactive surface species that is electrochemically consumed upon initial charge.

Task #2: Impacts of Treatment on NMC (Again)

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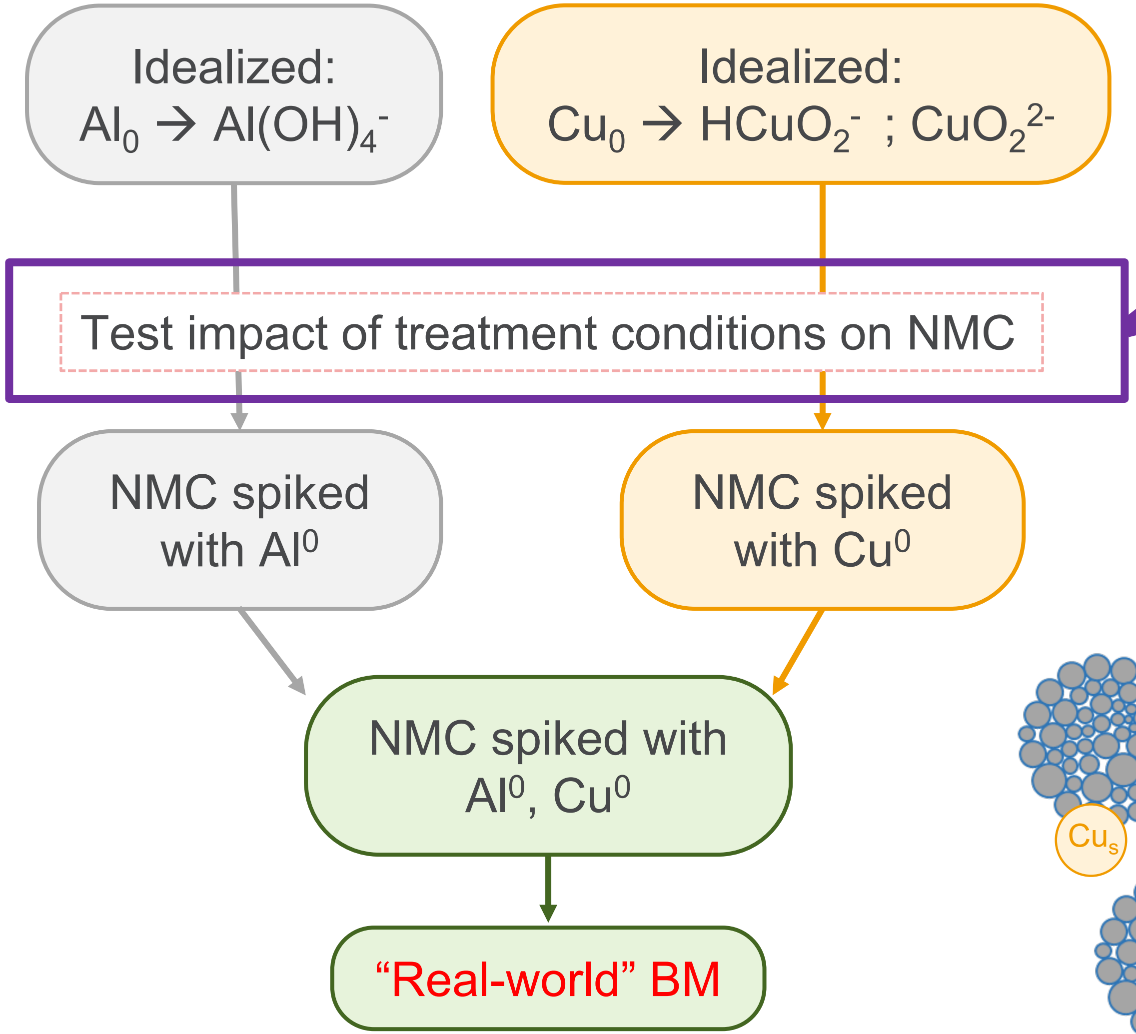
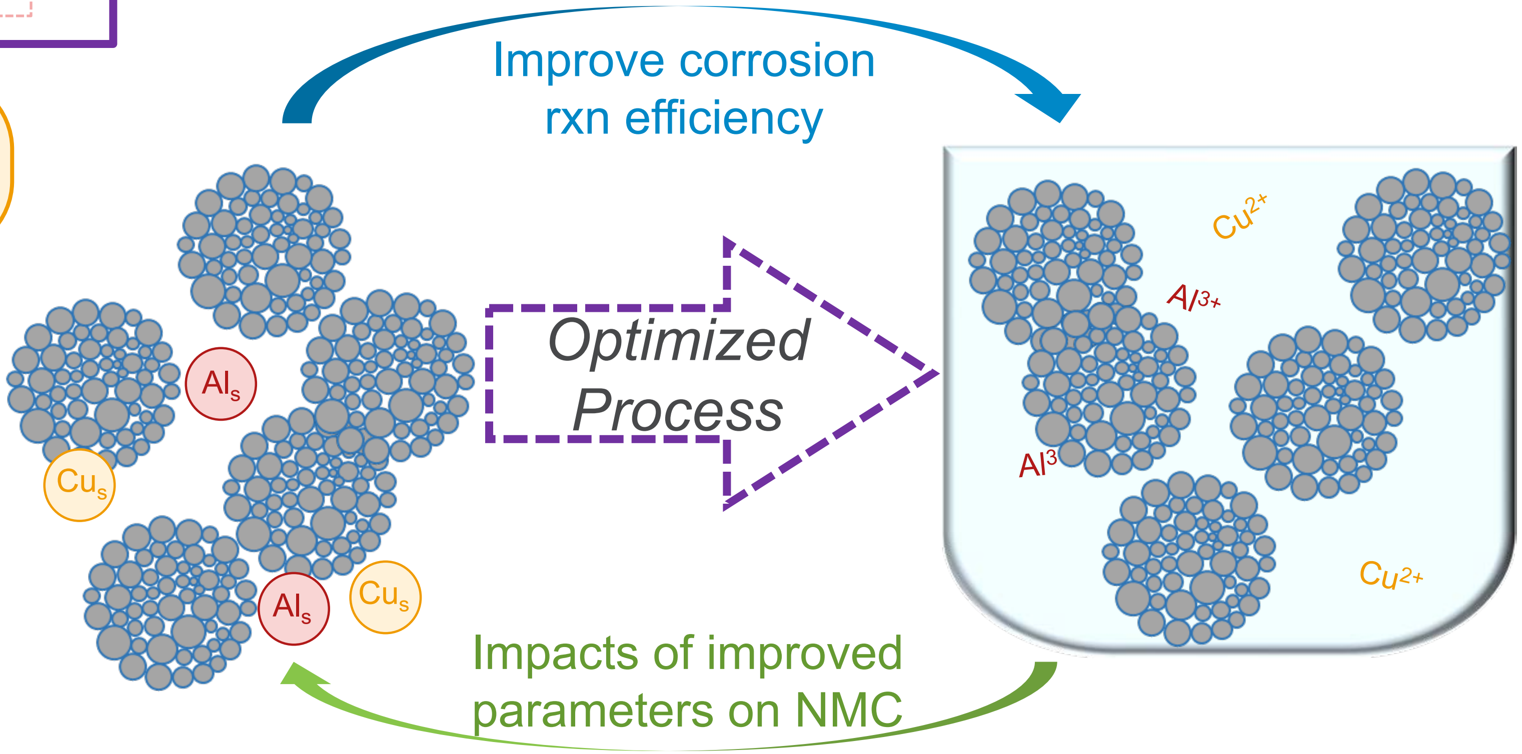


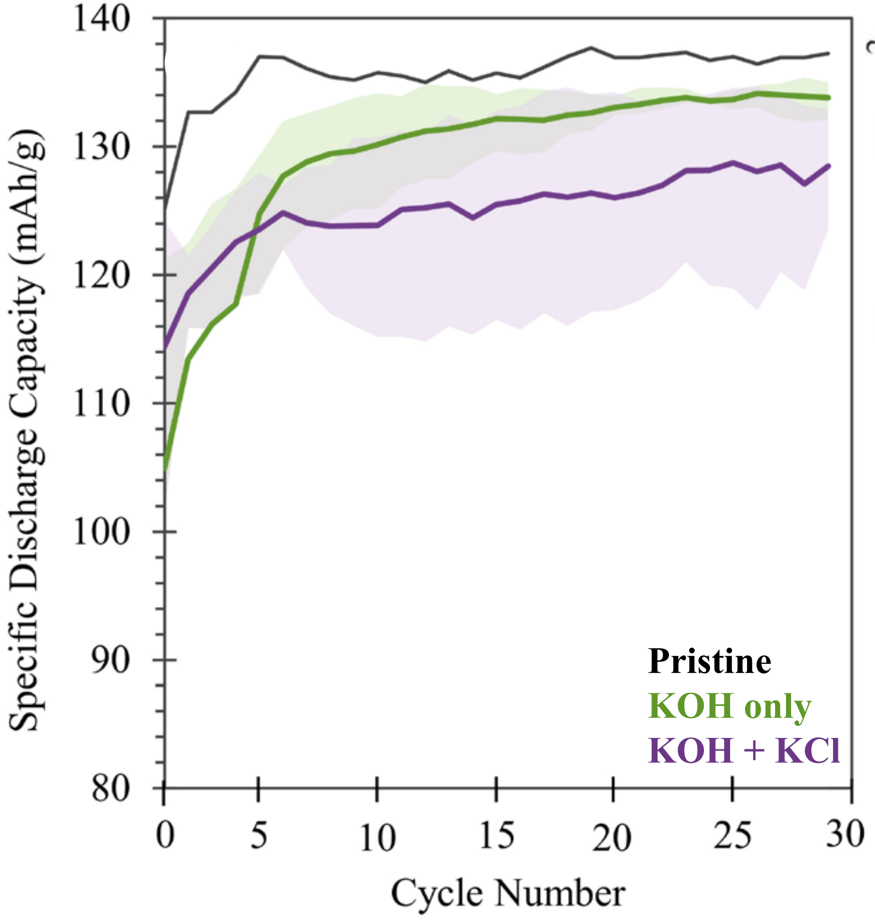
Electrochemical Performance

Structural/Morphological Changes
- -XRD
- -SEM

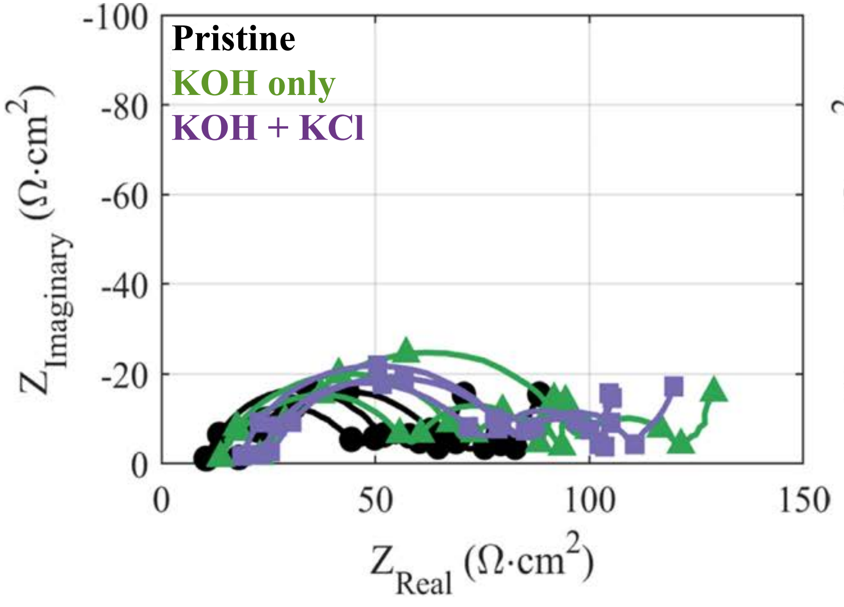
Chemical Changes
- -ICP (*pending*)



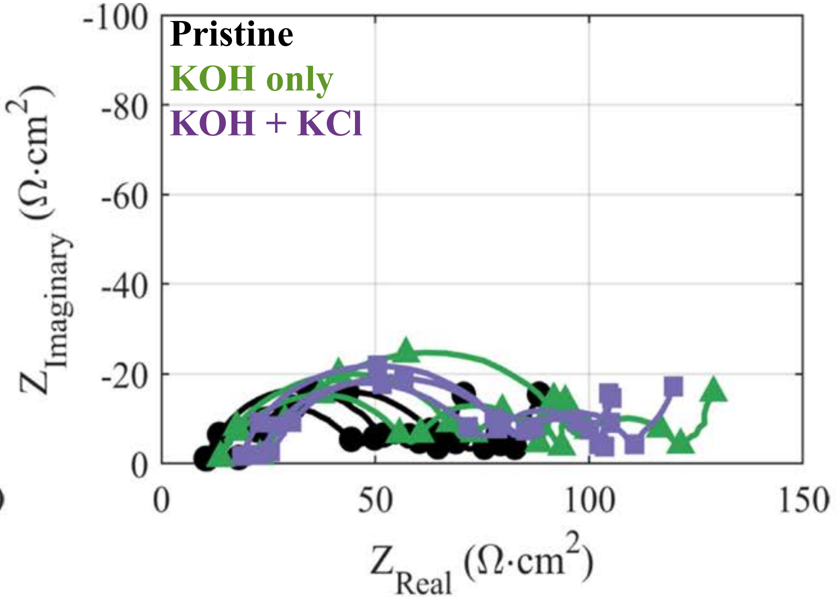
Full-Cell Performance: C/10 Cycling & Impedance



Post-Formation



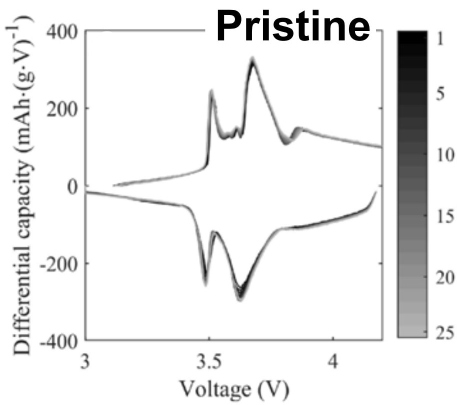
25 Cycles Post-Formation

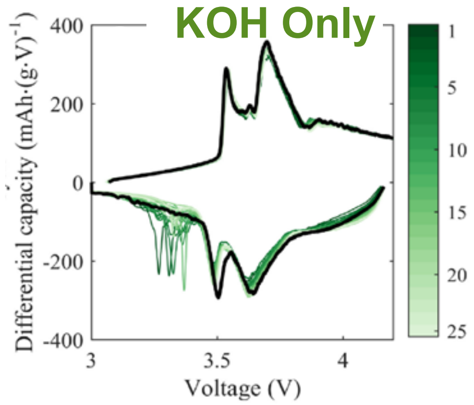


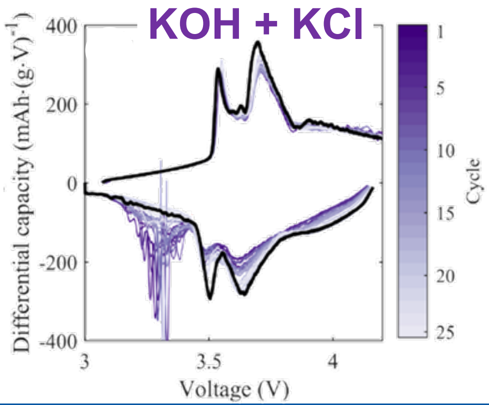
- Capacity reduction & impedance growth observed in full cells (vs pristine graphite) – but not in half cells
- This suggests the presence of *soluble* reactive contaminant(s) in the treated cathode material, which cross over & act adversely at the anode
- Surface contaminants initially prevent effective utilization Li inventory, but do not deplete significant Li through reaction (capacity recovery)

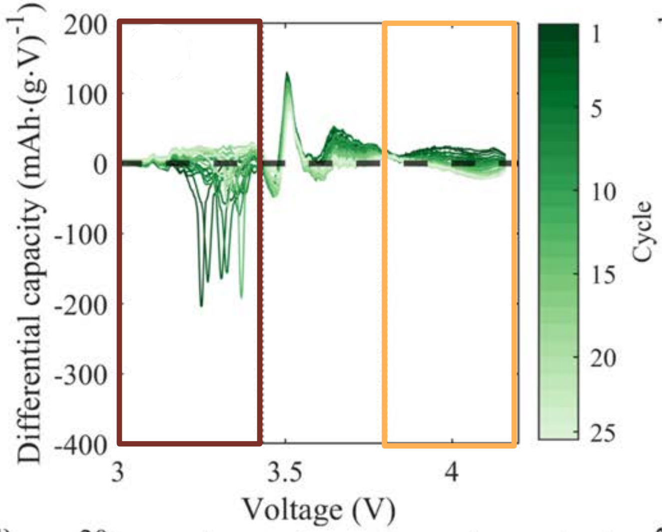
Full-Cell Differential Capacity Analysis

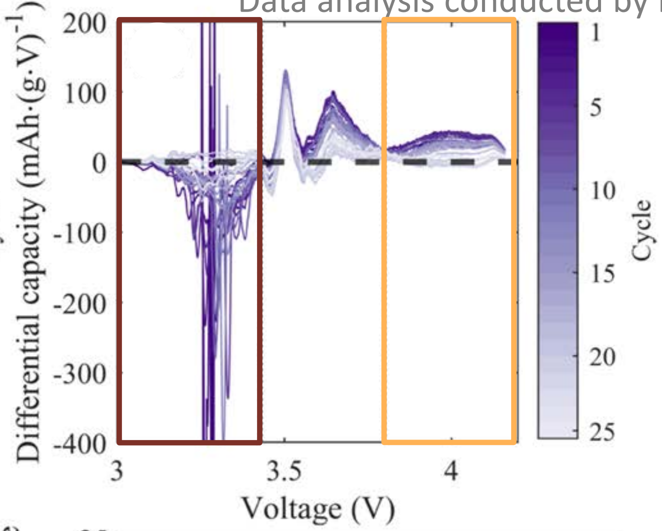
Data analysis conducted by Paul Gasper (NREL)



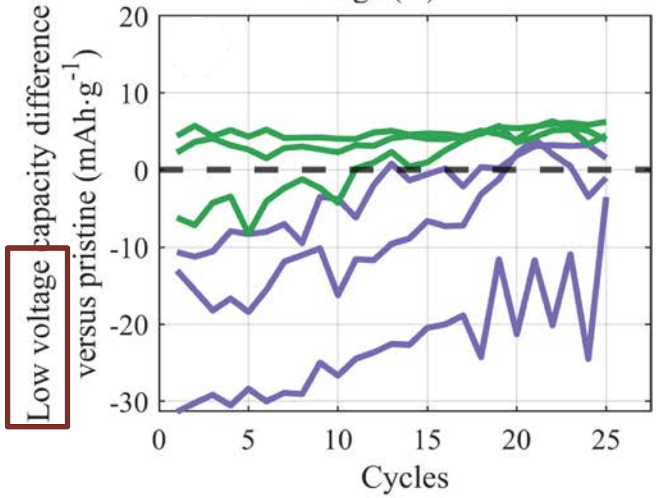


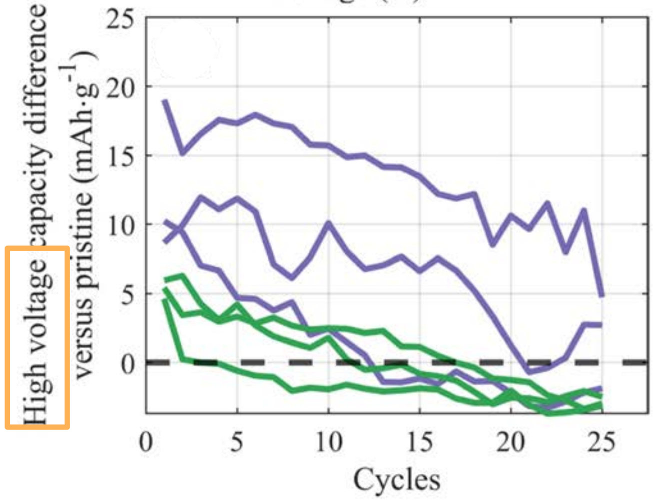






reduced side reactions





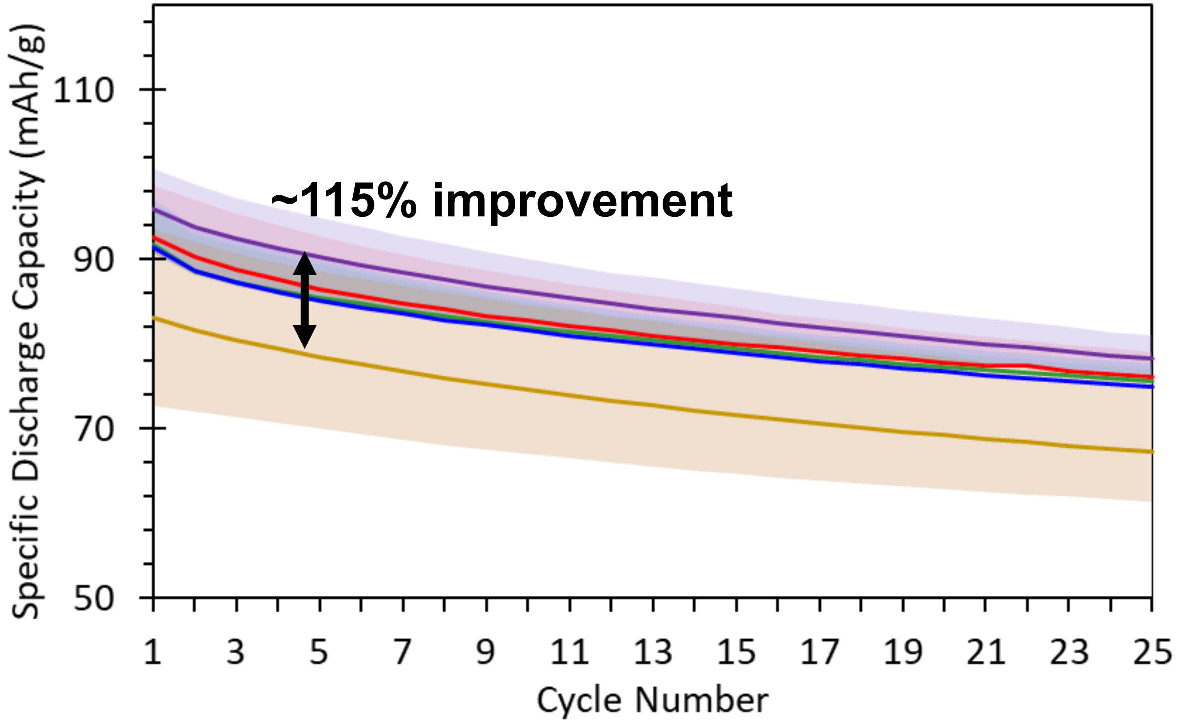
recovery of NMC capacity

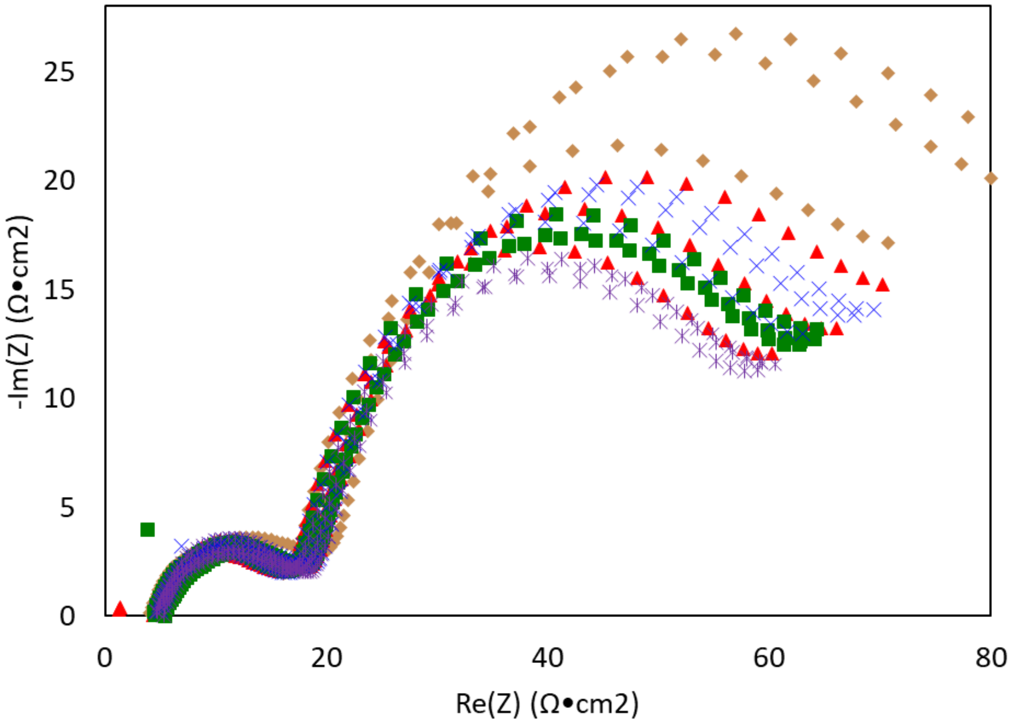
- KOH-only sample recovers pristine behavior with repeated electrochemical cycling; KOH+KCl sample shows continuous adverse reactivity
- Reaction in “non-NMC” electrochemical window: intercalation of K^+/Cl^- into graphite; LiOH oxidation

Ongoing Effort: Post-Treatment Solvent Choice

Base Treatment Only (KOH)

Base Treatment + Various Post-Treatment Solvent Rinses





- Combining (electro)chemical analysis and chemical rationale, we attribute the reduced capacity observed in full cells primarily to the *use of DI water* as a post-treatment rinse solvent:
  - -Surface-structural rearrangement
  - -Ineffective removal of solubilized contaminants (Al) and treatment solvents (K)
- Evaluation of alternative post-treatment solvents is underway, with promising initial results for practical BM

Task #4: Treatment Efficacy on Practical BM

SEM/EDS imaging conducted by Max Schulze (NREL)

Idealized: $Al_0 \rightarrow Al(OH)_4^-$

Idealized: $Cu_0 \rightarrow HCuO_2^-$; CuO_2^{2-}

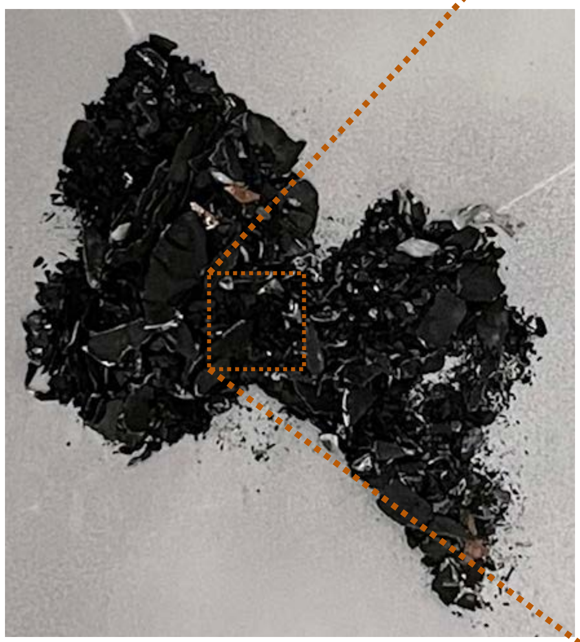
Test impact of treatment conditions on NMC

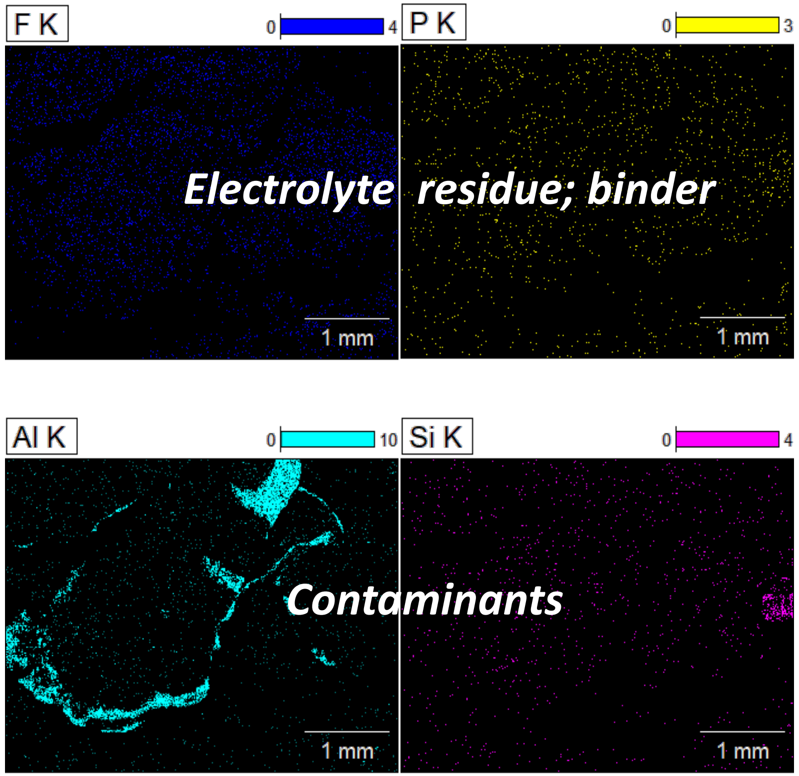
NMC spiked with Al^0

NMC spiked with Cu^0

NMC spiked with Al^0, Cu^0

"Real-world" BM

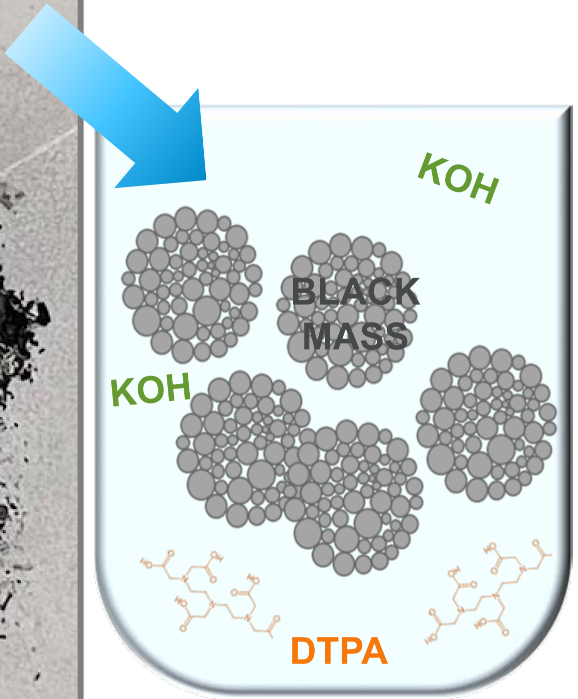




May contain additional metallic impurities not tested in idealized studies and/or non-NMC components (graphite, polymer separator, casing scraps, etc.)

Ongoing: Purification of (Practical) BM

- Larger shreds of NMC double-coated onto current collector
- Visible contaminant chunks
- Separator pieces present

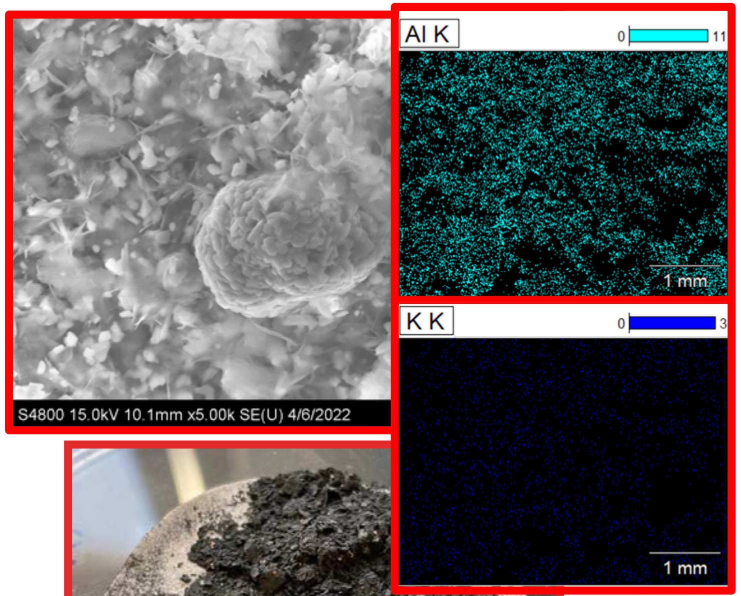


"BM Purification":

- KOH → pH 13
- DTPA*
- 60 °C
- 2.5 hr stirring
- Sonication

**2x molar conc. of "worst-case" total est. contaminants (Cu + Mg + Fe) from fines (as determined via ICP)*

Supernatant (recovered liquid phase) shows bluish color, indicating successful Cu ionization & binding



- Visible improvements to BM purity:
  - -Dissolution of Al current collector
  - -Major size reduction in Cu chunks
- However, some contamination still present (Cu particles; separator) and residual treatment species

Conclusions & Continuing Work

Summary of Completed Work:

- ✓ Complete ionization of practically relevant concentrations of Al^0, Cu^0 achieved under idealized conditions using low-cost, relatively mild processes
  - Sonication (Al^0, Cu^0) and use of a strong chelating agent accelerate corrosion kinetics & reaction extent
- ✓ Cl^- salts found to *inhibit,* rather than enhance, Cu^0 corrosion at mildly elevated temperatures
- ✓ Salts with larger cationic radius (i.e., K^+) reduce Li substitution and improve performance of treated material
- ✓ Optimized purification process has successfully been demonstrated for NMC spiked with 1% Al^0 and 1% Cu^0, with bulk structure and half-cell capacity of treated material matching pristine material
- ✓ Variability and reduced capacity in full-cells is attributed to surface changes (structure, chemistry) induced by post-treatment conditions (DI water washing) rather than the treatment process itself
  - Residual products are electrochemically consumed upon repeated cycling, restoring pristine behavior
- ✓ Demonstration of first application to industrial practical mass; optimization continues!

Ongoing Efforts:

- ☐ Optimized post-treatment conditions for applications to industrial BM (shredded end-of-life batteries)
- ☐ Scale up for demonstration at ReCell direct recycling pilot plant (current max: 15 g)
- ☐ Development of tailored sorbents for selective recovery of Al and Cu from solution

Thank you for your attention!

Further questions:

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ReCell
ADVANCED BATTERY RECYCLING

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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

VEHICLE TECHNOLOGIES OFFICE

NREL/PR-5700-84258

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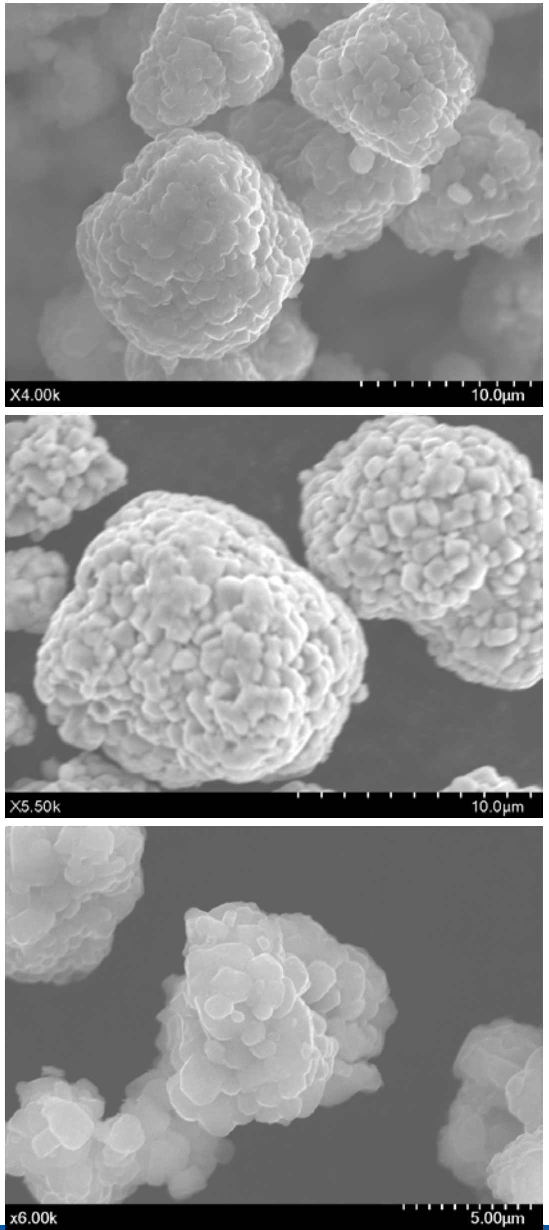
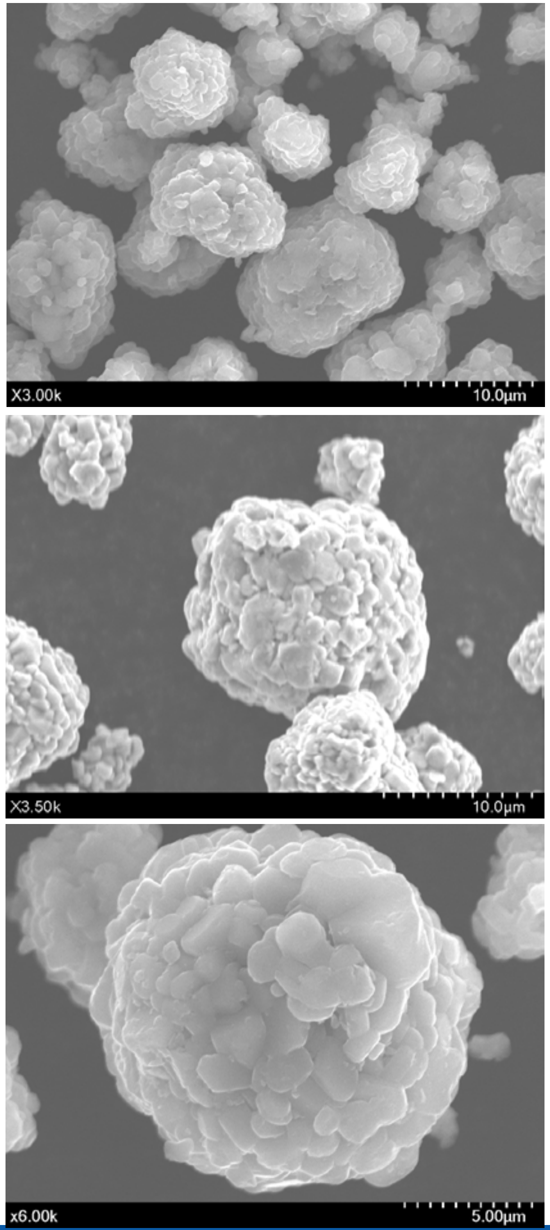
NREL Transforming ENERGY

Morphological Impacts of Treatment on NMC

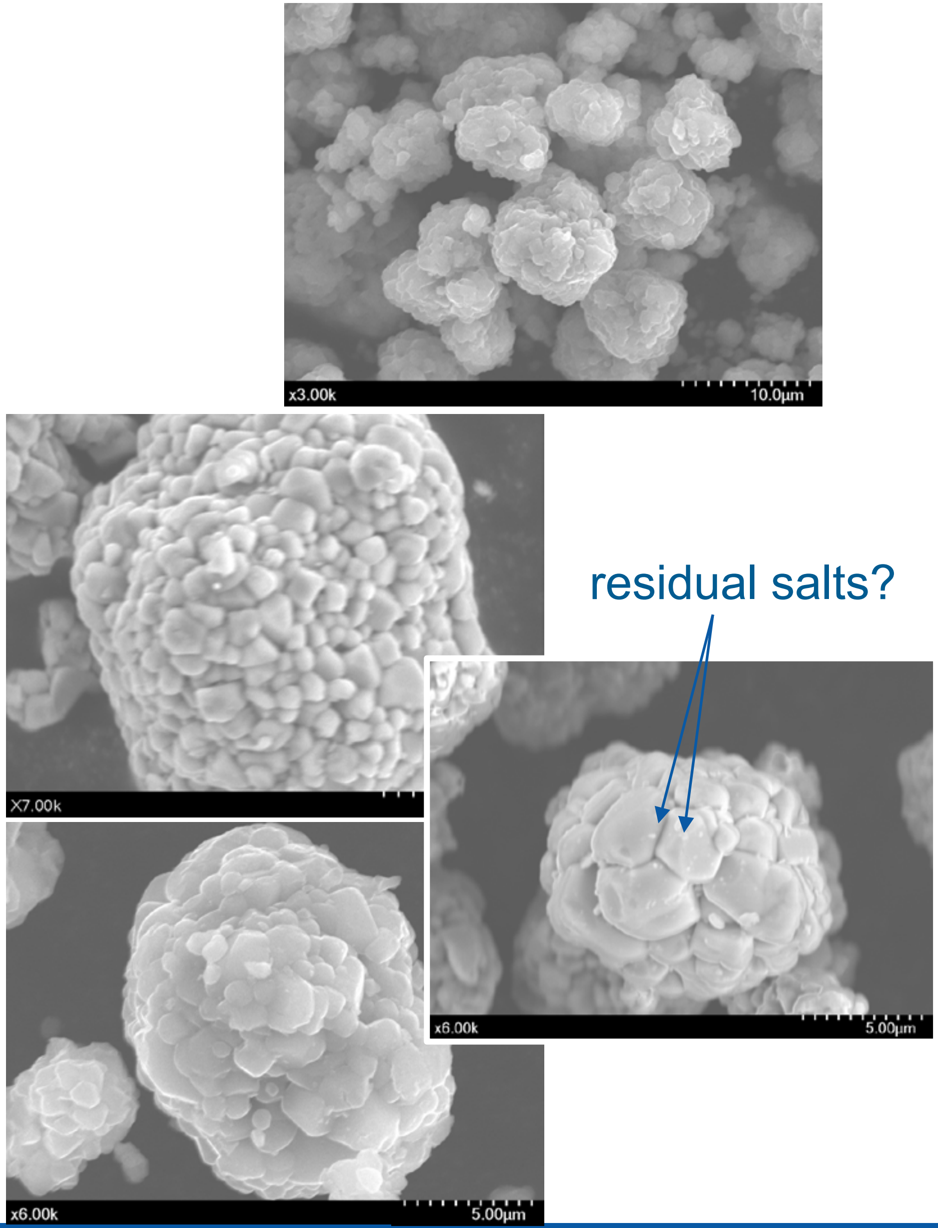
Pristine



KOH Treatment

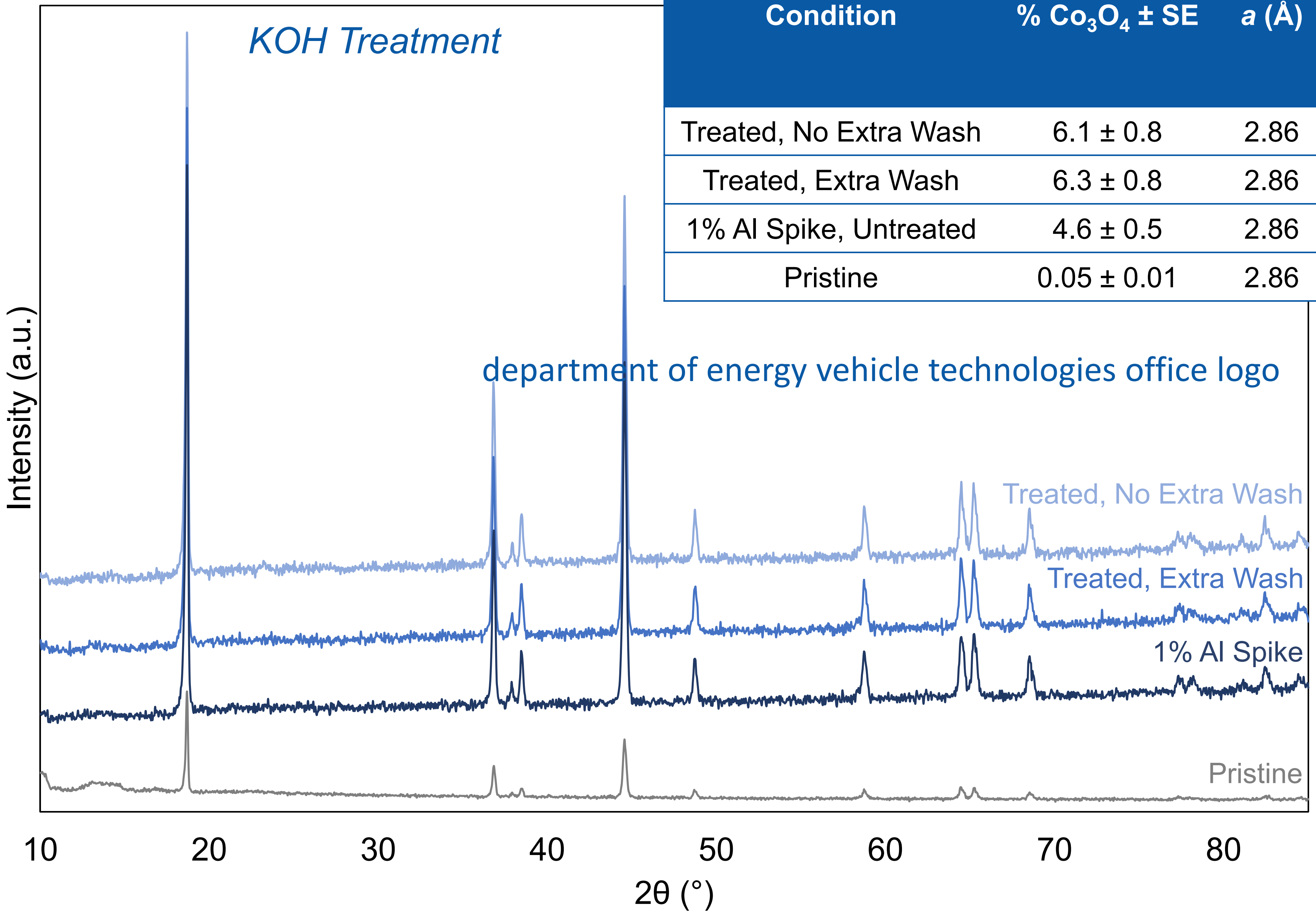


KOH + KCl Treatment



Structural Impacts of Treatment on NMC

Condition	% Co_3O_4 ± SE	*a* (Å)	*c* (Å)	*I*(003)/*I*(104)	"R-factor": {*I*(006)+*I*(012)}/*I*(101)
Treated, No Extra Wash	6.1 ± 0.8	2.86	14.23	1.19	0.360
Treated, Extra Wash	6.3 ± 0.8	2.86	14.23	1.20	0.401
1% Al Spike, Untreated	4.6 ± 0.5	2.86	14.23	1.20	0.426
Pristine	0.05 ± 0.01	2.86	14.23	1.05	0.379

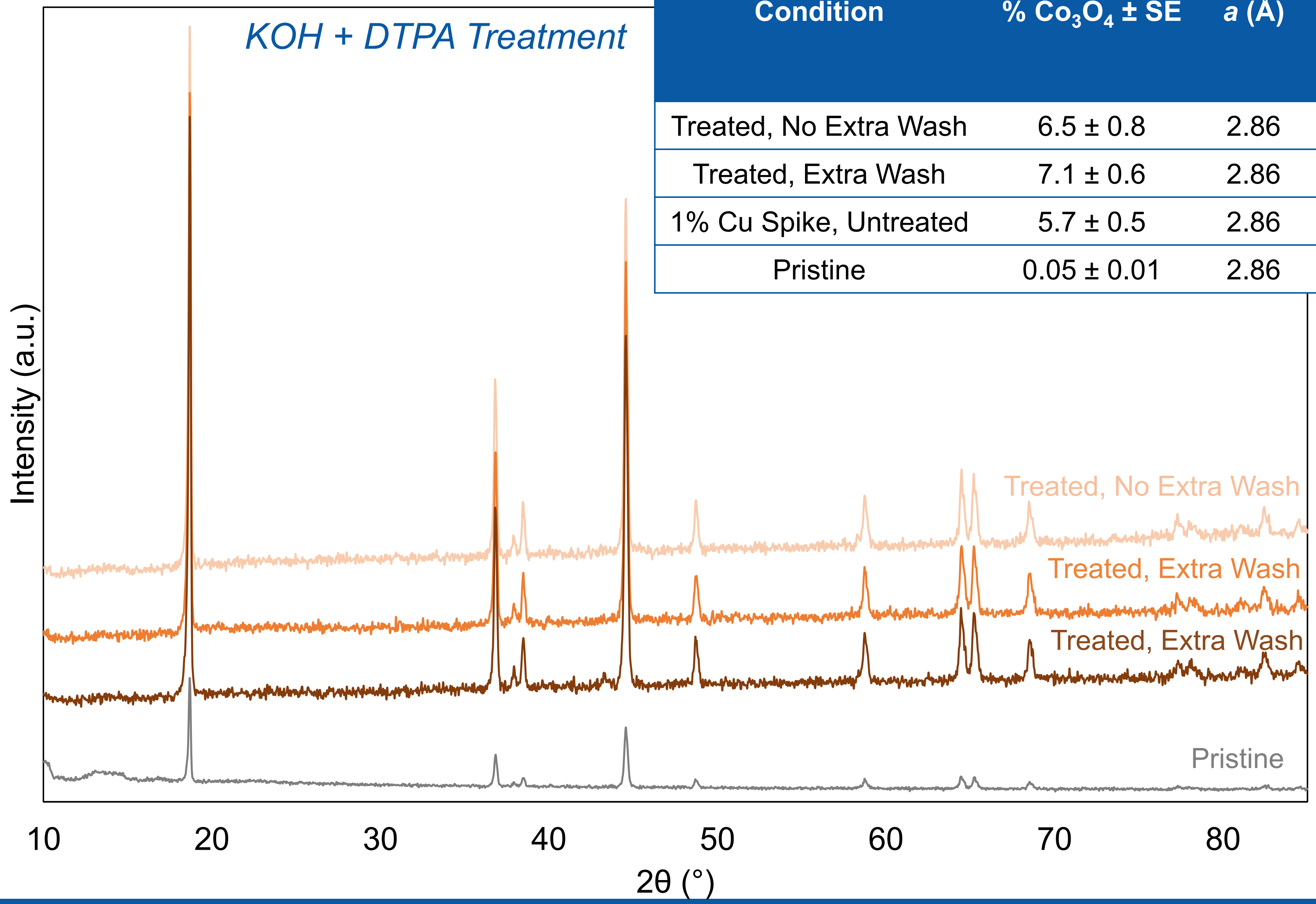


Rietveld refinement suggests no impact of treatment on cation mixing or lattice parameters (i.e., no evidence of bulk Li loss, even with supplemental DI H_2O rinse).

Some evidence of spinel phase transformation; impacts to long-term electrochemical stability are under investigation.

Structural Impacts of Treatment on NMC

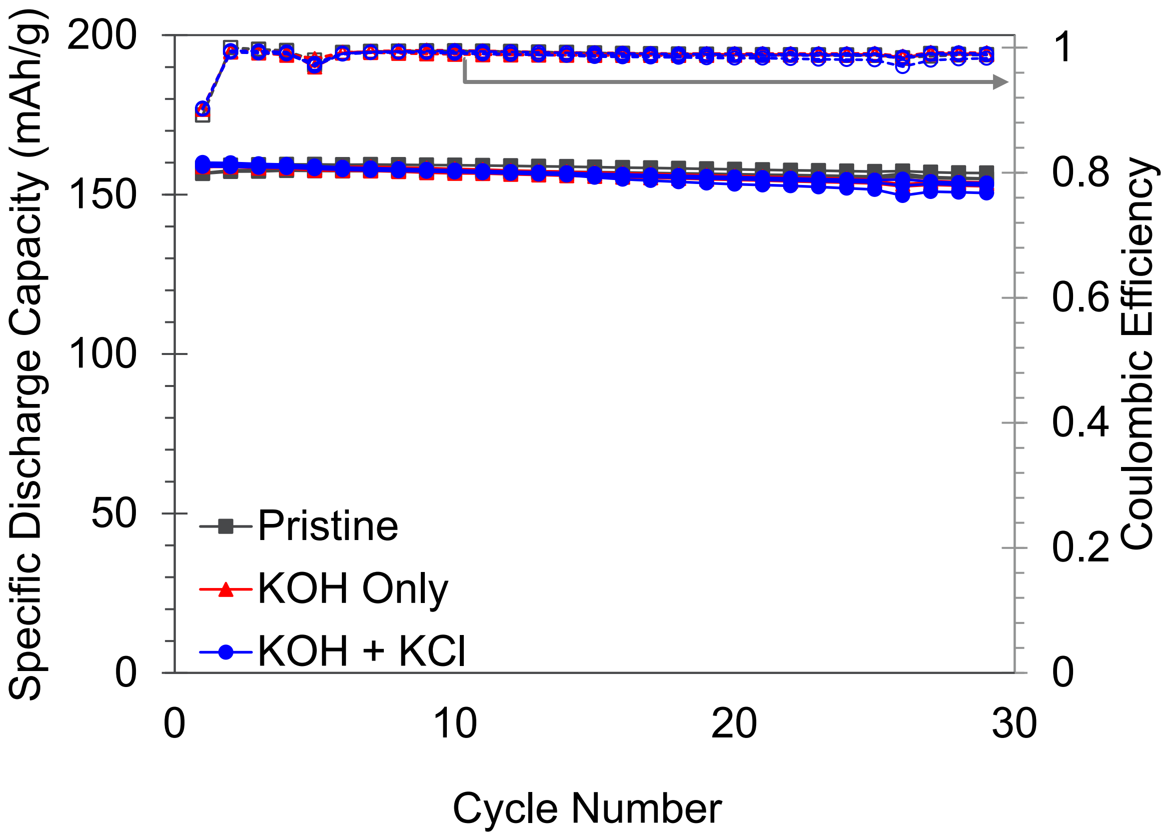
Condition	% Co_3O_4 ± SE	*a* (Å)	*c* (Å)	*I*(003)/*I*(104)	"R-factor": {*I*(006)+*I*(012)}/*I*(101)
Treated, No Extra Wash	6.5 ± 0.8	2.86	14.23	1.16	0.385
Treated, Extra Wash	7.1 ± 0.6	2.86	14.23	1.16	0.387
1% Cu Spike, Untreated	5.7 ± 0.5	2.86	14.23	1.20	0.378
Pristine	0.05 ± 0.01	2.86	14.23	1.05	0.379



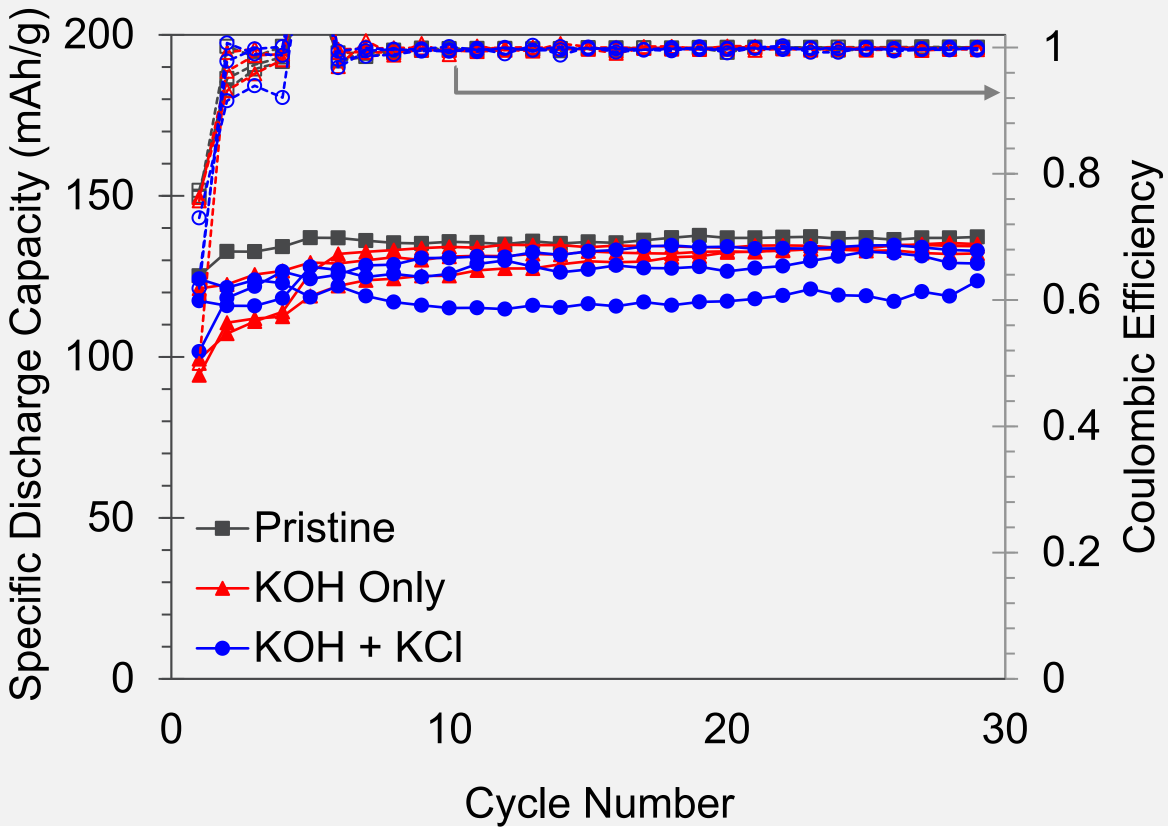
No additional impact of DTPA presence on cation mixing or lattice parameters (i.e., no evidence of bulk Li loss caused by chelating agent).

Electrochemical Impacts of Treatment on NMC

Half Cells: NMC-111; K^+ Salts



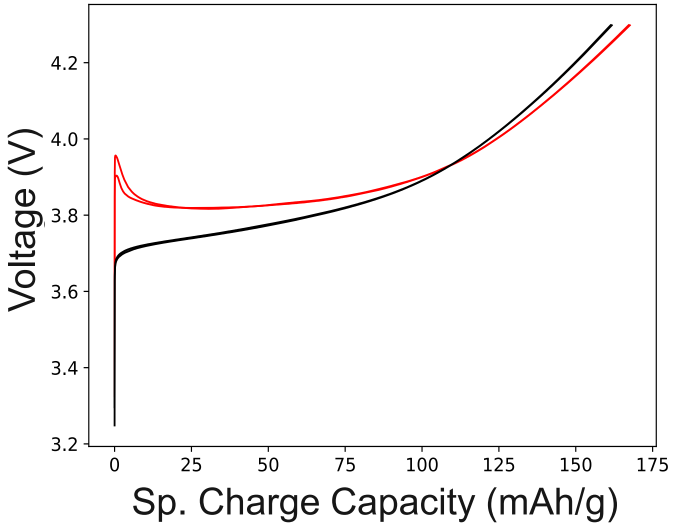
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)

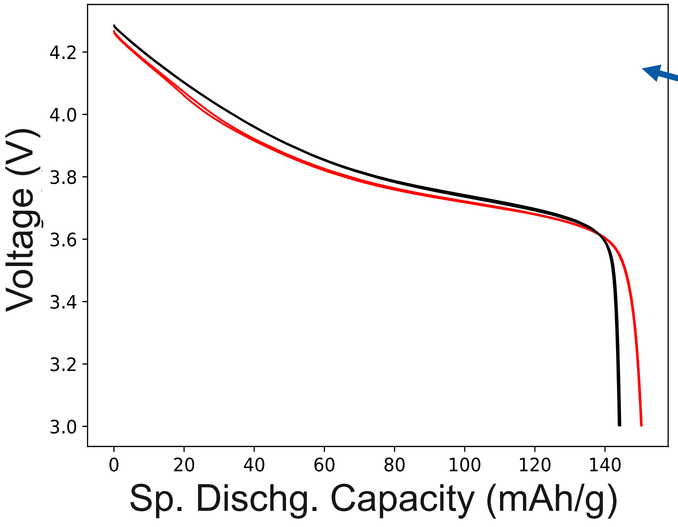


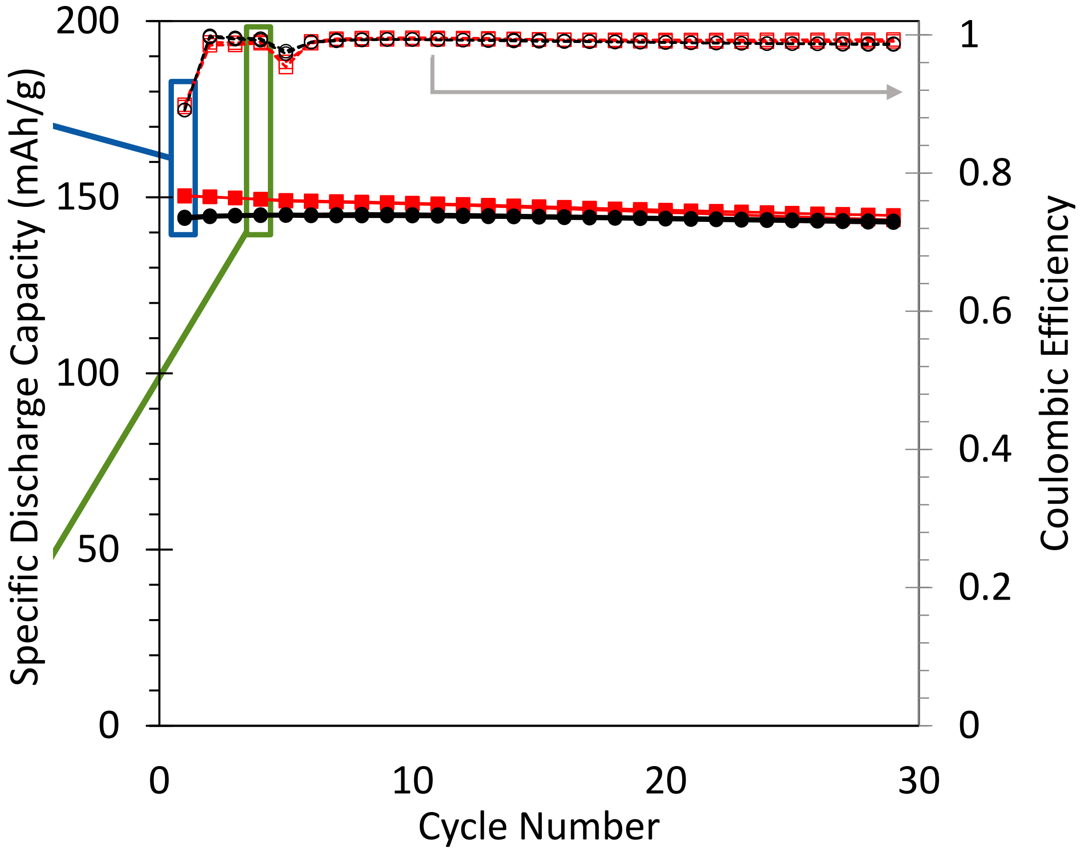
- NMC treated with K^+ salts shows improved performance over NMC treated with Na^+ salts (reduced cationic substitution)
- Reduced capacity in full cells may be attributable to residual Cl^- salts on the surface of NMC (irregular SEI formation).
- Mitigation strategies for residual salts under investigation; simple DI H_2O wash may leach Li^+

Electrochemical Impacts of Treatment on NMC

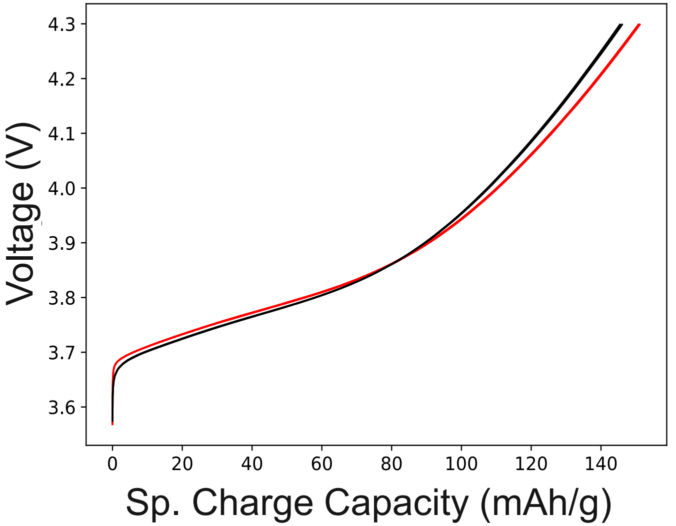
Cycle 1

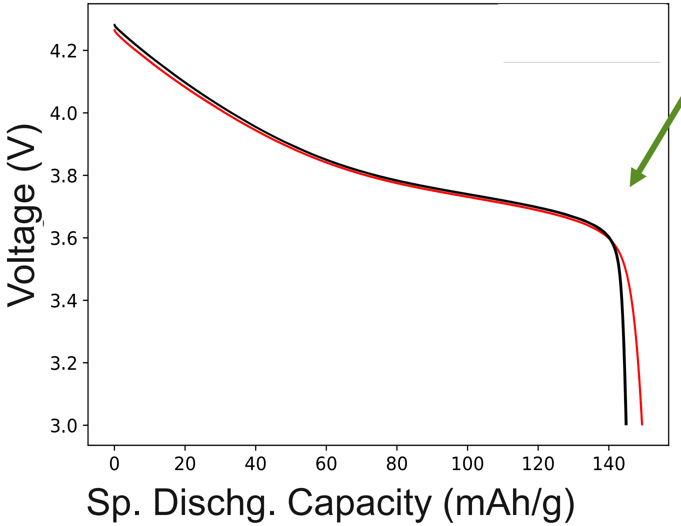






Cycle 4



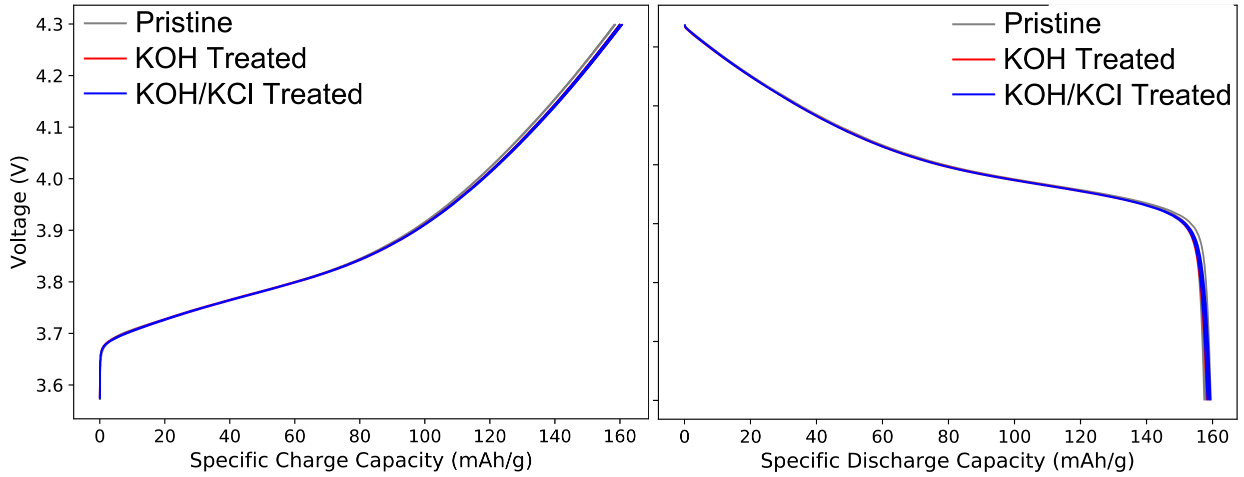


- Irregular first-cycle behavior may be attributable to residual salts on the surface of NMC (affecting SEI evolution). Performance stabilizes after formation.
- Mitigation strategies for residual salts under investigation; simple DI H_2O wash may leach Li^+.

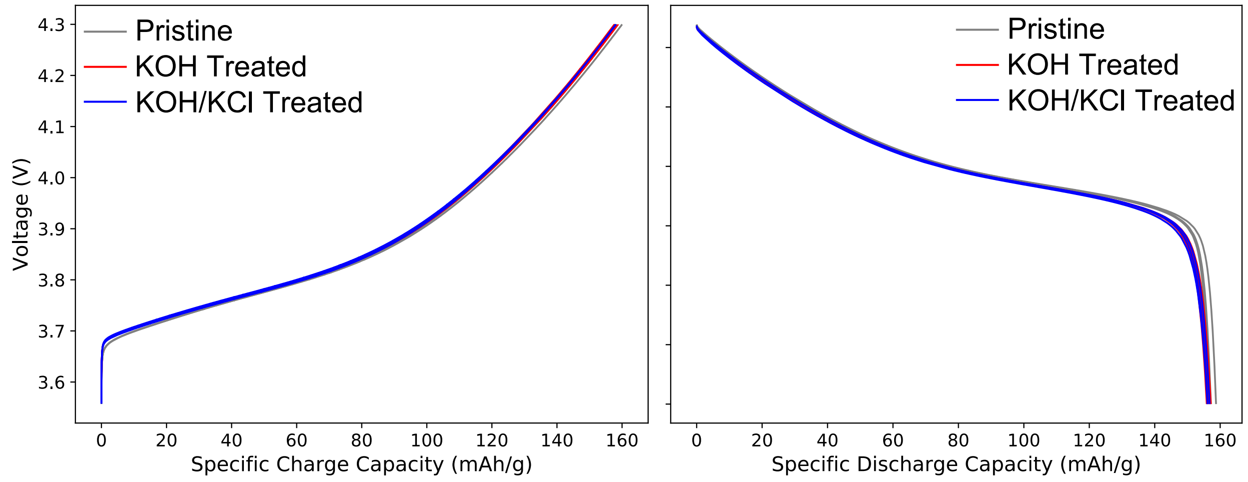
Electrochemical Impacts of Treatment on NMC

Half Cells: NMC-111; K^+ Salts

Cycle 4 (end of formation)

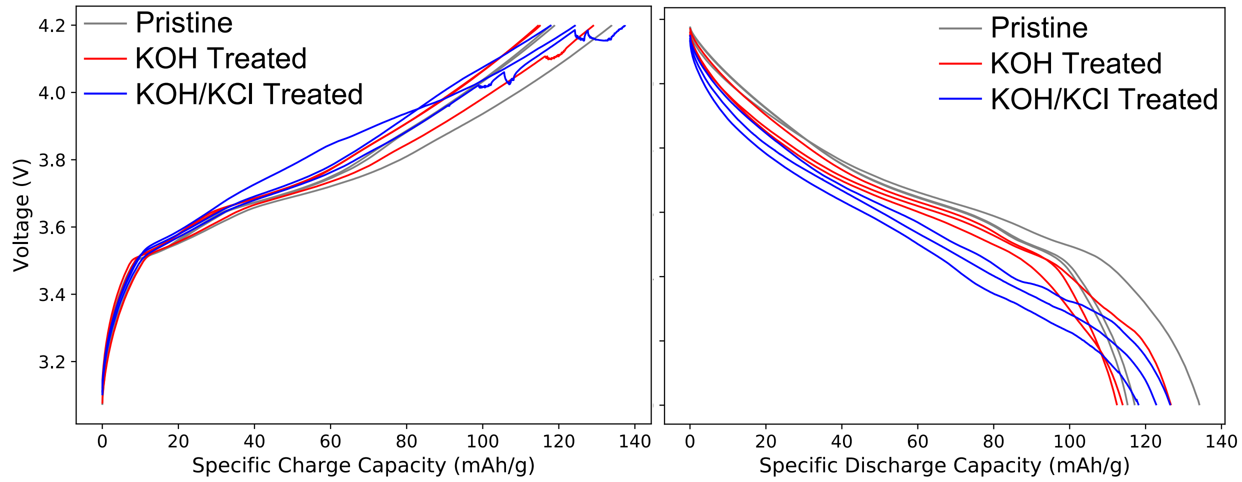


Cycle 14 (10 cycles @ C/10)

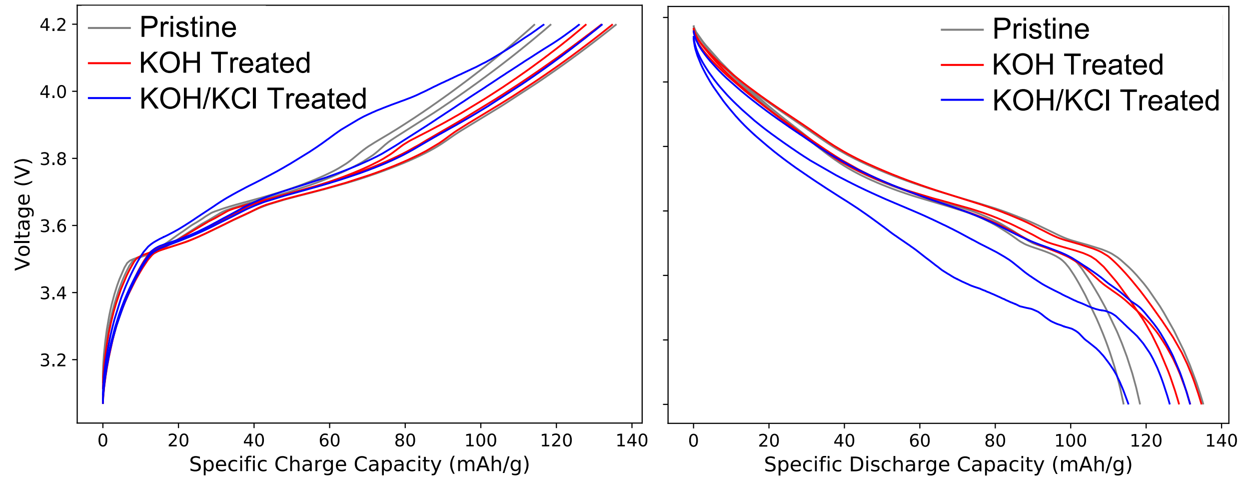


Full Cells: NMC-111; K^+ Salts

Cycle 4 (end of formation)



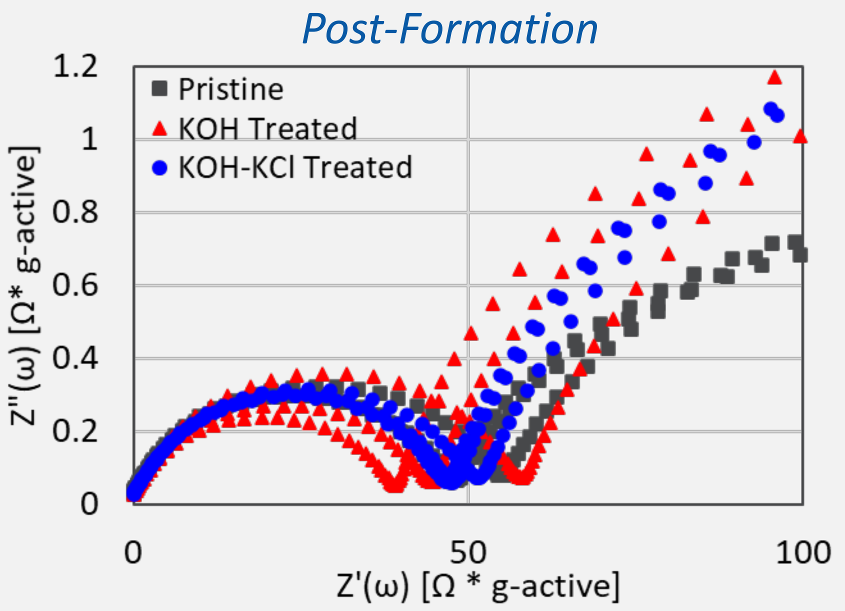
Cycle 14 (10 cycles @ C/10)

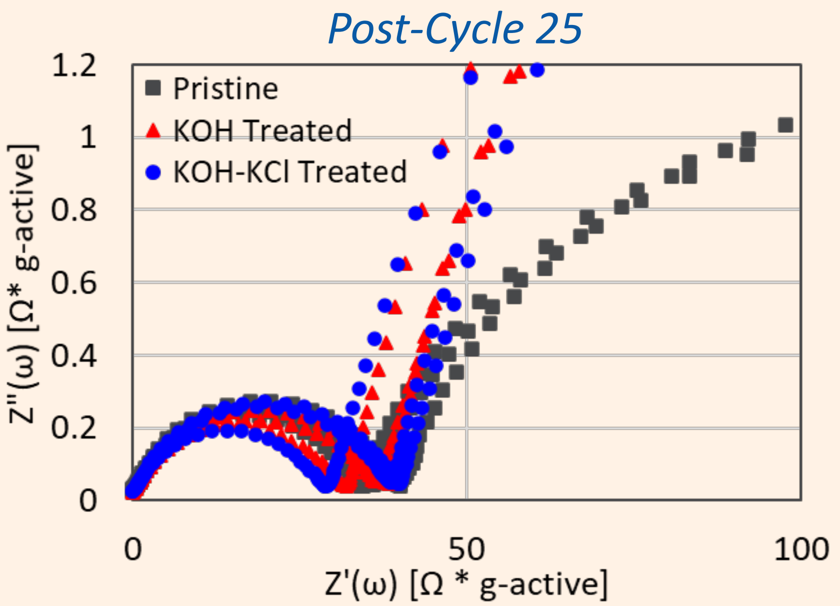


Change in voltage profiles for treated full cells is thought to be from residual salts, and not cathode degradation.

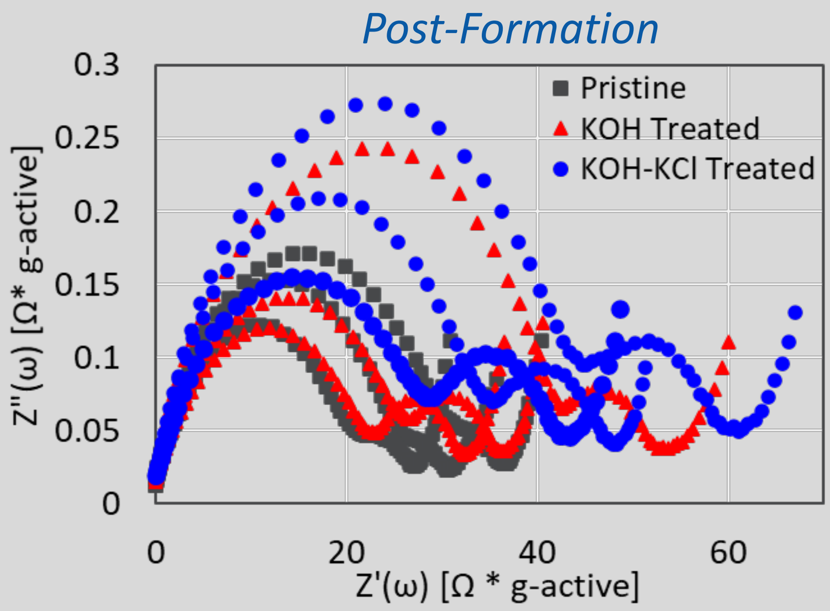
IMPEDANCE DATA (EIS); TREATED NMC-111 & NMC-532; POST-FORM.

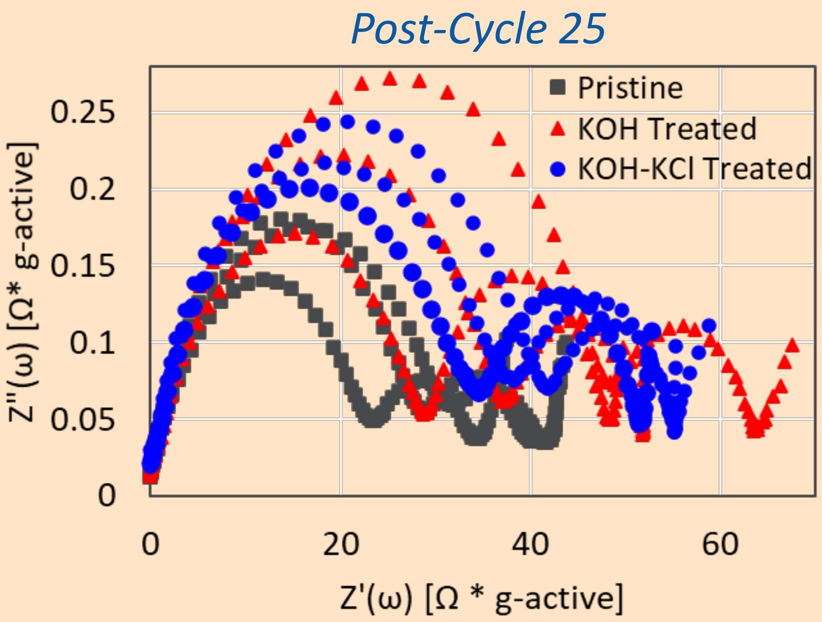
Half Cells: NMC-111; K^+ Salts





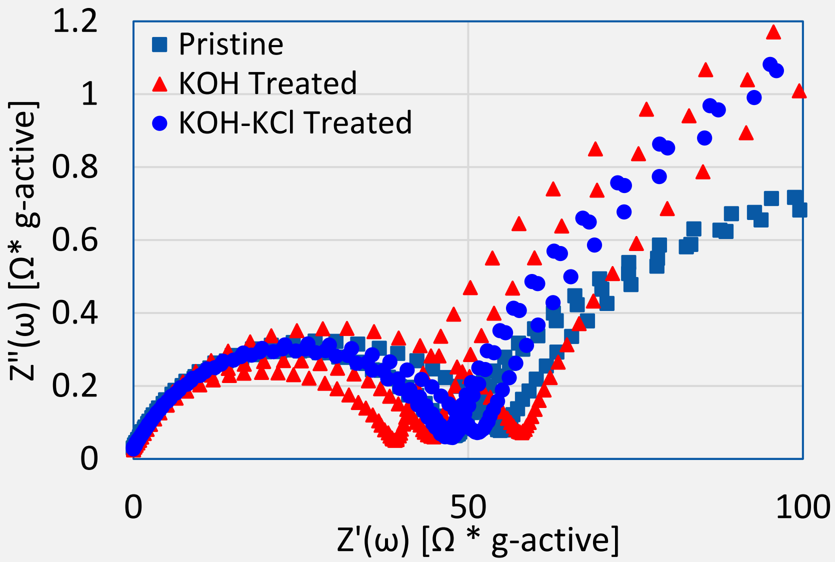
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)



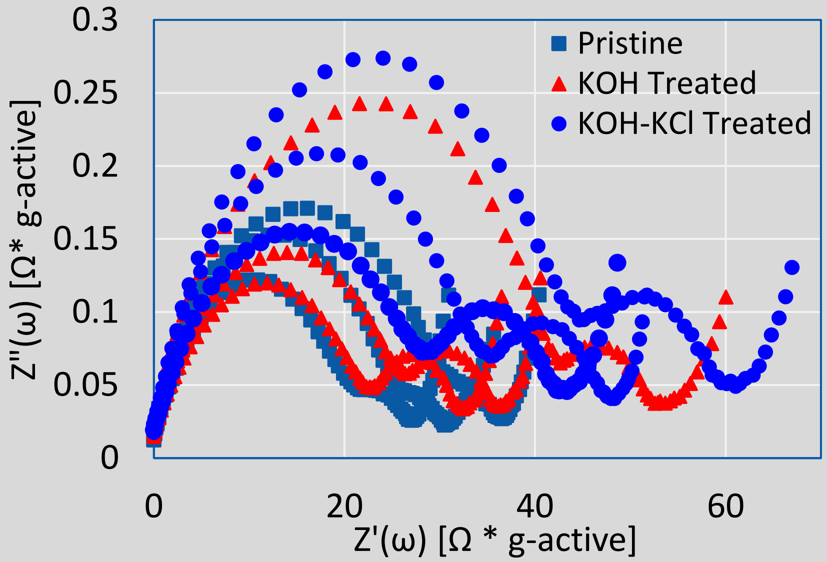


IMPEDANCE DATA (EIS); TREATED NMC-111 & NMC-532; POST-FORM.

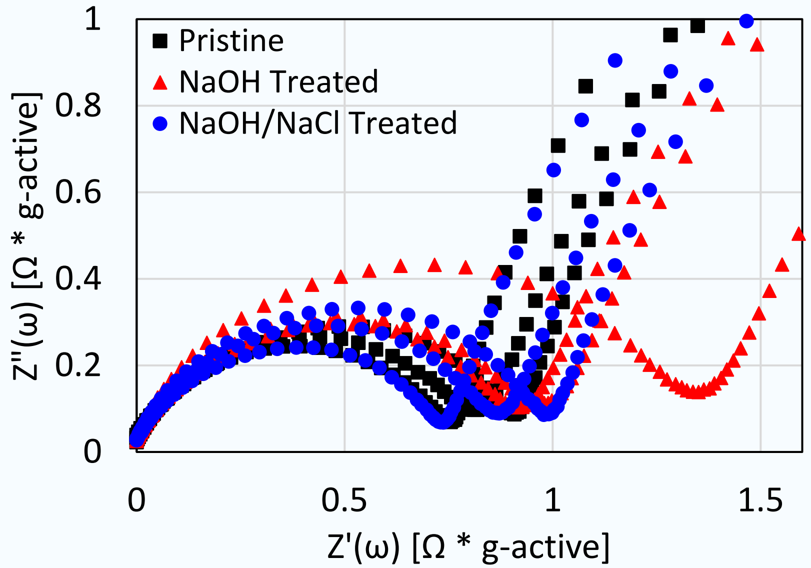
Half Cells: NMC-111; K^+ Salts



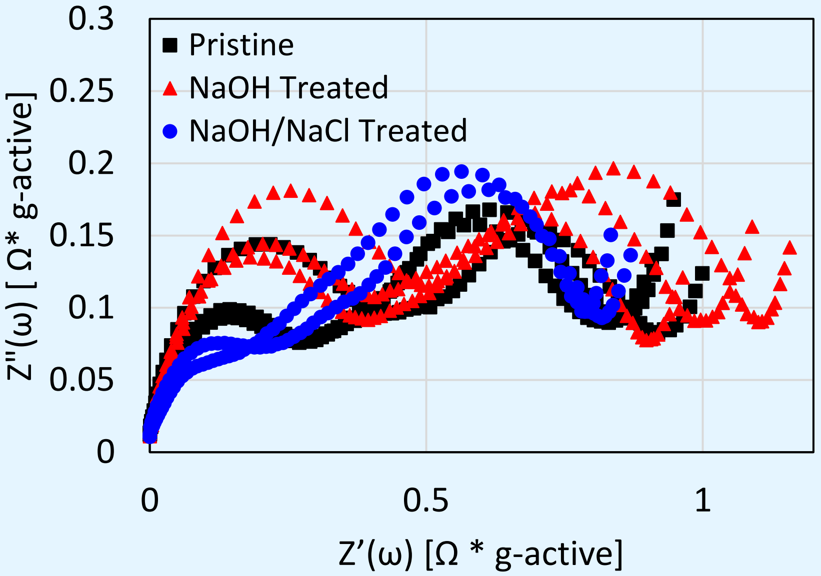
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)



Half Cells: NMC-532; Na^+ Salts

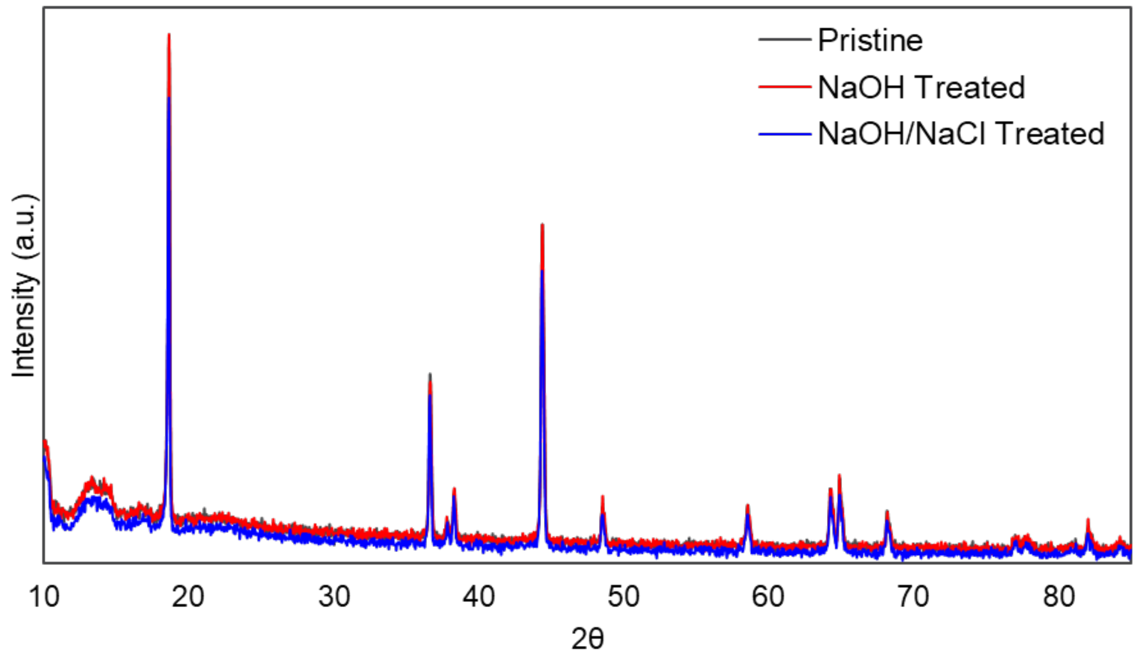


Full Cells: NMC-532; Na^+ Salts (n/p: ~1.25)



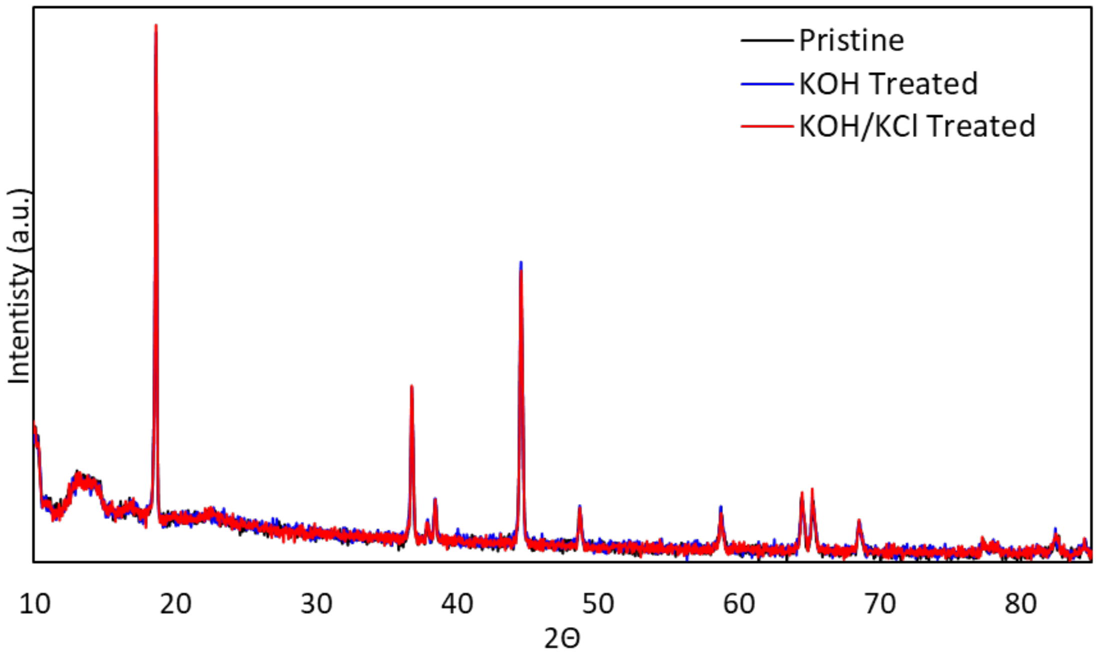
Structural Impacts of Treatment on NMC

NMC-532; Na^+ salts; pH 11



Condition	% Co_3O_4 ± SE	*a*	*c*	*I(003)/I(104)*
Pristine	1.0 ± 0.7	0.288	1.426	1.03
NaOH	1.5 ± 0.9	0.289	1.425	1.06
NaOH/NaCl	1.1 ± 0.5	0.288	1.426	1.12

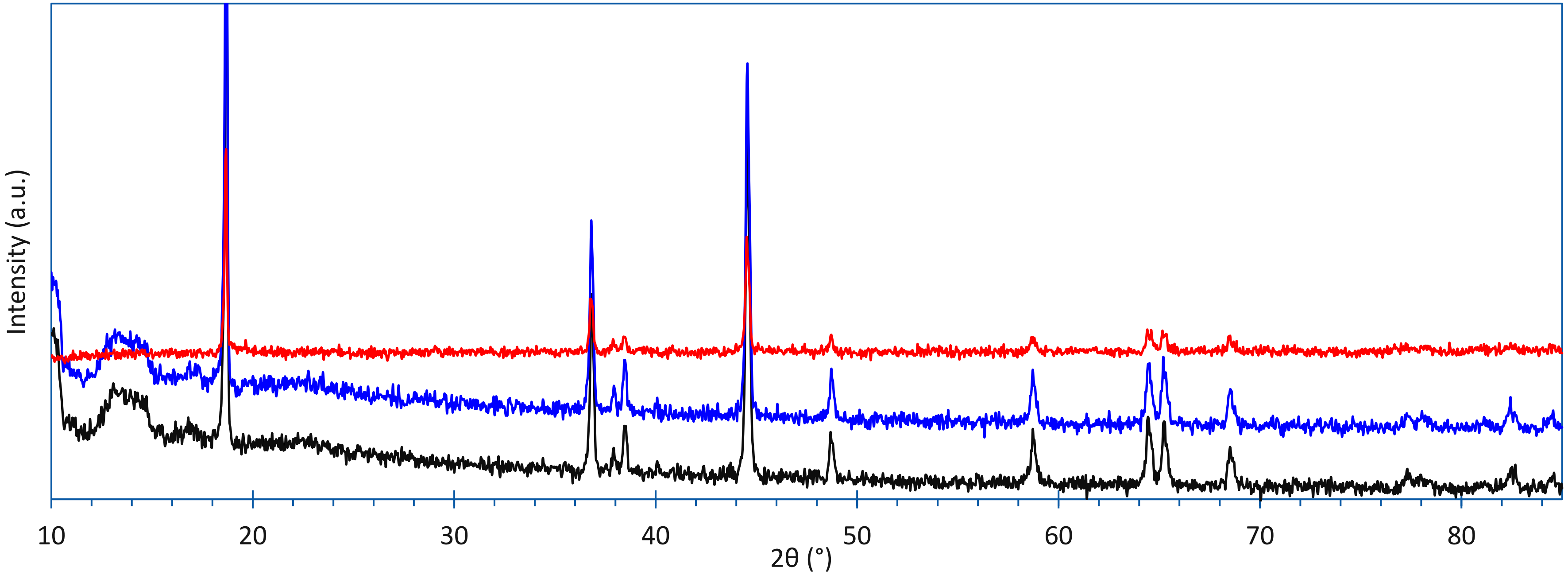
NMC-111; K^+ salts; pH 13



Condition	% Co_3O_4 ± SE	*a*	*c*	*I(003)/I(104)*
Pristine	0.05 ± 0.01	0.286	1.423	1.05
KOH	0.04 ± 0.01	0.286	1.423	1.08
KOH/KCl	0.05 ± 0.01	0.286	1.422	1.09

No significant bulk structural transformations (cation mixing, lattice expansion, phase change) observed for treated NMC.

Structural Impacts of Treatment on NMC, Cont'd



Impacts of Optimized Treatment Conditions on NMC Structure:

- No observed change to bulk lattice parameters; no significant peak shifting
- Conflicting evidence around cation mixing…may need to repeat sample due to low intensity
- Possible increase in spinel phase (within range of refinement error)

	NMC	Treatment Type	pH	Temperature	Agitation	Sonics?	Time (hr)	% Co_3O_4 ± SE	*a*	*c*	*I*(003)/*I*(104)	"R-factor": {*I*(006)+*I*(012)}/*I*(101)
	532	Pristine	---	---	---	---	---	1.0 ± 0.7	0.288	1.426	1.03	0.408
	532	NaOH	11	Ambient	Shaking	No	1	1.5 ± 0.9	0.289	1.425	1.06	0.458
	532	NaOH/NaCl	11	Ambient	Shaking	No	1	1.1 ± 0.5	0.288	1.426	1.12	0.443
*	**111**	**Pristine**	**---**	**---**	**---**	**---**	**---**	**0.05 ± 0.01**	**0.286**	**1.423**	**1.05**	**0.379**
*	**111**	**KOH**	**13**	**Ambient**	**Shaking**	**No**	**1**	**0.04 ± 0.01**	**0.286**	**1.423**	**1.08**	**0.376**
	111	KOH/KCl	13	Ambient	Shaking	No	1	0.05 ± 0.01	0.286	1.422	1.09	0.333
*	**111**	**KOH**	**13**	**60 °C**	**Overhead Stir**	**Yes**	**2**	**0.07± 0.01**	**0.286**	**1.422**	**1.18**	**0.505**

*Reduced intensity of red sample due to smaller divergence slit (low sample volume); repeat analysis planned