NREL Transforming ENERGY

ReCell ADVANCED BATTERY RECYCLING

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

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VEHICLE TECHNOLOGIES OFFICE

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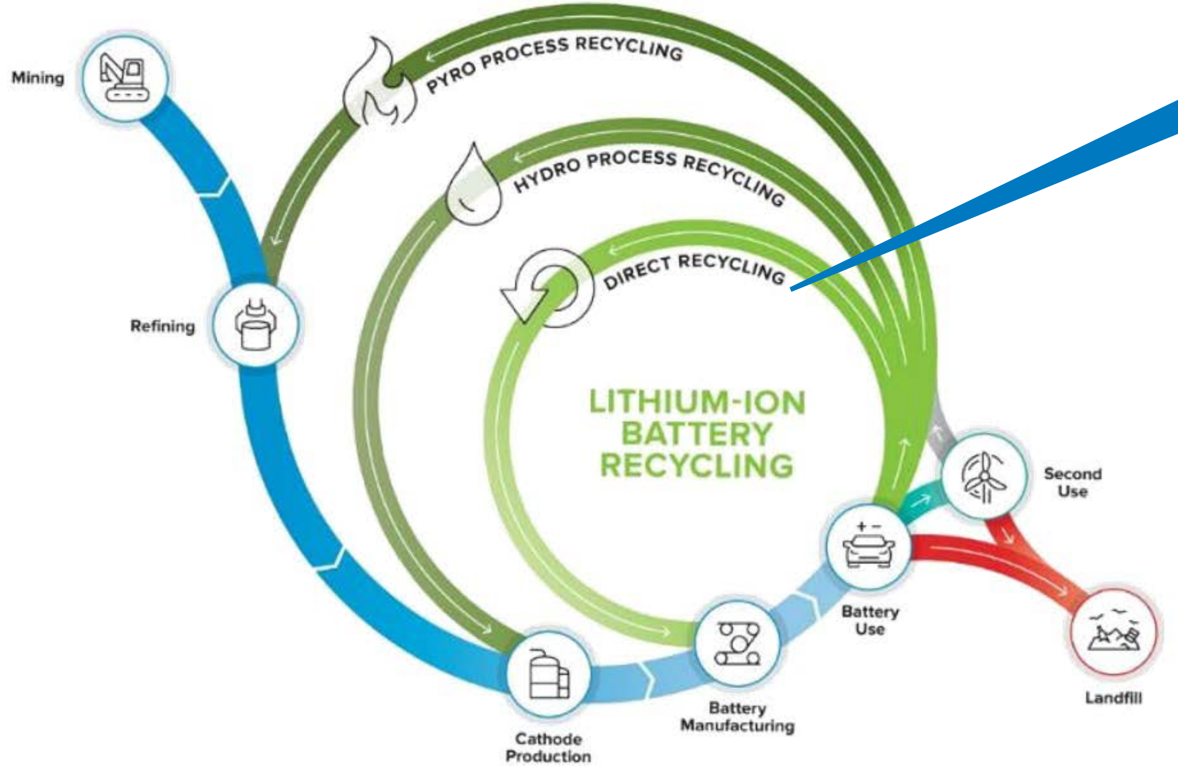
Direct Recycling of Li-Ion Batteries

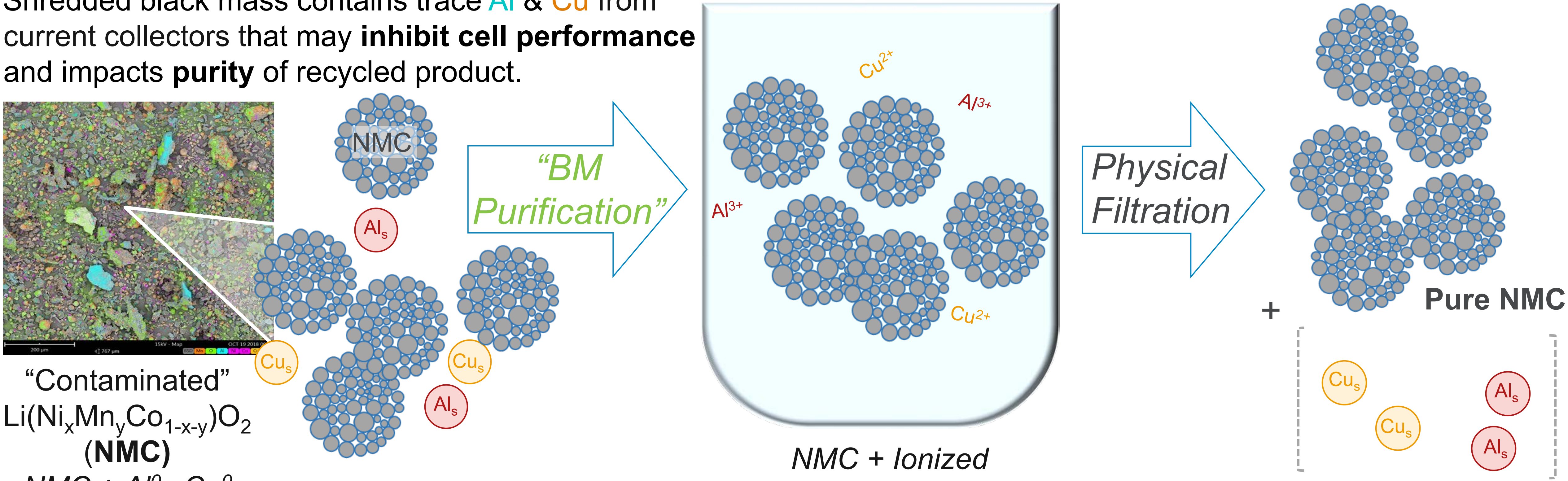
- Burgeoning demand for Li-ion batteries induces **supply chain instability** and raises concerns regarding **end-of-life disposal**.
- <u>DOE goal:</u> "Reduce the cost of electric vehicle battery packs to <$150/kWh with technologies that significantly reduce or eliminate **dependency on critical materials**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



"Contaminated" $Li(Ni_xMn_yCo_{1-x-y})O_2$ (**NMC**)
NMC + Al^0, Cu^0

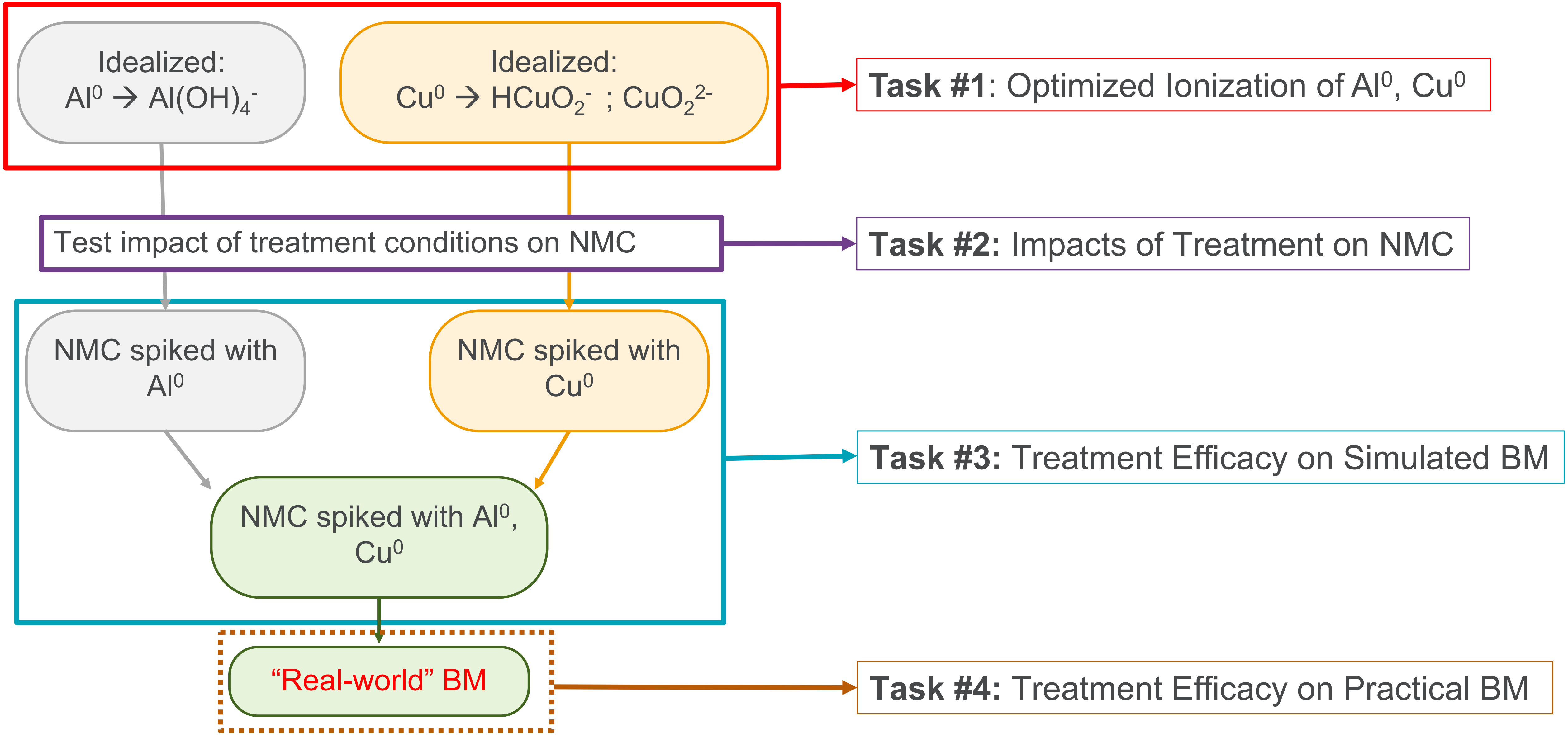
NMC + Ionized Al^{3+}, Cu^{2+}

Pure Recovered Al^0, Cu^0

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



Task #1: Optimized Ionization of Al_0, Cu_0

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")*

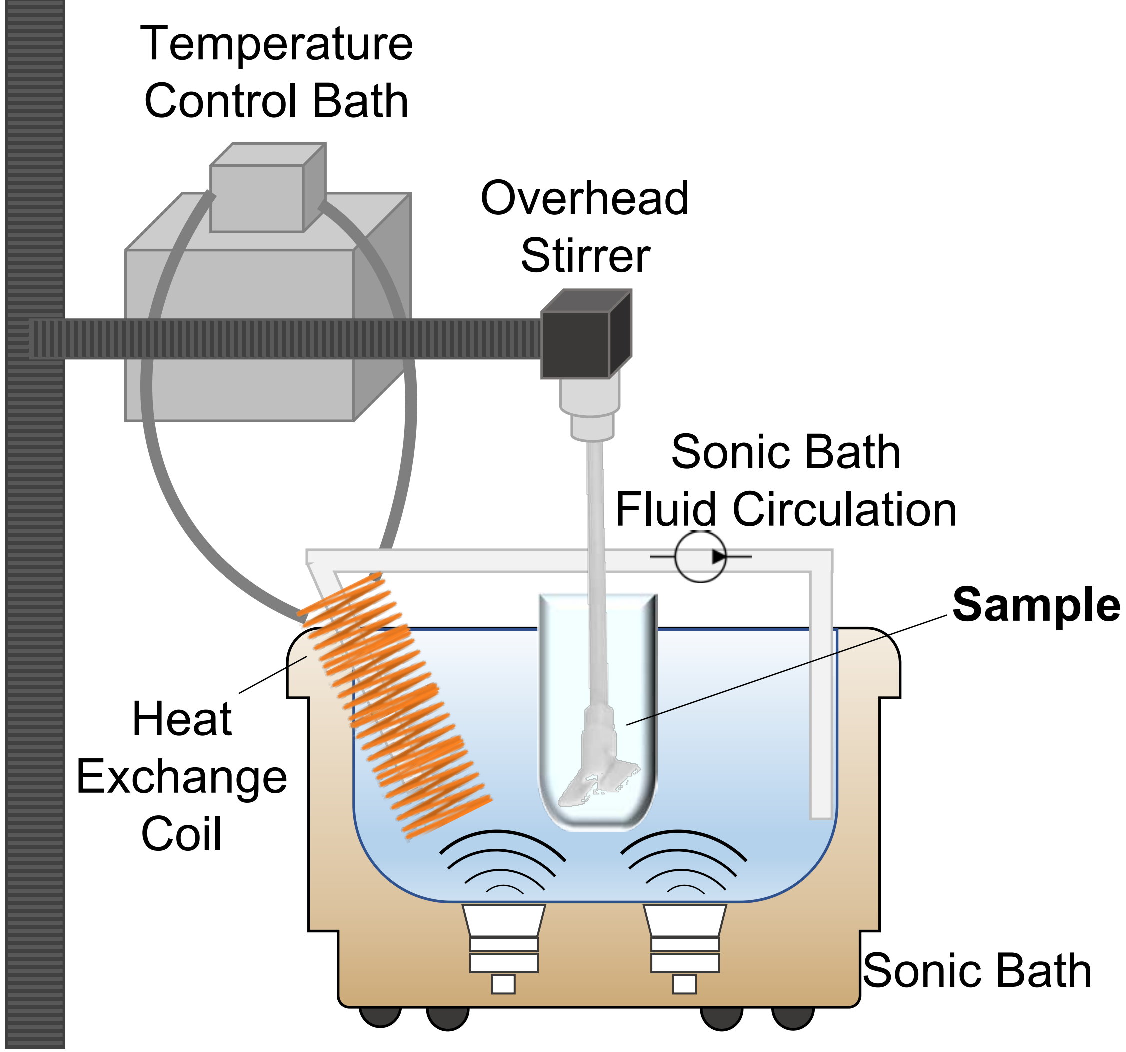
Cl^- *(saturated; ~4.5 M)*

DTPA *(2x molar equivalent)*

"Bench-scale" testing:

- 40-45 mL solution
- 10 mg contaminant

Modular overhead sonic-stirrer



Al^0 & Cu^0 Corrosion: Theoretical Foundations

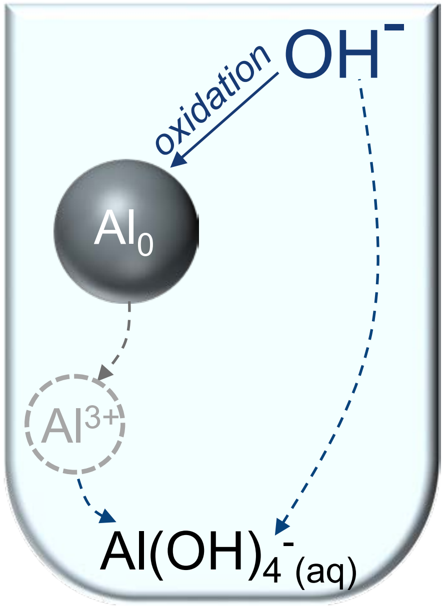
Al^0 Corrosion:

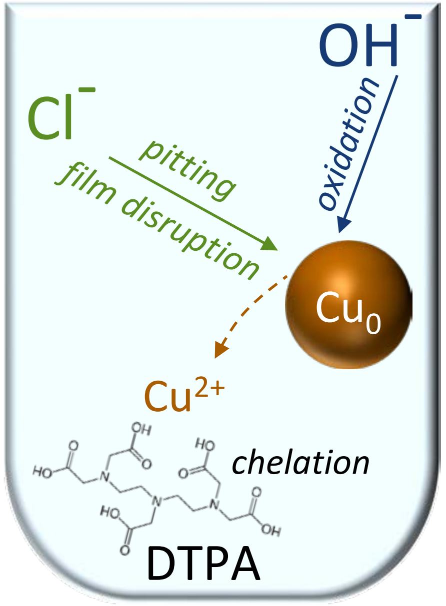
-Rapid, strongly pH-dependent reaction under ambient oxidative conditions

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

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

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



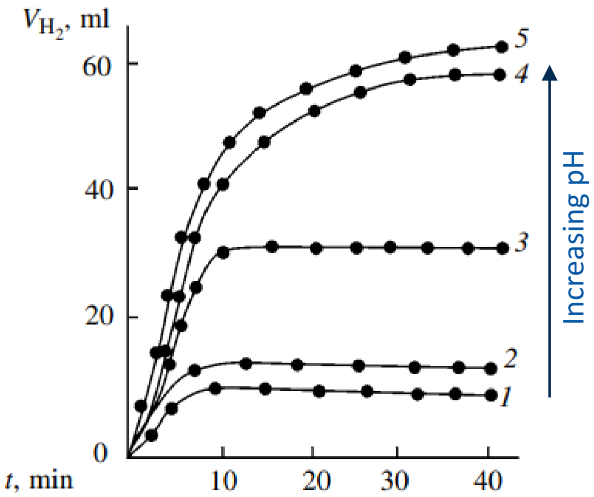


Cu^0 Corrosion:

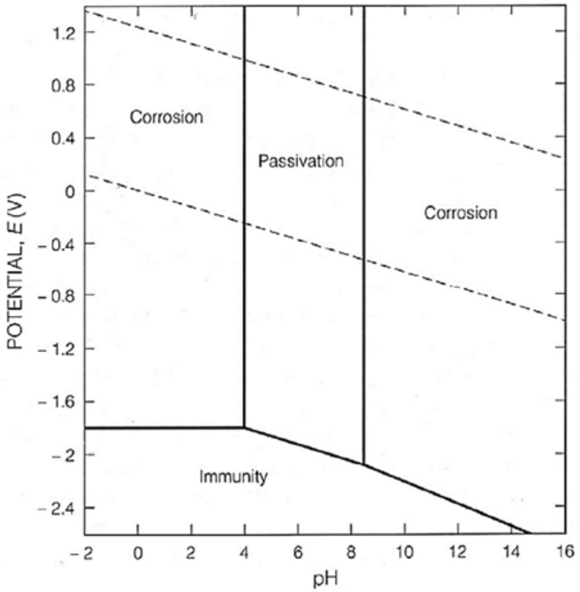
-Kinetically slow and thermodynamically unfavorable

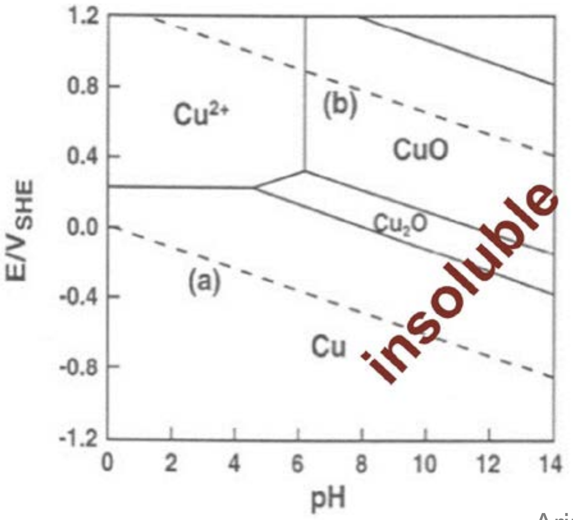
-Low solubility of Cu^{2+} species and formation of passivating surface films

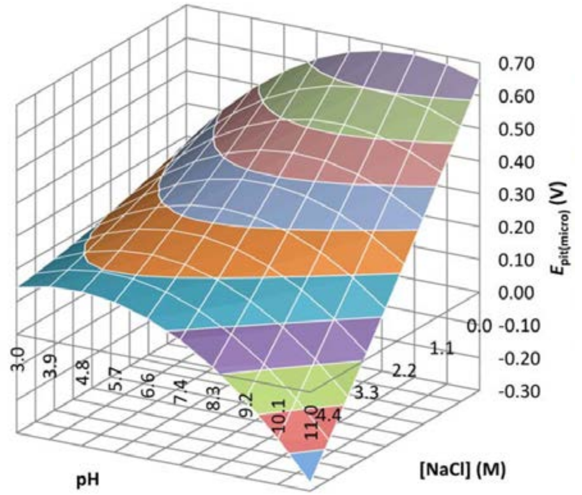
-**Chloride** reportedly enhances corrosion in alkaline media through pitting and surface film disruption



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*)

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

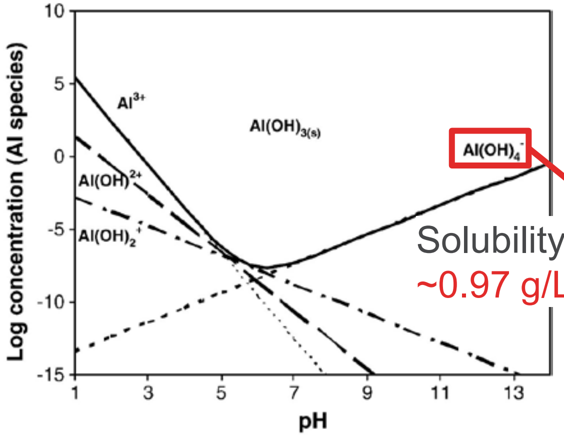
Each extent of reaction consumes Al_0 and OH^- on a 1:1 molar basis

Reaction kinetics and extent may be quantified by **tracking solution pH**

log K_f $[Al(OH)_4^-]$ = 33.0 (25 °C)

Al^{3+} preferentially and strongly binds OH^- in alkaline solution to form soluble $Al(OH_4)^-$.

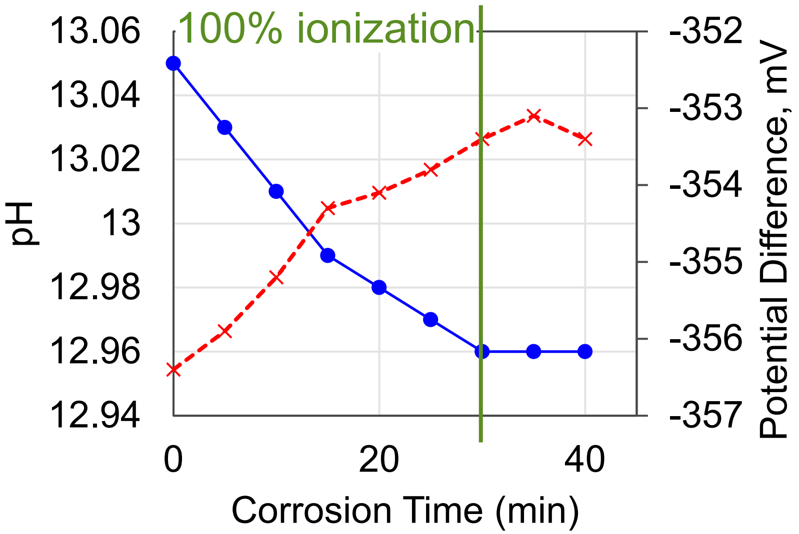
***Thermodynamically favorable** reaction; room for **kinetic tuning**.*



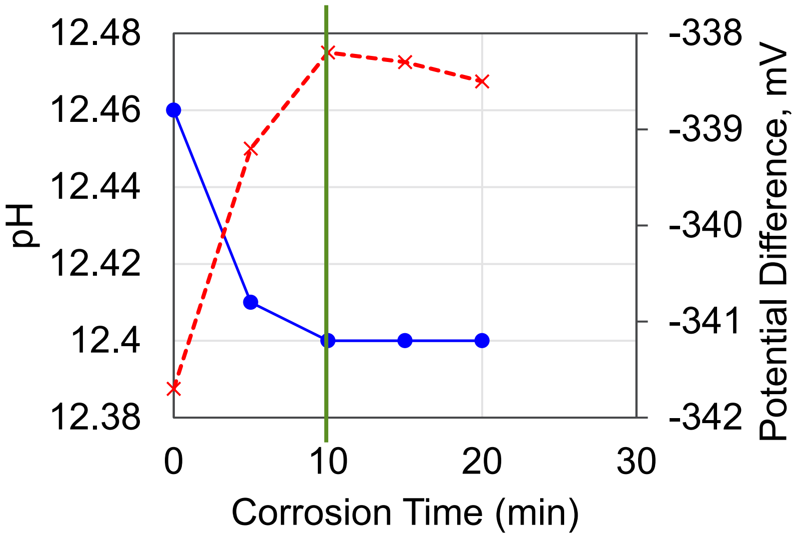
Emamjomeh et al, *Desalination* 275, 1-3 (2011), 102-106.

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

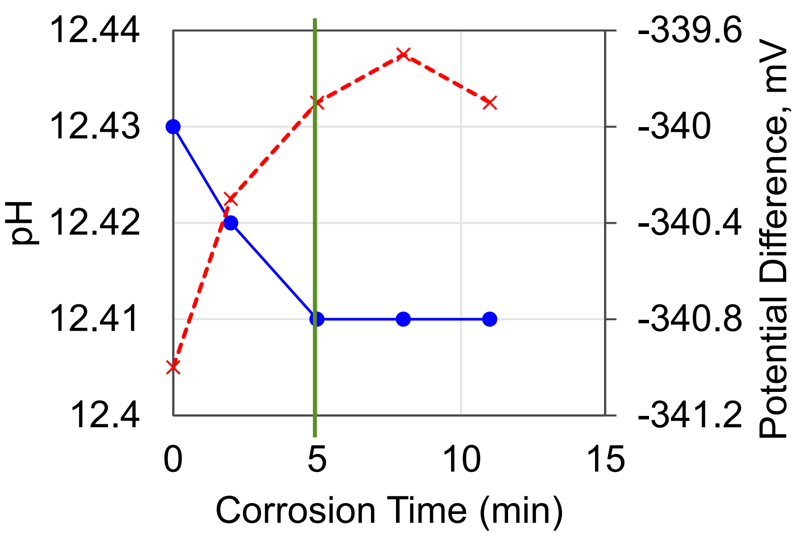
RT, no T control *(20–22 °C)*



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*)

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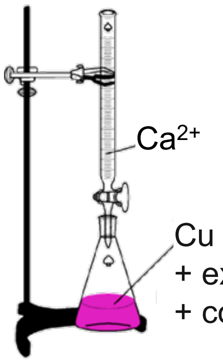


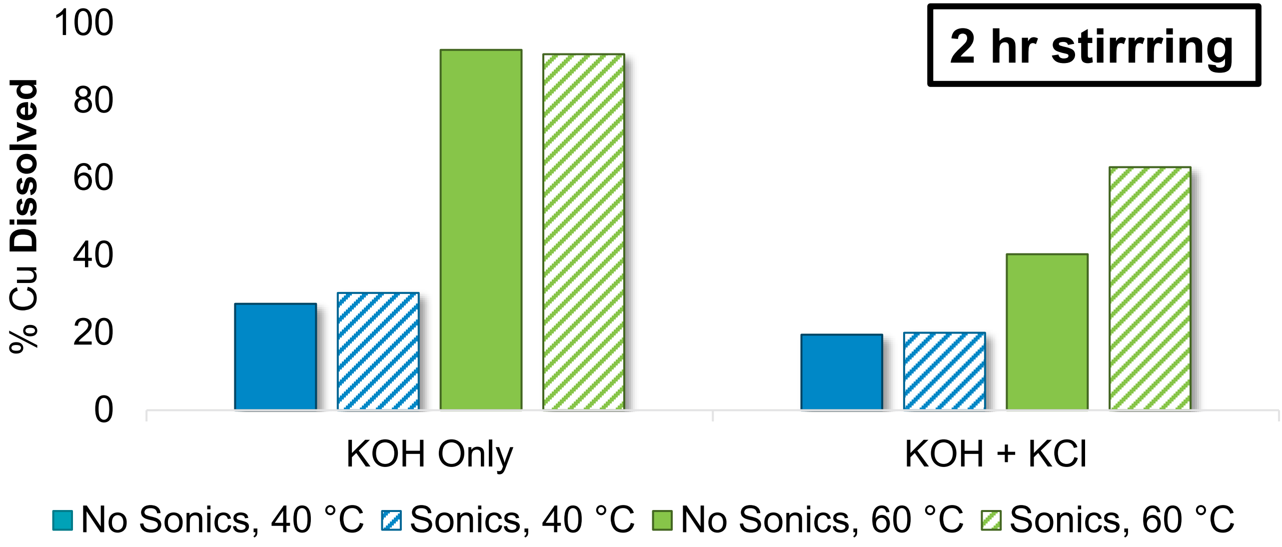
Approach:
colorimetric titration
(± *1-2 wt % Cu*)

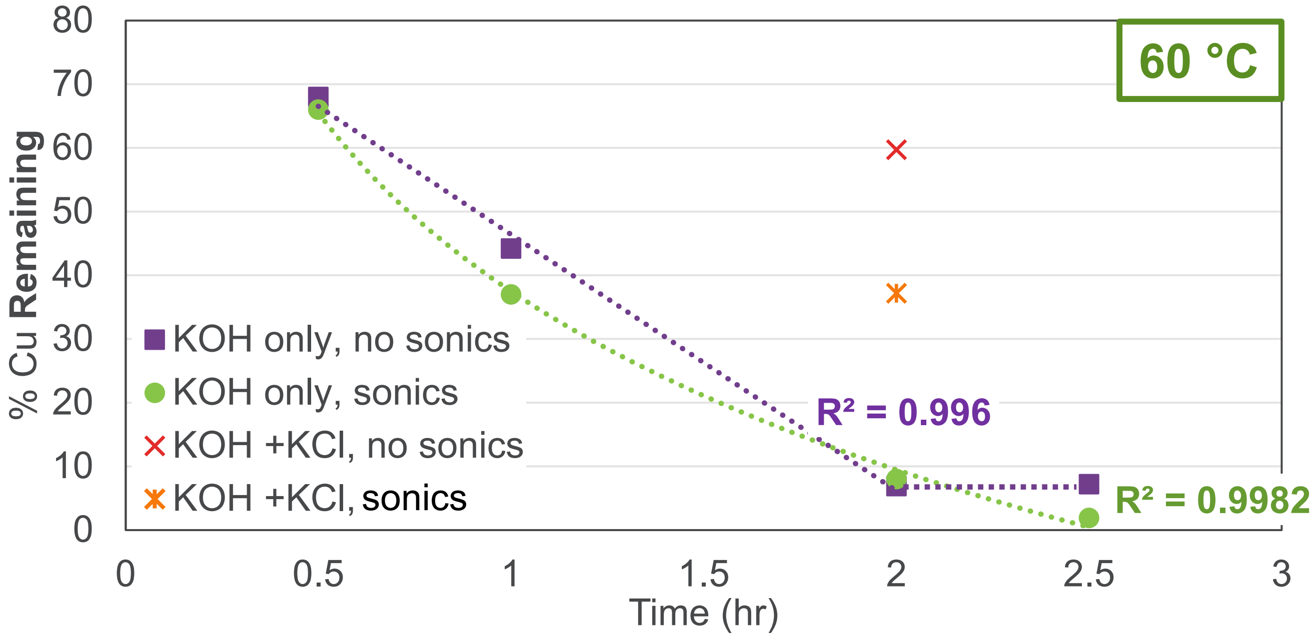
Cu + DTPA (complexed)
+ excess DTPA
+ colorimetric indicator

"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.

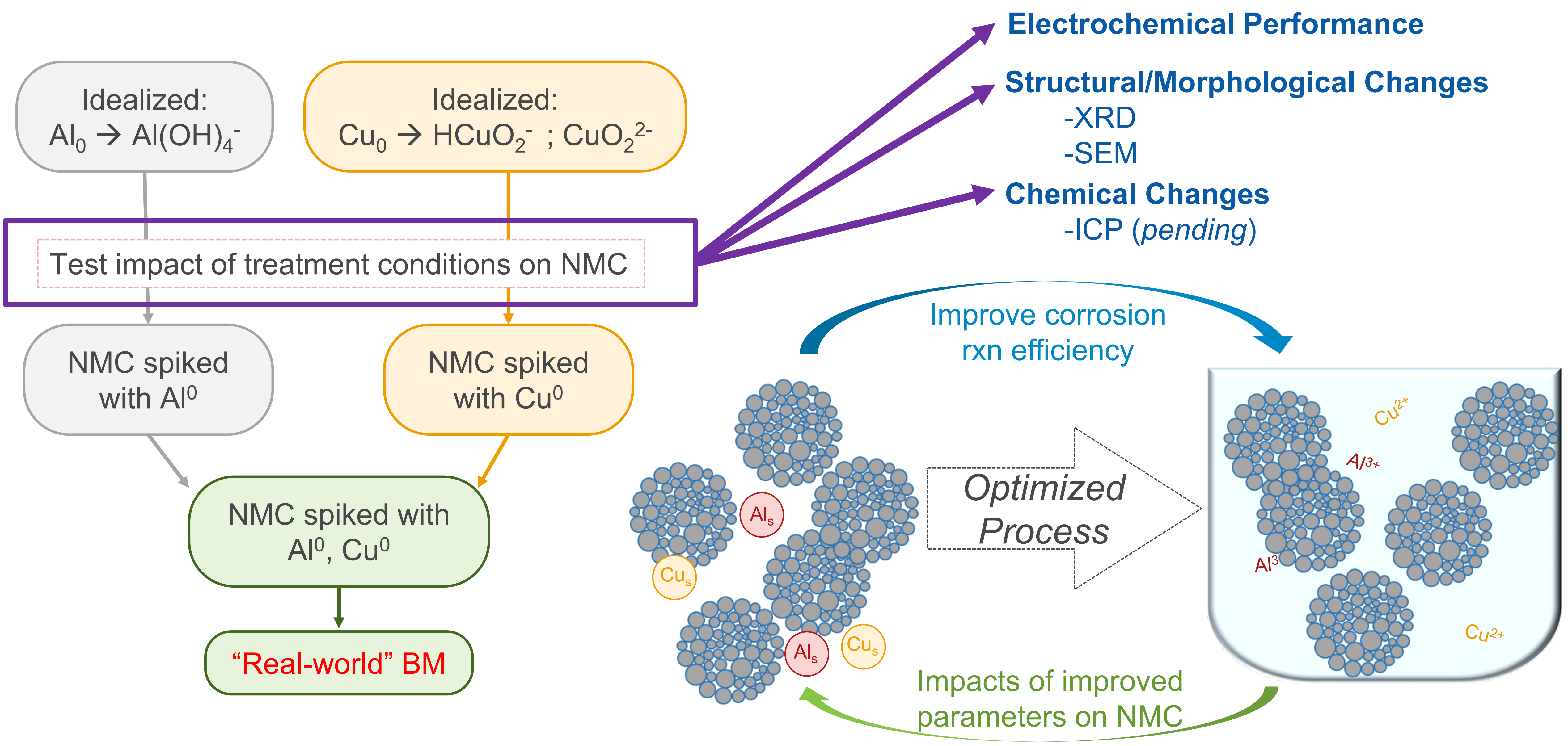
Without Sonication:

- **Linear (0^{th} order)** kinetics until ~93% ionization
- Thermodynamic maximum <100% ionization

With Sonication:

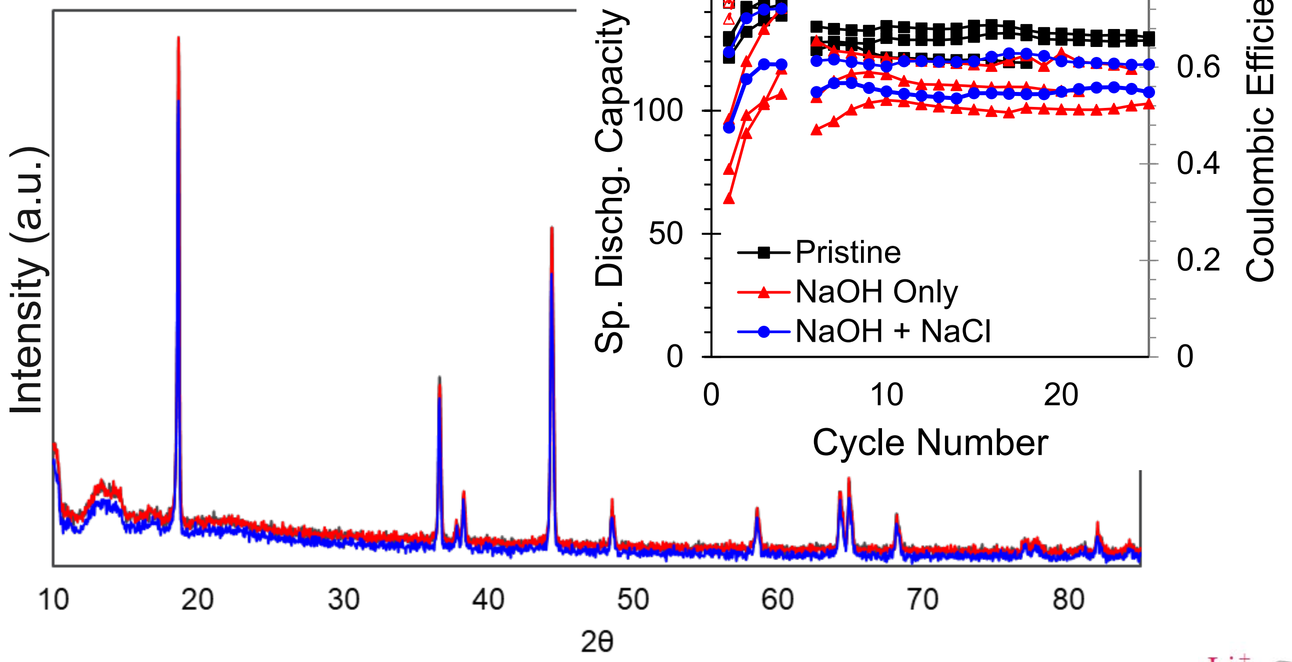
- **Logarithmic (1^{st} order)** kinetics (conc. dependence on ionized product)
- ~100% corrosion achieved after **2.5 hr** (*within error*)

Task #2: Impacts of Treatment on NMC

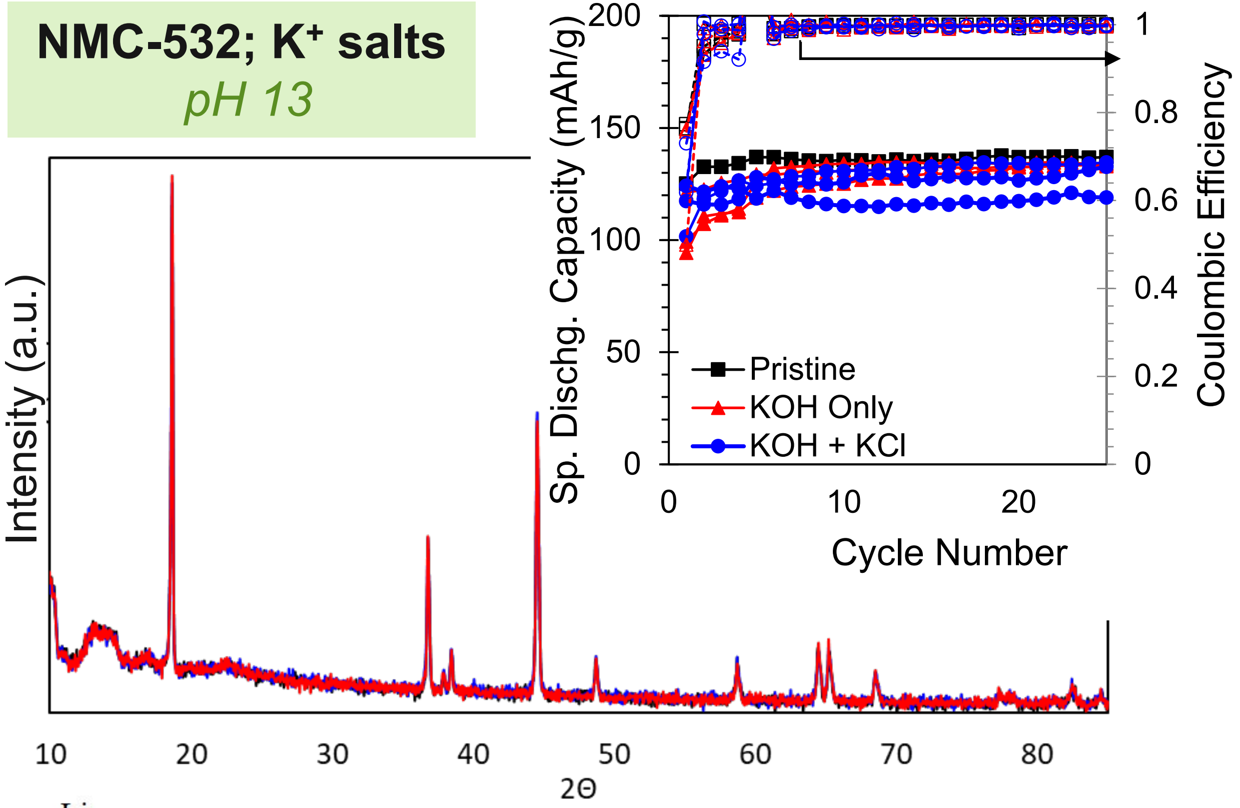


Iterative Process Optimization

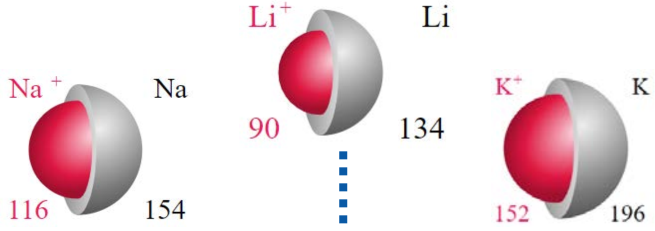
NMC-532; Na^{+} salts
pH 11



NMC-532; K^{+} salts
pH 13



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



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.

In Progress: Treatment Efficacy on BM

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

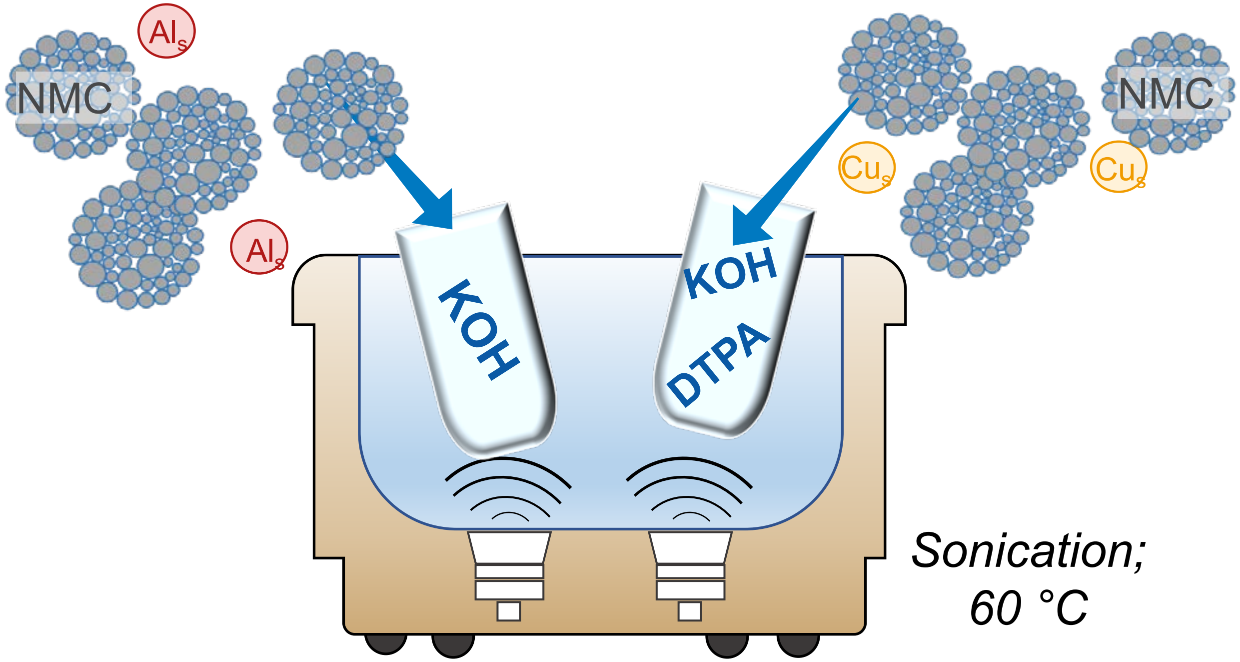
Idealized: $Cu_0 \rightarrow HCuO_2^-$; CuO_2^{2-}

NMC spiked with Al_0

NMC spiked with Cu_0

NMC spiked with Al_0, Cu_0

"Real-world" BM



Sonication; 60 °C

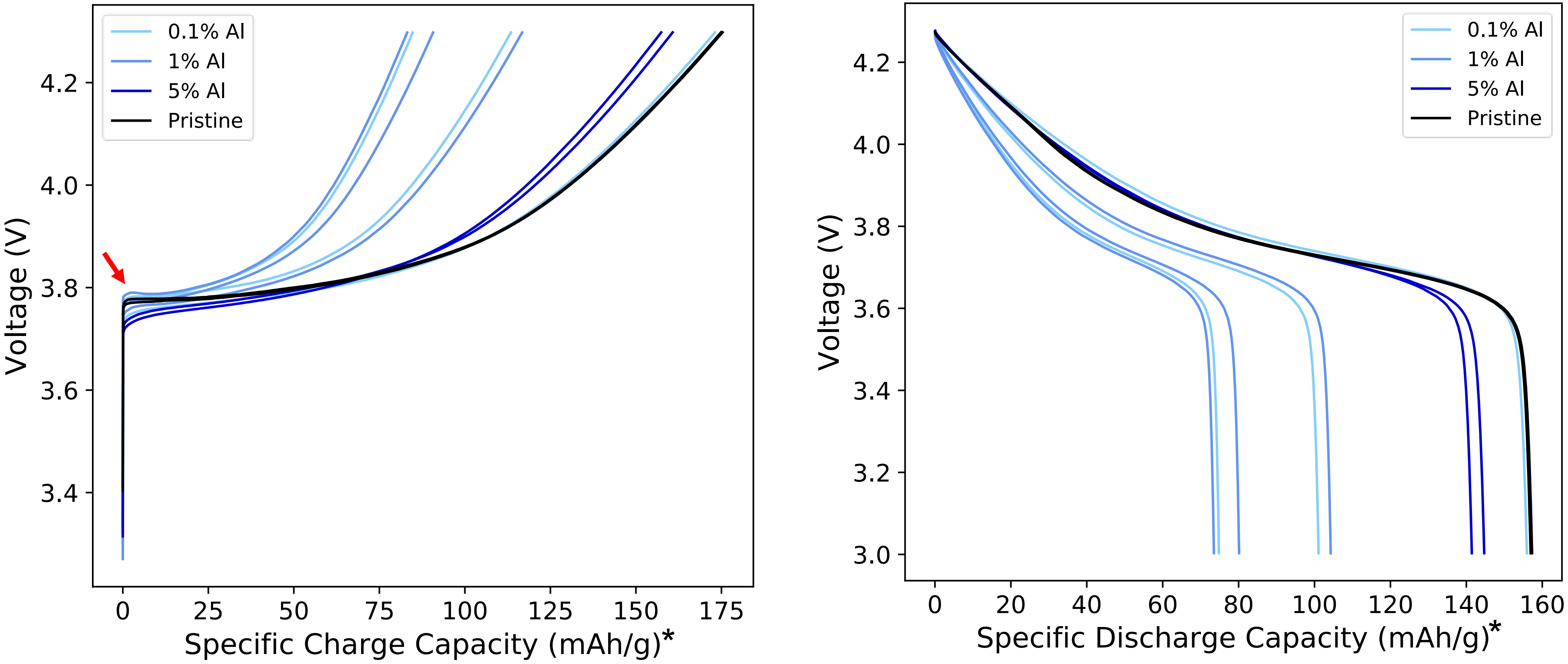
Prepare batches of NMC spiked with relevant contaminant loadings (0.1 – 5 wt%)

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

May contain additional metallic impurities not tested in idealized studies

Impacts of treatment conditions on residual graphite?

Pre-Treatment Baselining: Al^0-Contaminated NMC

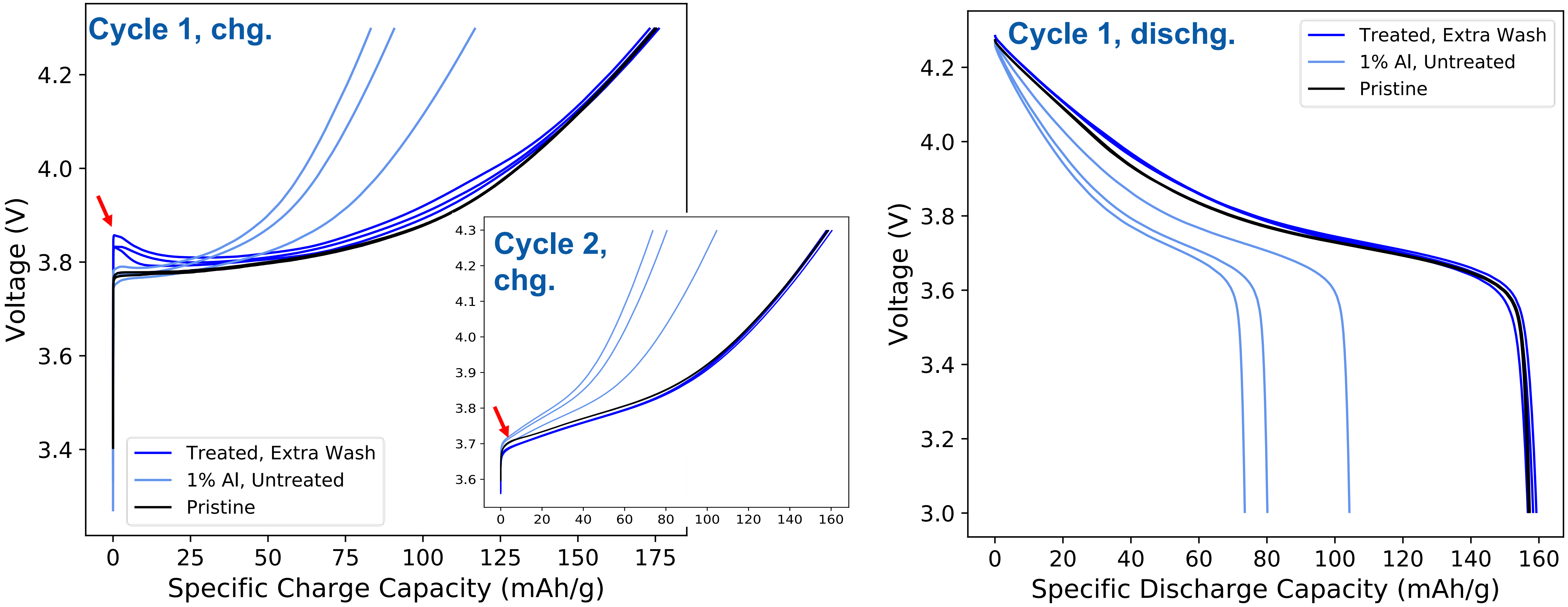


Specific capacity normalized with respect to mass of NMC (contaminant mass excluded)

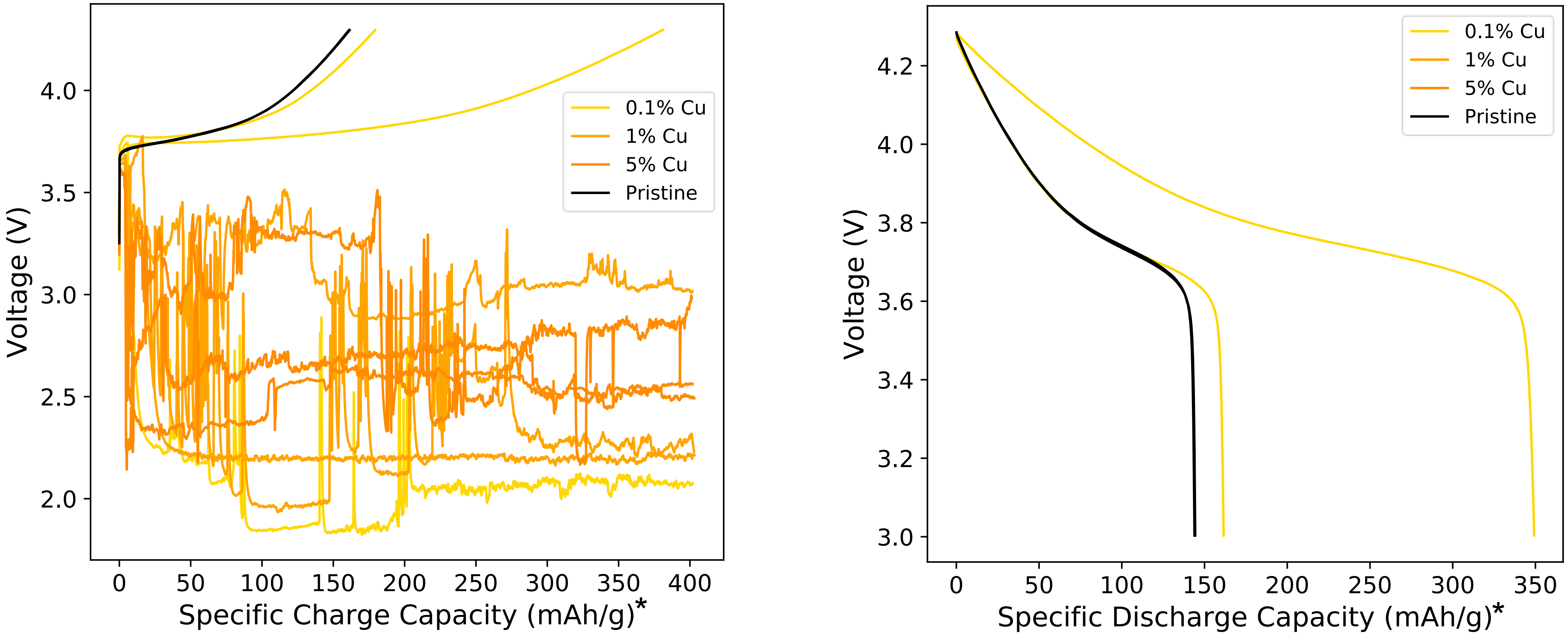
- Al^0 contamination may function as a conductive dopant (reduces initial charge resistance), particularly at higher impurity concentrations,[1] but negatively impacts cell capacity (kinetic losses)
- Interestingly, the worst impact on performance is seen between 0.1% - 1% Al^0…i.e., the practically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

Treatment of Al^0-Contaminated NMC



- Initial discharge is nearly identical to pristine material, suggesting a **successful Al^0 purification process** that **does not adversely impact NMC performance**.
- Higher impedance on cycle 1 shifts to lower impedance on cycle 2 with treatment; cause is under investigation.

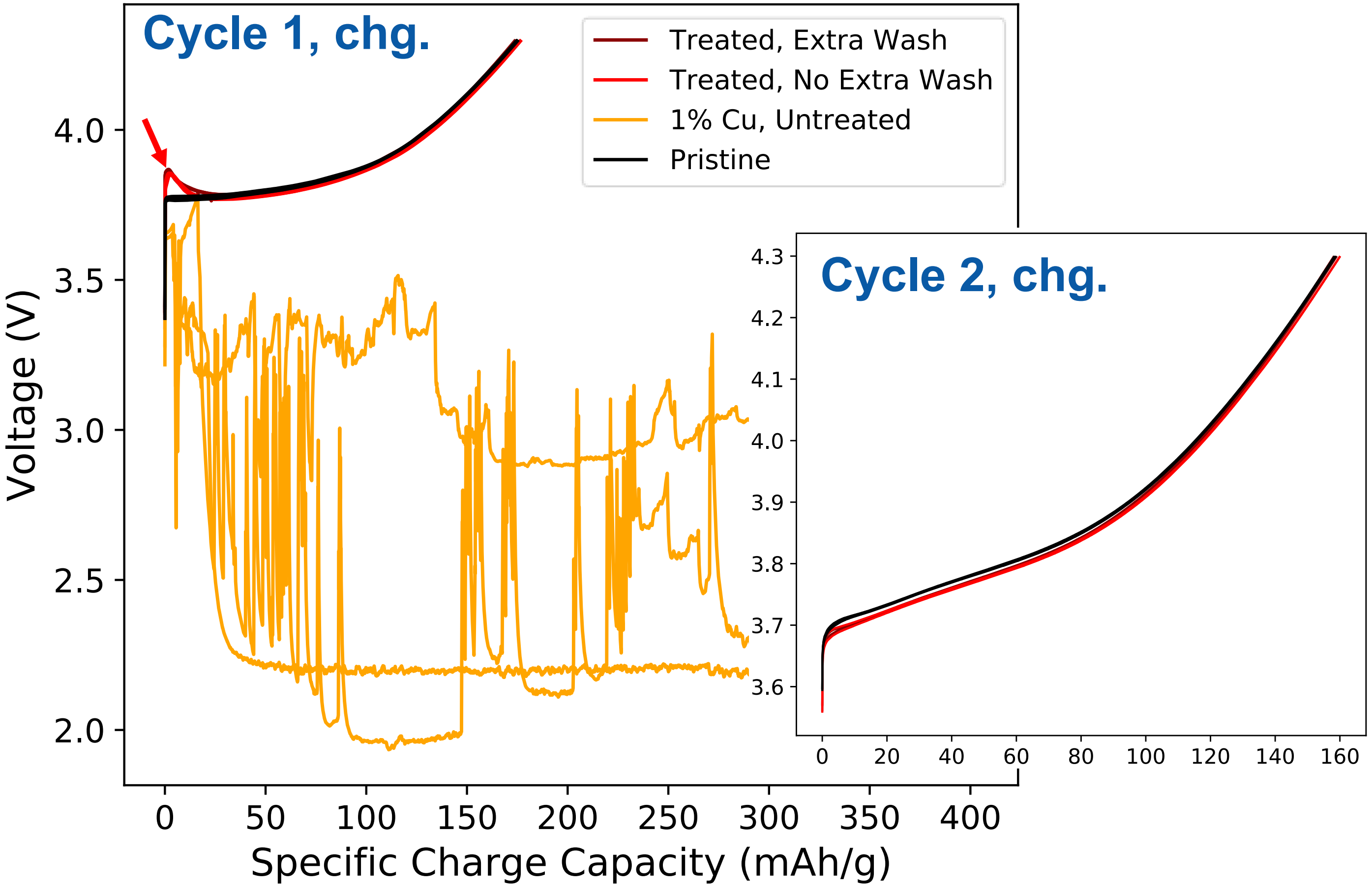


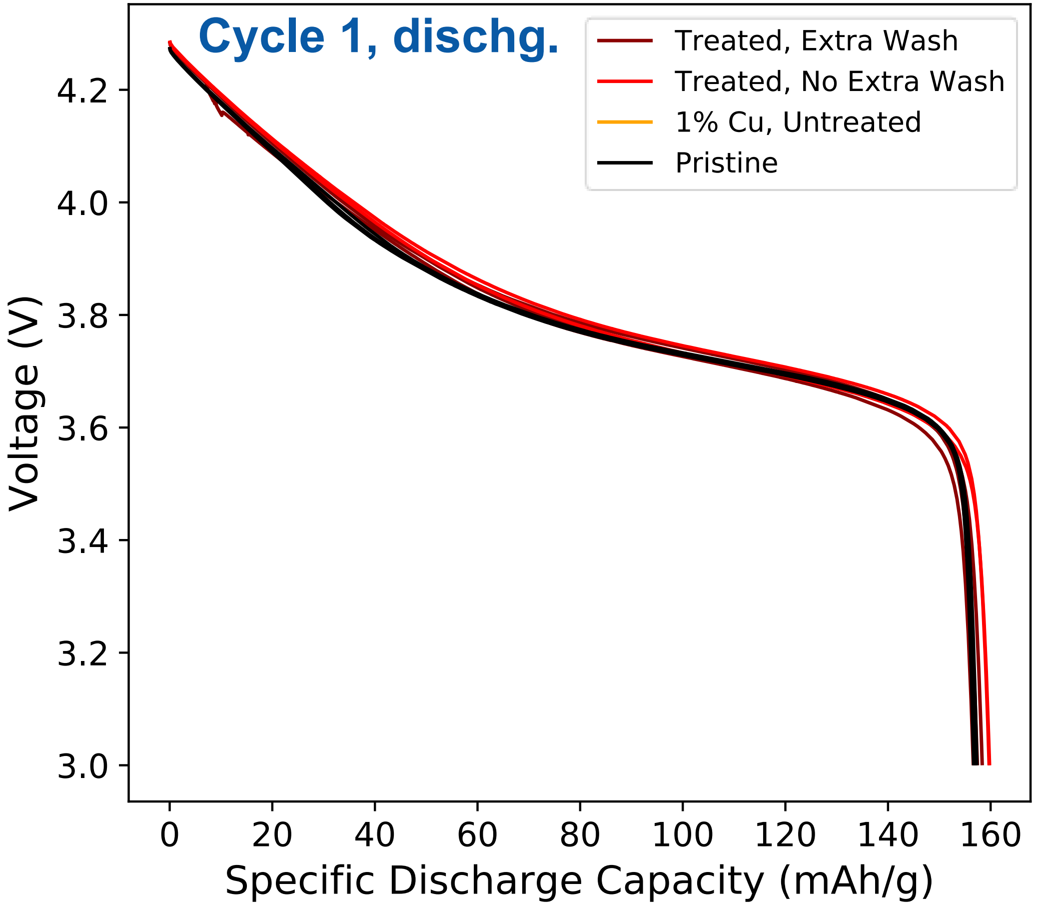
**Specific capacity normalized with respect to mass of NMC (contaminant mass excluded)*

- 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*)

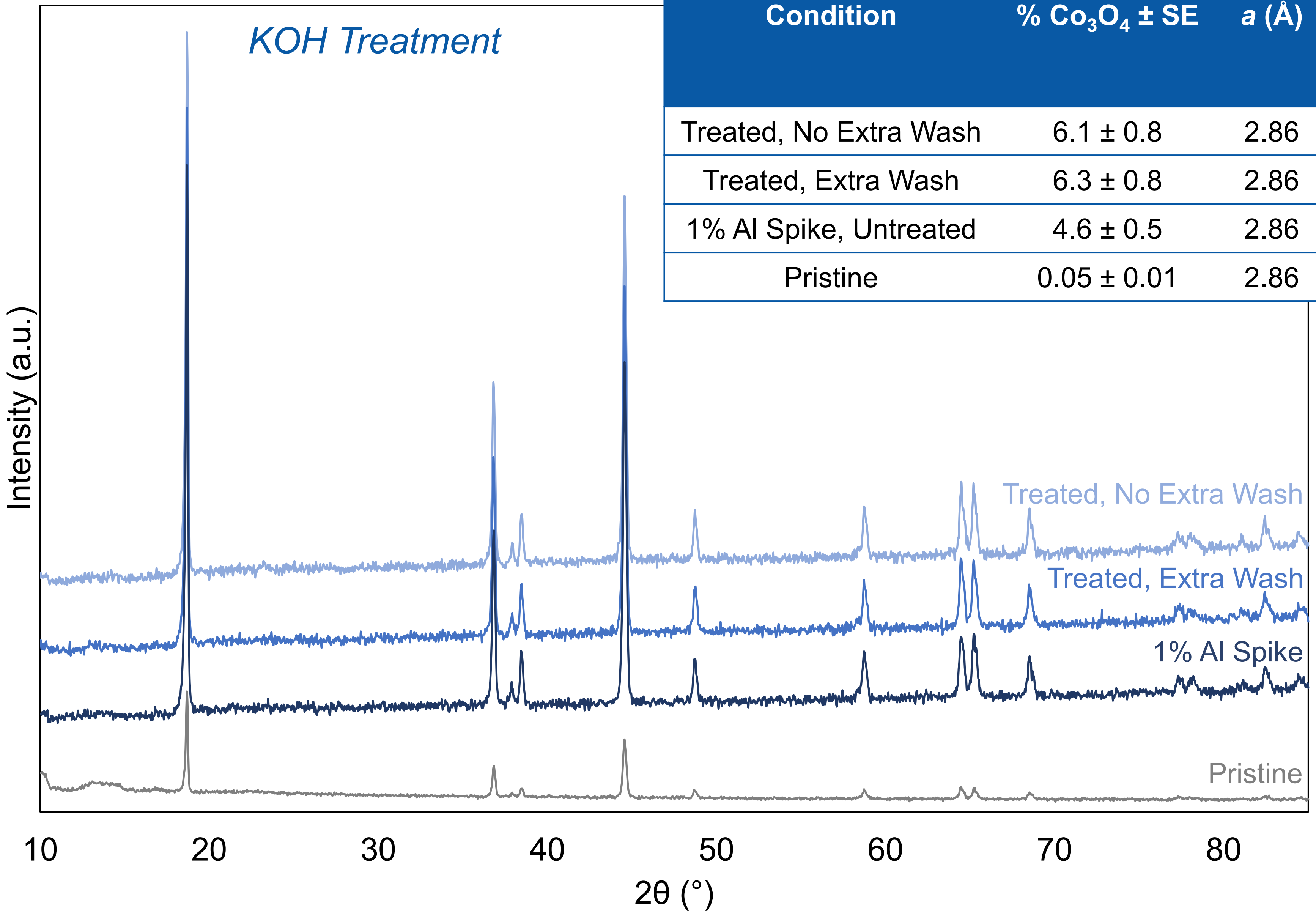
Treatment of Al^0-Contaminated NMC





- Cu^0 removal is also proven to be successful, with pristine capacity restored.
- Similar pattern of initial impedance between 1st and 2nd cycles observed as for treated Al^0 samples.
- Supplemental rinse with DI H_2O (to remove residual salts) does not resolve; further investigation is underway.

Structural Impacts of Treatment on NMC

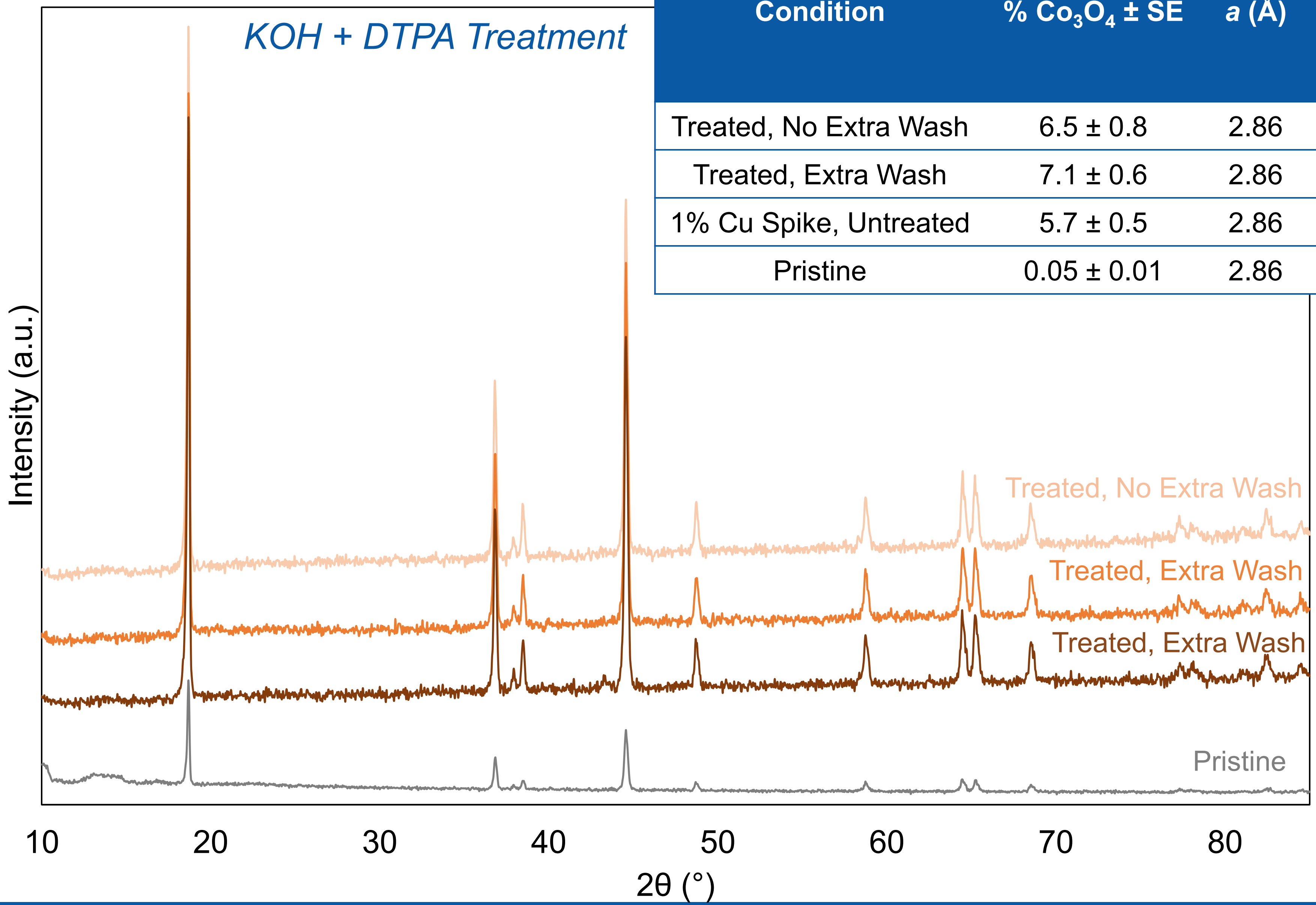


Condition	% Co_3O_4 ± SE	*a* (Å)	*c* (Å)	*I*(003)/*I*(104)	"R-factor": {*I*(006)+*I*(012)}/*I*(101)
Treated, No Extra Wash	6.1 ± 0.8	2.86	14.23	1.19	0.360
Treated, Extra Wash	6.3 ± 0.8	2.86	14.23	1.20	0.401
1% Al Spike, Untreated	4.6 ± 0.5	2.86	14.23	1.20	0.426
Pristine	0.05 ± 0.01	2.86	14.23	1.05	0.379

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).

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
  - Al → Al^{3+} is a rapid, strongly pH-dependent reaction under ambient oxidative conditions
  - Cu → Cu^{2+} is kinetically slow and thermodynamically unfavorable
  - 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 electrochemical capacity of treated material matching pristine during initial formation cycling
  - Some evidence of bulk structural rearrangement to spinel phase; however, no apparent impact on performance
  - Source of first-cycle irregularity in voltage profiles of treated material is under continued investigation

Upcoming Studies:

- ☐ Validation of purification process on industrial BM (shredded end-of-life batteries)
- ☐ Scale up for demonstration at ReCell direct recycling pilot plant
- ☐ Development of tailored sorbents for selective recovery of Al and Cu from solution

Thank you for your attention!

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Further questions:
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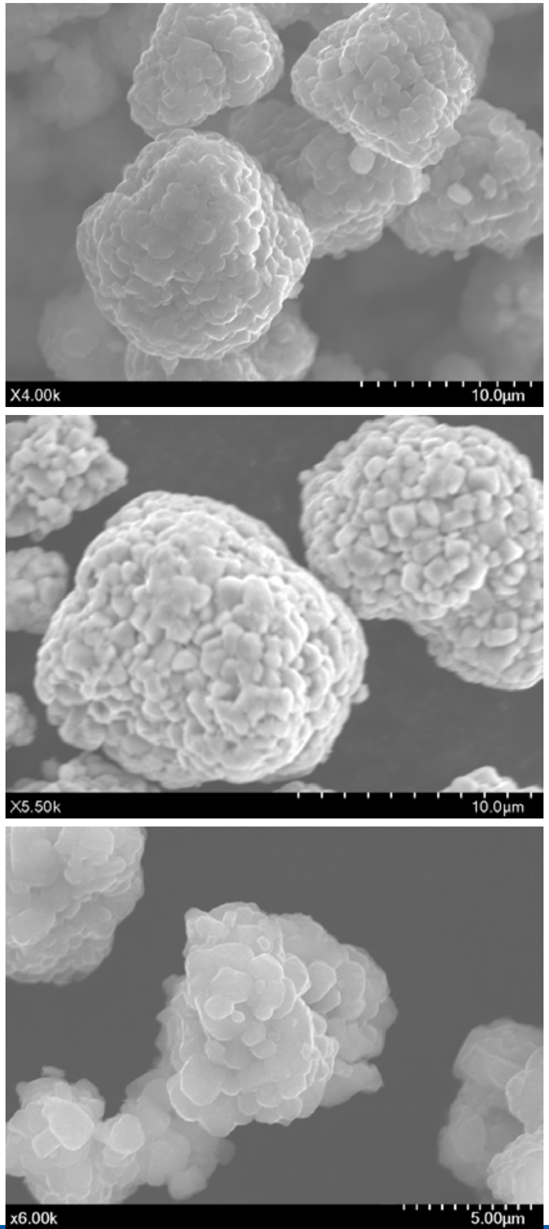
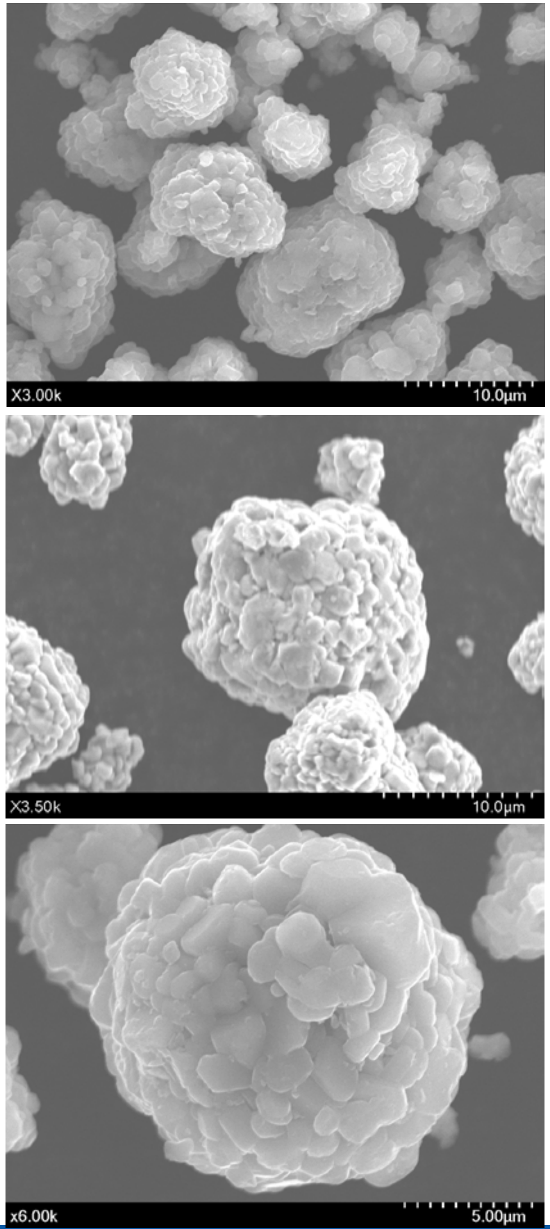
Morphological Impacts of Treatment on NMC

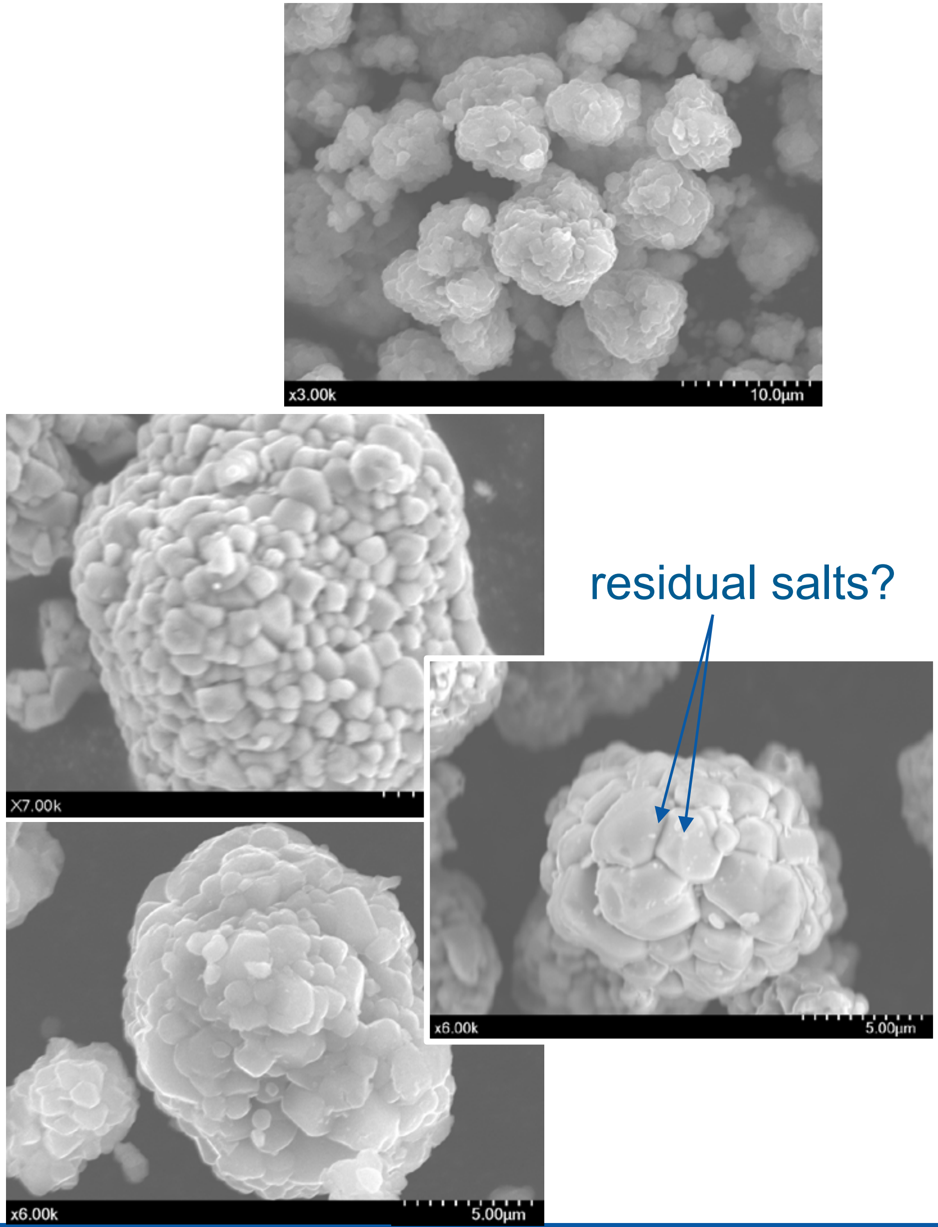
Pristine



KOH Treatment



KOH + KCl Treatment



Electrochemical Impacts of Treatment on NMC

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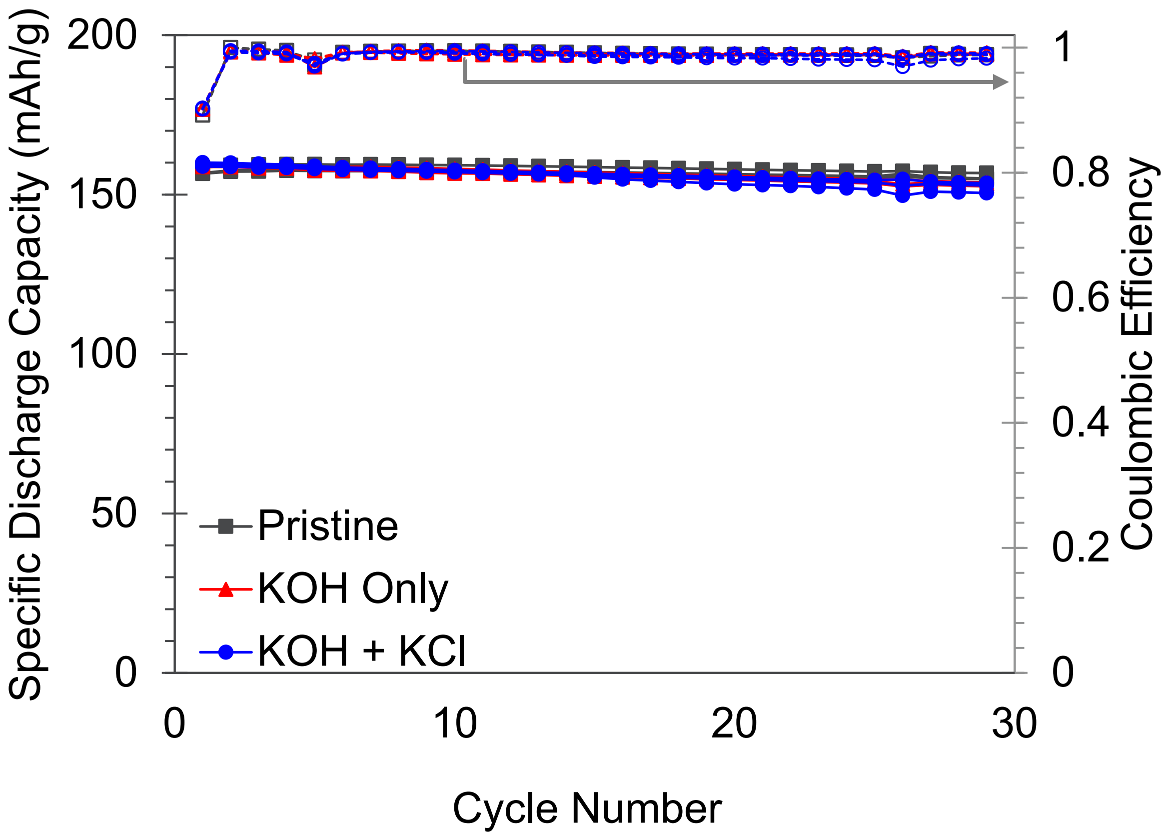
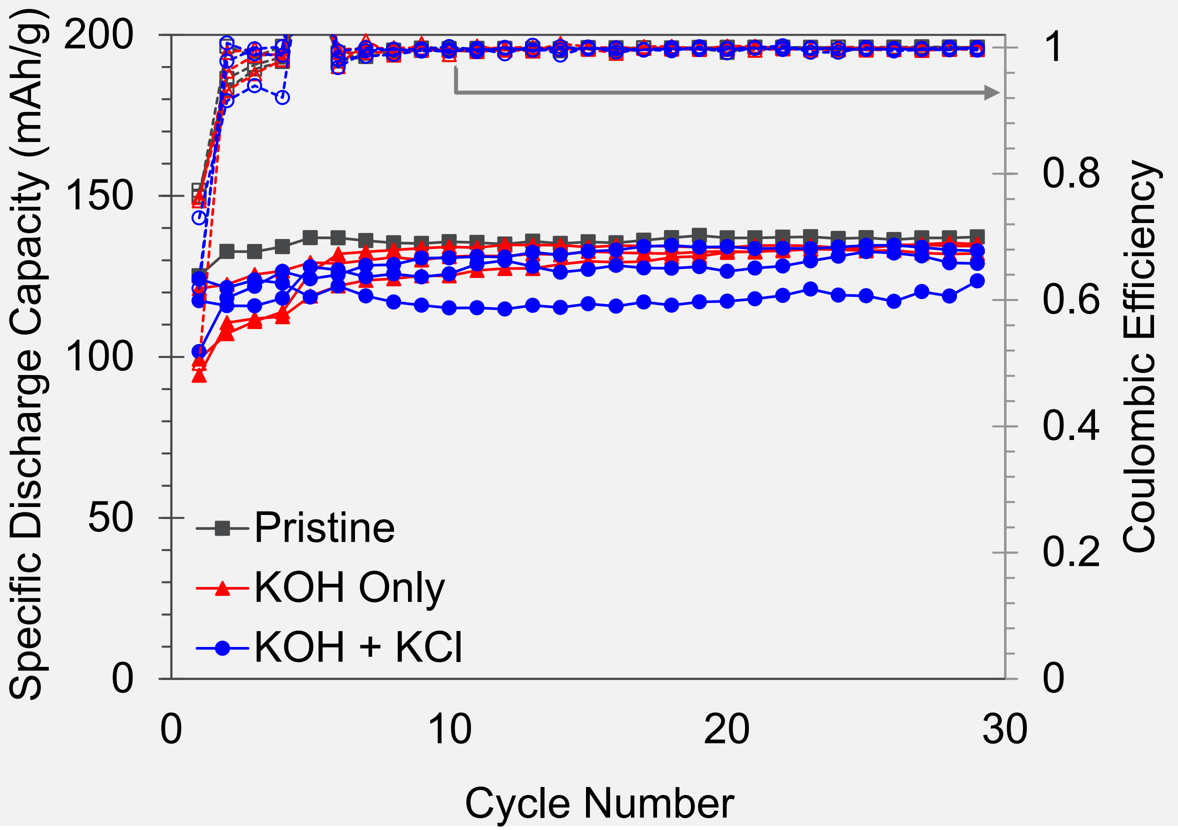
Half Cells: NMC-111; K^+ Salts



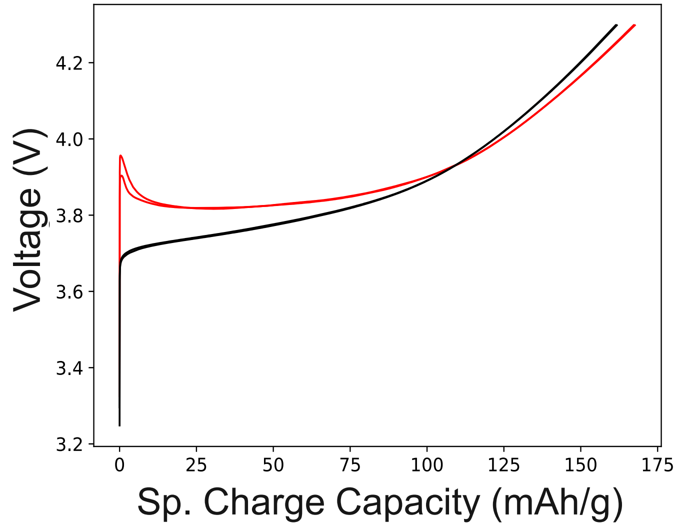
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)

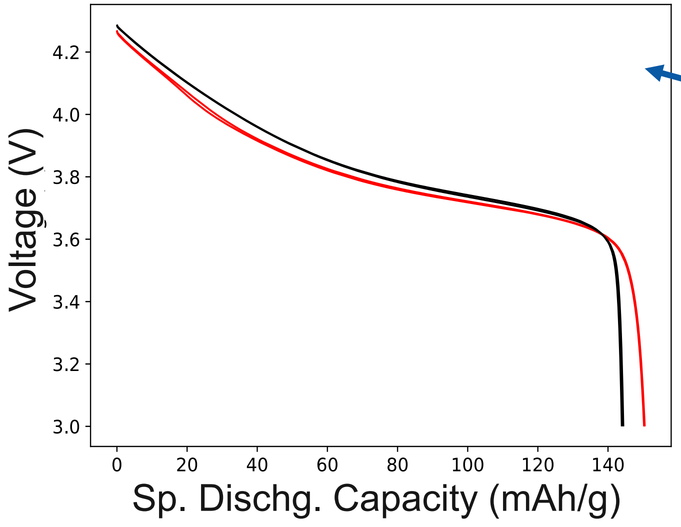


- NMC treated with K^+ salts shows improved performance over NMC treated with Na^+ salts (reduced cationic substitution)
- Reduced capacity in full cells may be attributable to residual Cl^- salts on the surface of NMC (irregular SEI formation).
- Mitigation strategies for residual salts under investigation;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

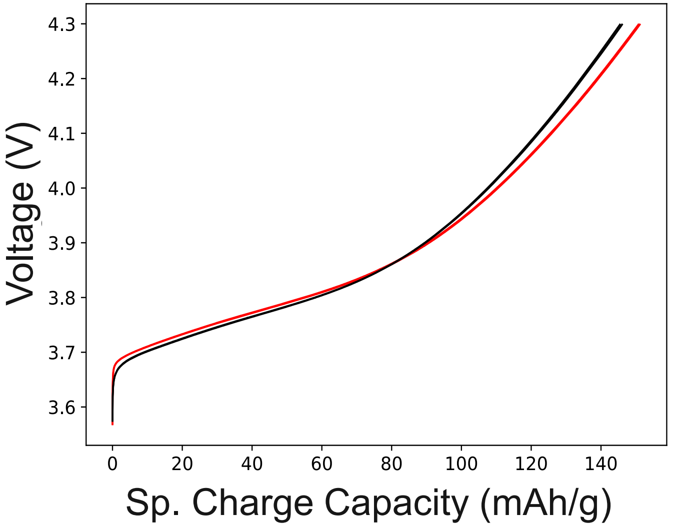
Electrochemical Impacts of Treatment on NMC

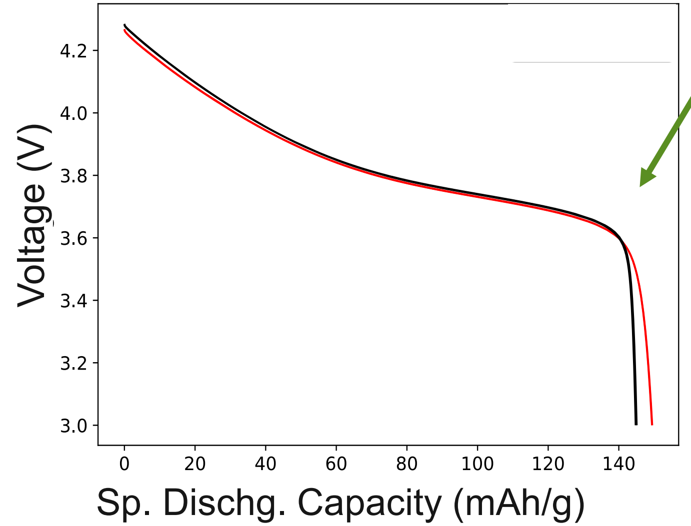
Cycle 1

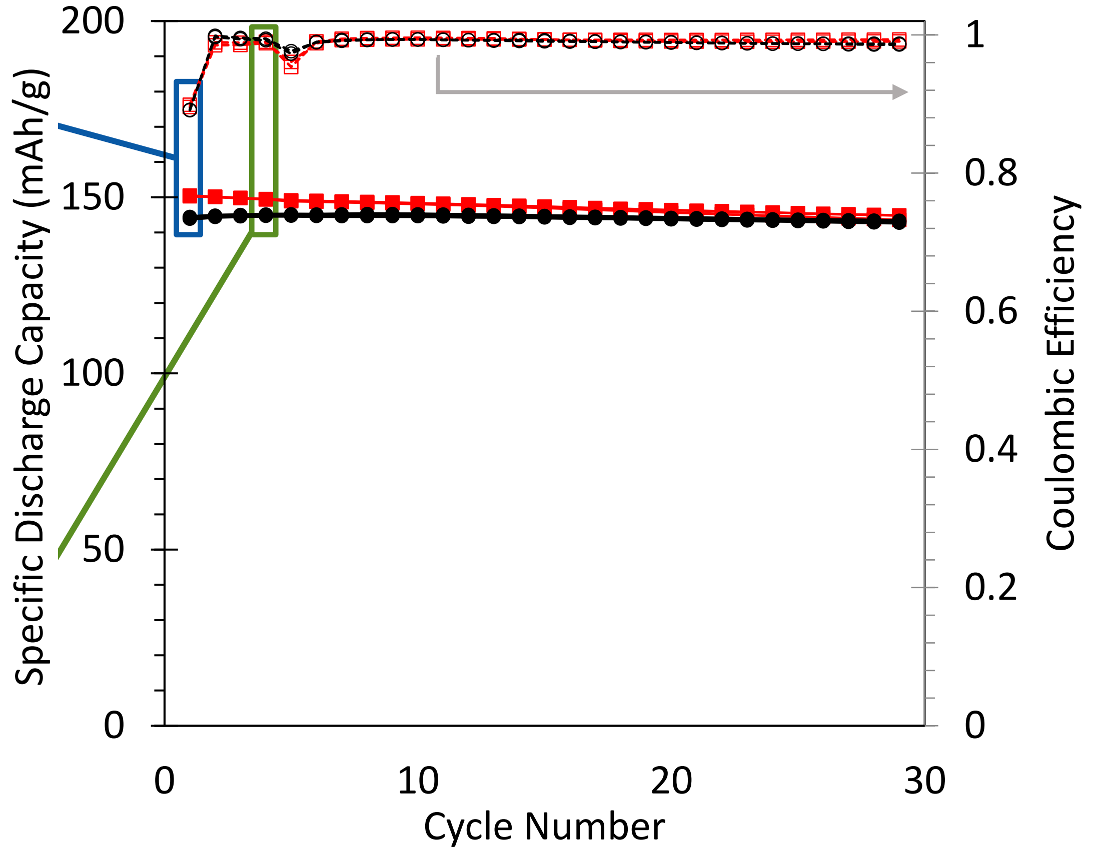




Cycle 4





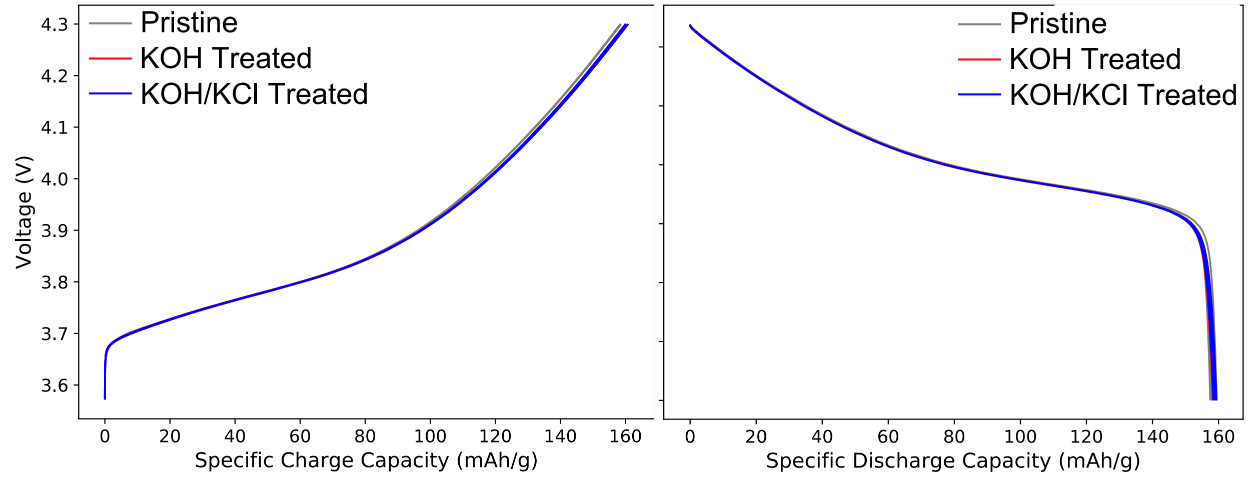


- Irregular first-cycle behavior may be attributable to residual salts on the surface of NMC (affecting SEI evolution). Performance stabilizes after formation.
- Mitigation strategies for residual salts under investigation; simple DI H_2O wash may leach Li^+.

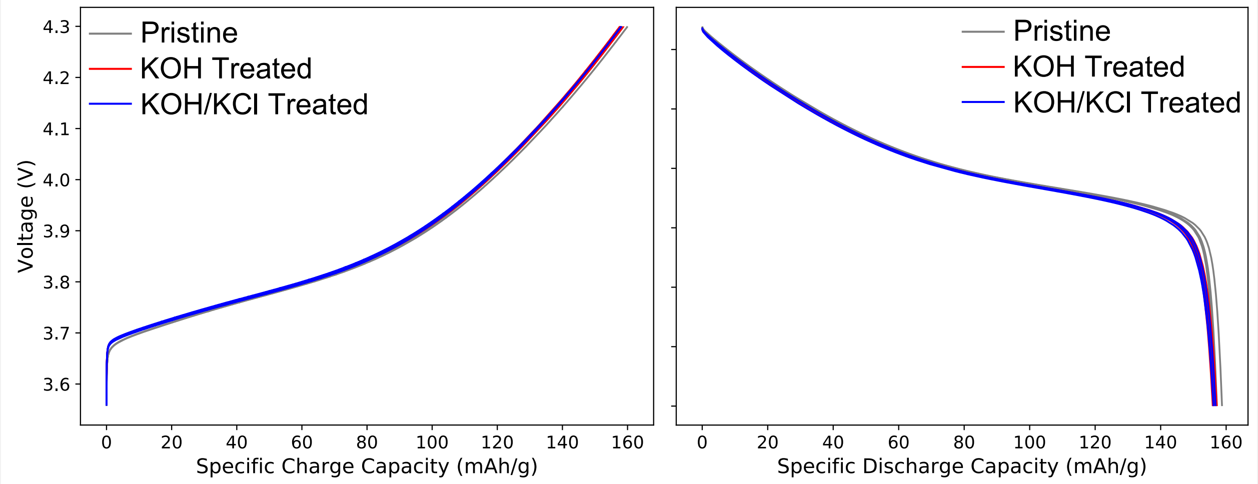
Electrochemical Impacts of Treatment on NMC

Half Cells: NMC-111; K^+ Salts

Cycle 4 (end of formation)

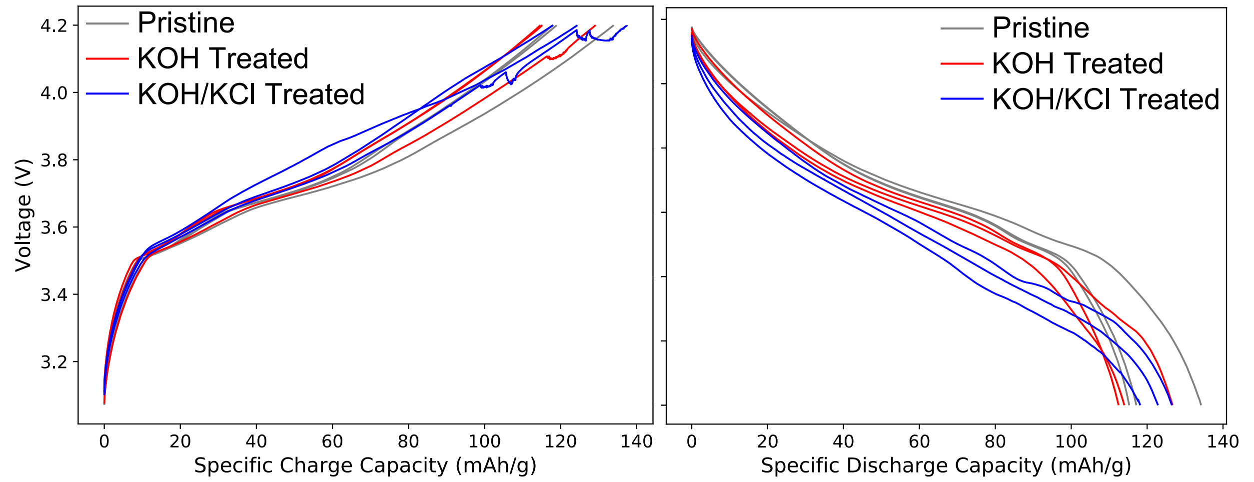


Cycle 14 (10 cycles @ C/10)

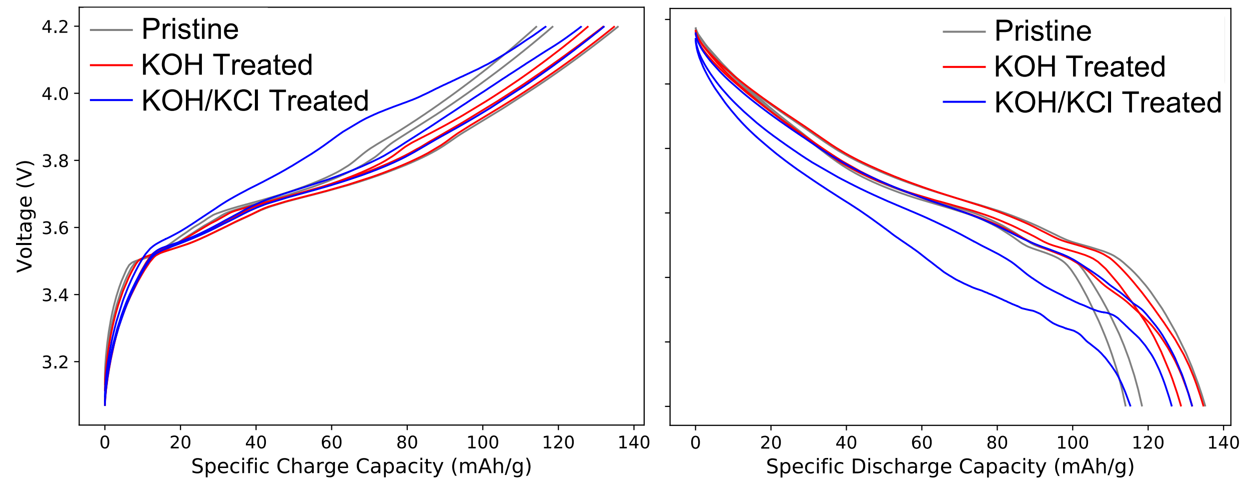


Full Cells: NMC-111; K^+ Salts

Cycle 4 (end of formation)



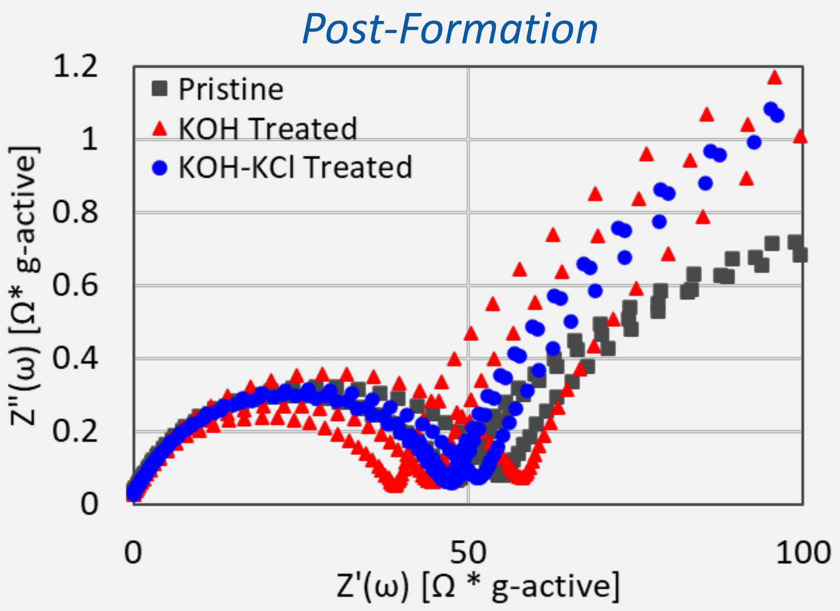
Cycle 14 (10 cycles @ C/10)

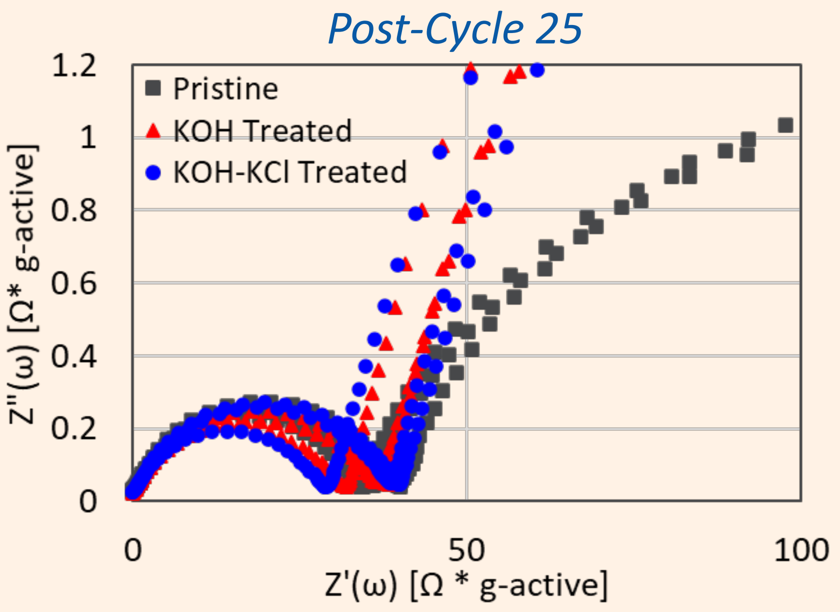


Change in voltage profiles for treated full cells is thought to be from residual salts, and not cathode degradation.

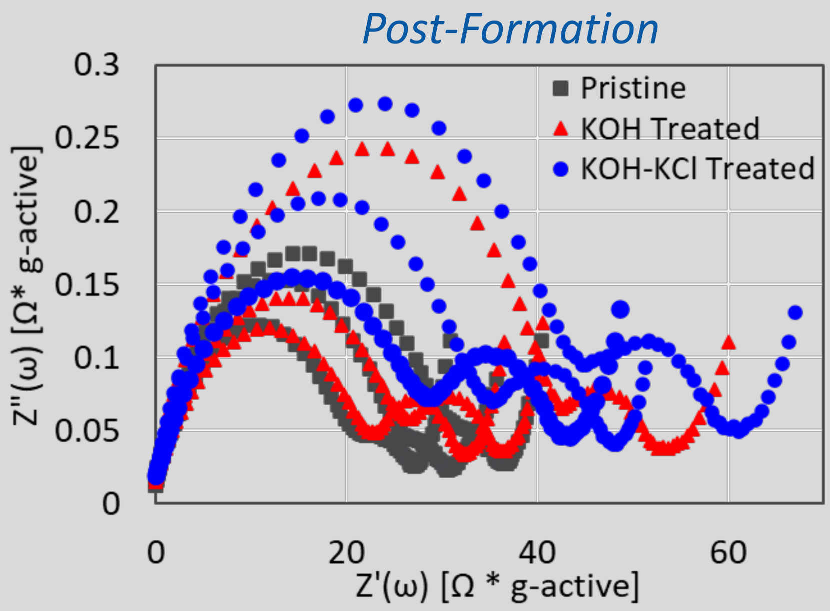
IMPEDANCE DATA (EIS); TREATED NMC-111 & NMC-532; POST-FORM.

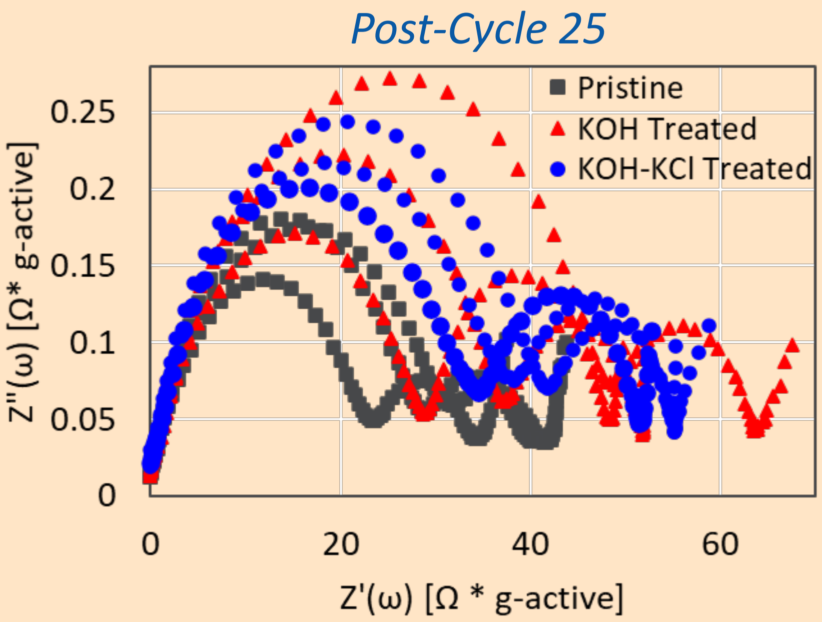
Half Cells: NMC-111; K^+ Salts





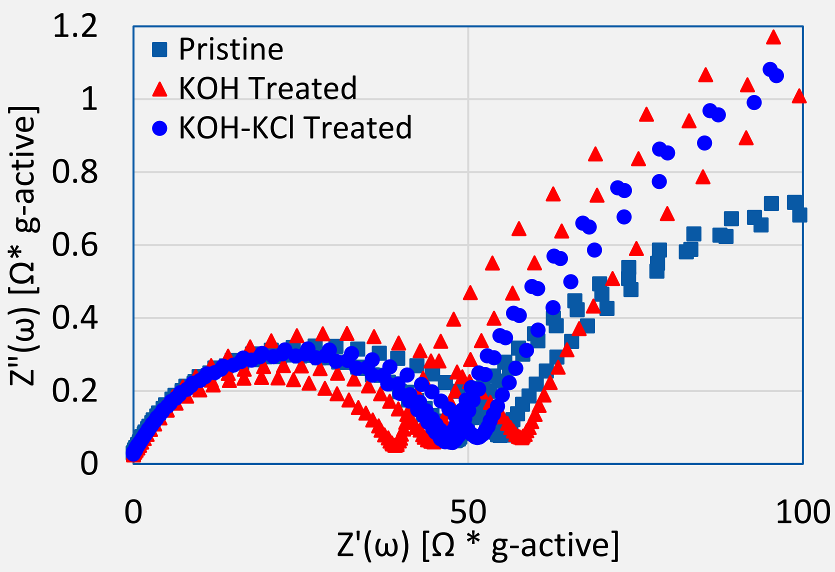
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)



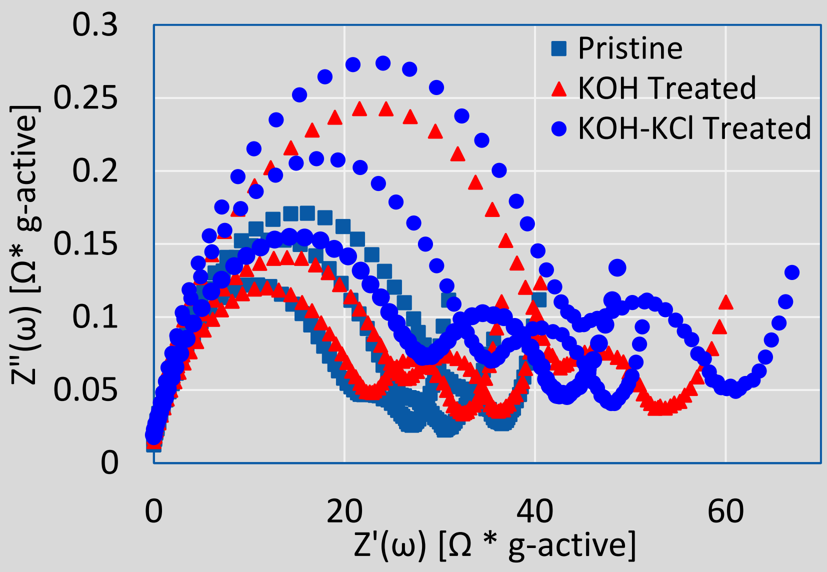


IMPEDANCE DATA (EIS); TREATED NMC-111 & NMC-532; POST-FORM.

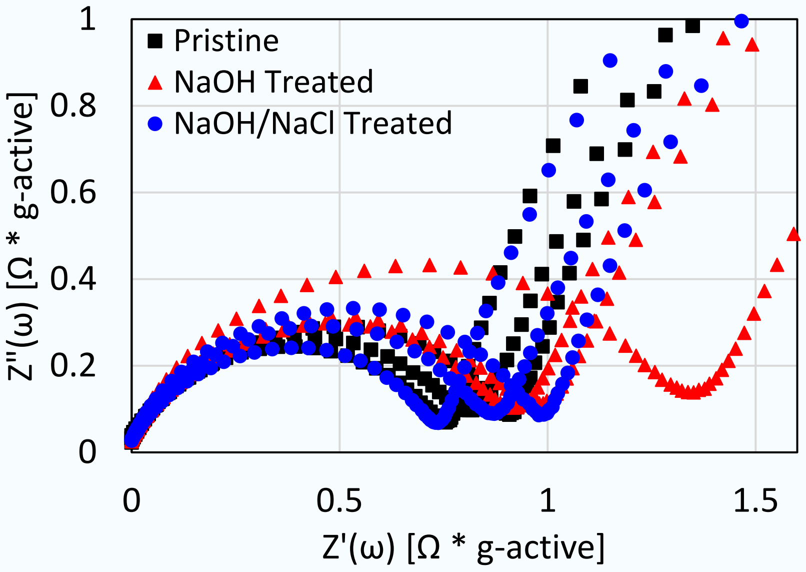
Half Cells: NMC-111; K^+ Salts



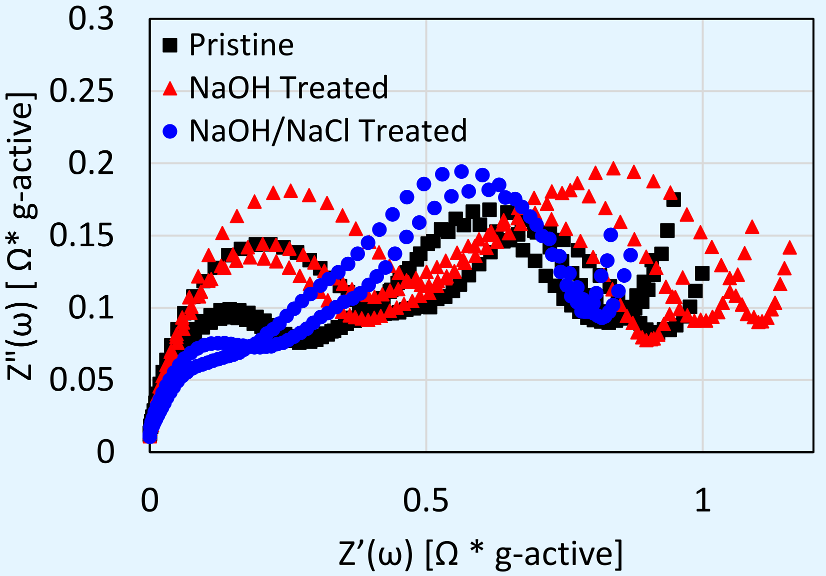
Full Cells: NMC-111; K^+ Salts (n/p: ~1.15)



Half Cells: NMC-532; Na^+ Salts

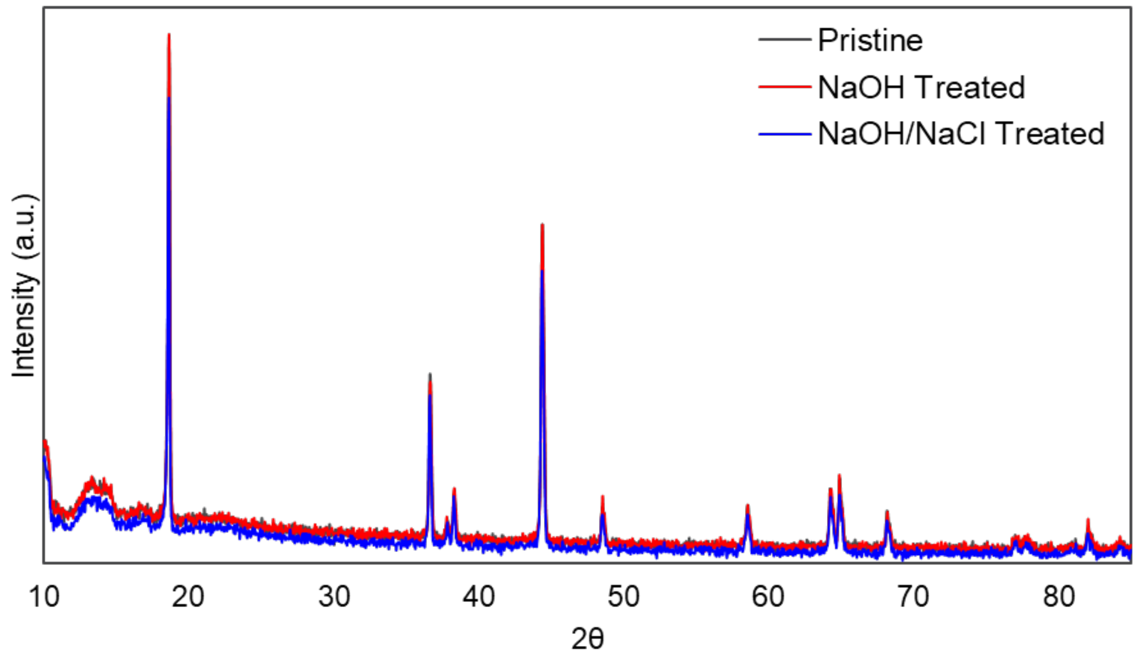


Full Cells: NMC-532; Na^+ Salts (n/p: ~1.25)



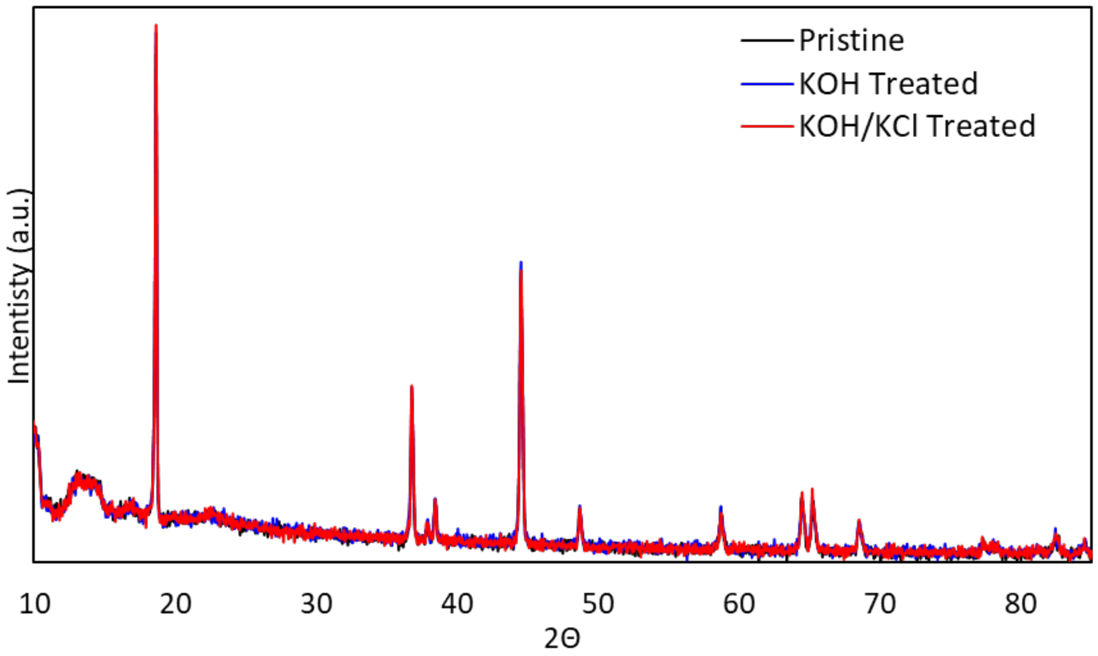
Structural Impacts of Treatment on NMC

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

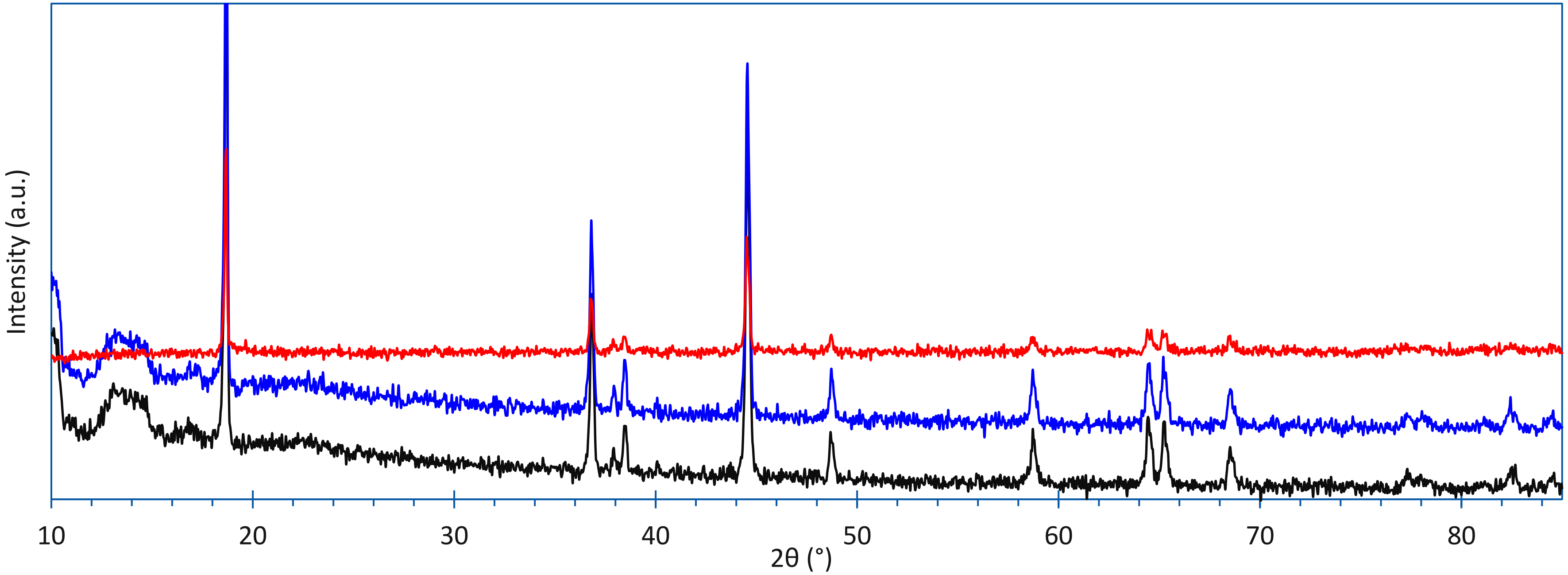
NMC-111; K^+ salts; pH 13



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