

# DIRECT CATHODE-TO-CATHODE RECYCLING EFFORTS

Project ID bat379

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Argonne National Laboratory

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Annual Merit Review



# OVERVIEW

## Timeline

- Project start: October 2018
- Project end: September 2021
- Percent complete: ~15%

## Barriers

- Recycling and Sustainability
  - Cost to recycle is currently 5-15% of battery cost
  - Material shortage (Li, Co, and Ni)
  - Varying chemistries result in variable backend value

## Budget

Year 1	\$4,615k
<i>Argonne</i>	<i>\$2650k</i>
<i>NREL</i>	<i>\$965k</i>
<i>ORNL</i>	<i>\$550k</i>
<i>UCSD</i>	<i>\$150k</i>
<i>WPI</i>	<i>\$150k</i>
<i>MTU</i>	<i>\$150k</i>

## Partners

- Argonne National Laboratory
- National Renewable Energy Laboratory
- Oak Ridge National Laboratory
- University of California, San Diego
- Worcester Polytechnic Institute
- Michigan Technological University

# RELEVANCE - RECELL CENTER

## Objective:

Foster the development of cost-effective and environmentally sound processes to recycle lithium-ion batteries

Bring together battery recycling experts to bridge technical and economic gaps to enable industry adoption

## Impact:

Reduced cost of ownership and helping to drive battery costs to DOE's \$80/kWh goal

Reduce primary material production to avoid material shortages and reliance upon foreign sources, increasing our nation's energy security

Minimize environmental impacts of the battery life cycle

# MILESTONES

Q1 (Center) Establish the battery recycling center's mission and include its targets and goals

✓ COMPLETED 12/21/18:

***“Decrease the cost of recycling lithium ion batteries to ensure future supply of critical materials and decrease energy usage compared to raw material production”***

Q2 (NREL) Provide an initial progress report on roll-to-roll relithiation

✓ COMPLETED 3/29/19: Roll-to-roll relithiation work is progressing and the concept is currently being tested using coin cells

Q3 (ORNL) Provide an initial progress report on design for recycle initiative

In progress

Q4 (ANL) Establish the ReCell Center's Battery Recycling Laboratory and Scale-up Facility

In progress

# APPROACH – DIRECT CATHODE RECYCLING

Several phenomena contribute to the gradual breakdown in lithium-ion battery performance, including surface degradation, cathode instability, reactivity with organic electrolyte components, and surface films. These phenomena need to be reversed and performance restored.

- Cathode Separation
  - Froth Flotation – L. Pan (MTU)
  - Magnetic Separation – E. Dahl (Argonne)
- Binder Removal – A. Lipson (Argonne)
- Relithiation
  - Electrochemical – J. Coyle, X. Li (NREL)
  - Solid State – J. Vaughey (Argonne)
  - Hydrothermal – Z. Chen (UCSD)
  - Ionothermal – S. Dai (ORNL)
- Compositional Change
  - Solid State – J. Vaughey (Argonne)
  - Role of Impurities – Y. Wang (WPI)



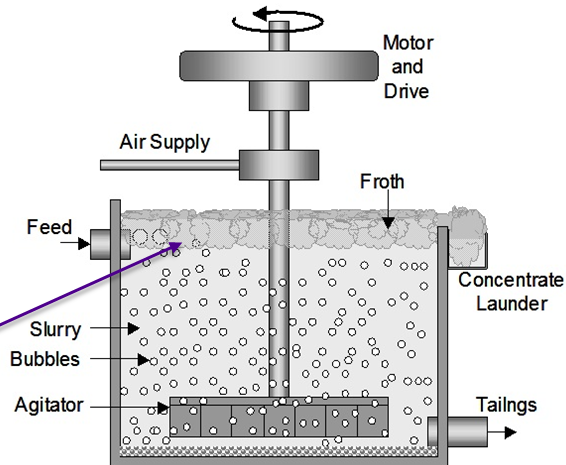
# CATHODE SEPARATION – FROTH FLOTATION

A commercial waste stream may represent different cathodes, from different users, from different eras, for different devices. Direct recycling requires single battery chemistries (or compatible chemistries) to be successful in the marketplace. This effort examines using surface chemistry, pH, and froth flotation to separate different battery cathodes.

Cathode	Natural pH	Recovery (%)
NMC 111	8.28	9%
NMC 811	10.48	<2%
LFP	10.50	100%
NCA	10.50	<2%
LMO	7.40	6%
D-NMC 111*	6.80	<2%

The hydrophobicity of LFP powders is attributed to carbon coatings on surfaces

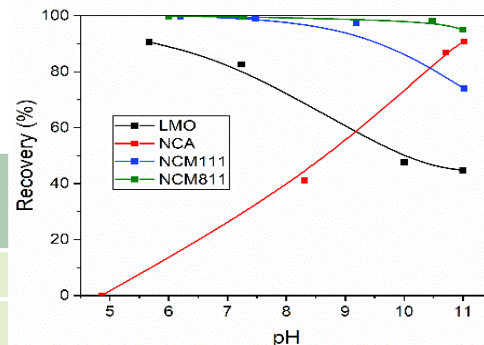
Cathode collected in froth layer (3min)



# CATHODE SEPARATION – FROTH FLOTATION

Froth flotation separation of individual cathode chemistries using different collectors at different pHs has been evaluated.

Condition		D-NMC 111	NMC 111	NMC 811	LMO
Collector	pH				
Salicylaidixime	Natural	18%	80%	0%	72%
Salicylaidixime	6	-	76%	18%	86%
Cupferron	Natural	22%	34%	16%	38%
Cupferron	6	<2%	60%	46%	43%
Hydroxamate	Natural	95%	93%	96%	68%
Hydroxamate	6	-	96%	91%	63%
Fatty acid	Natural	100%	100%	98%	63%
Fatty acid	6	-	99%	100%	96%
Phenylthiourea	Natural	56%	33%	67%	40%
Phenylthiourea	6	-	37%	27%	47%



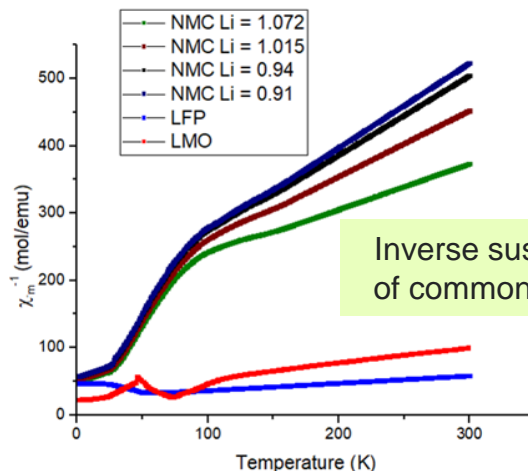
Preliminary results: both hydroxamate and fatty acid work effectively in rendering NMC 111 and NMC 811 hydrophobic. NCA at pH= 6 is hydrophilic regardless of types of collectors used.

These results suggest that both hydroxamate and fatty acid might be the candidates for separation of individual cathode chemistries.

# CATHODE SEPARATION - MAGNETIC

	Percentage of Retained Material by component	
	Average	
Residual Flux Density [G]	NMC111	LMO
7000	22.4%	77.6%
8300	25.0%	75.0%
9600	29.3%	70.7%
10300	33.7%	66.3%
12300	39.4%	60.6%
13050	42.1%	57.9%
14000	43.5%	56.5%
14800	46.1%	53.9%

1:1 mixtures of LMO and NMC111 were created and passed through magnetic fields of various strengths. The higher magnetic susceptibility of LMO relative to NMC111 allows for its separation. The purest fractions of LMO are obtained under the influence of magnetic fields that lack the strength to retain NMC111.



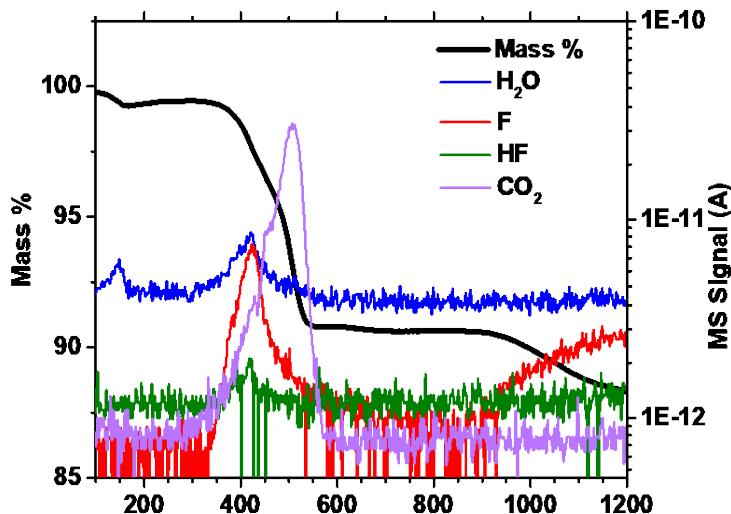
Inverse susceptibility of common cathodes



# BINDER REMOVAL

The cathode materials within the black mass are mixed with other electrode components and coated with polymeric binders, such as PVDF. Three possible methods of separation are thermal degradation, dissolution, and mechanical separation.

## Thermal Decomposition



## TGA-MS

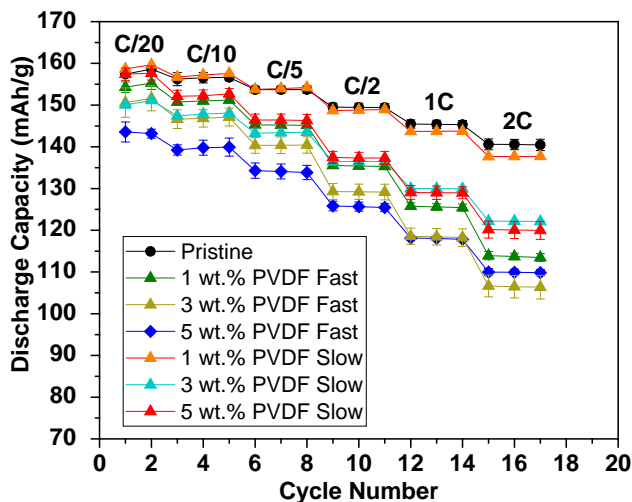
- PVDF decomposes near 400°C
- Carbon black burns near 500°C
- About 90.8% of the mass remains including 0.8 wt.% fluorides or other species remaining

## Fluoride Sequestration

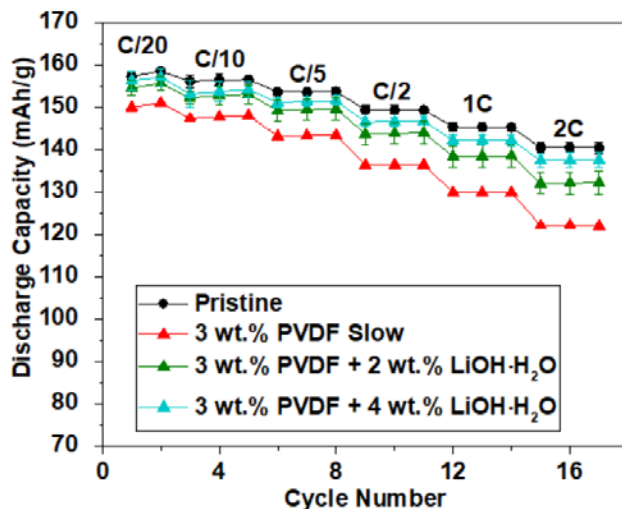
Adding LiOH to the binder burnout process sequesters the active fluoride from the PVDF decomposition as LiF, blocking a reaction with the NMC cathode.

# BINDER REMOVAL

Electrochemical evaluation of recovered cathodes: Best performance was using slow burnout (to 500 °C over 15h), with addition of a lithium source to tie up the fluoride formed during burnout before it can form LiF with lithium from the cathode.



Thermal Binder Removal  
(rate and % PVDF)



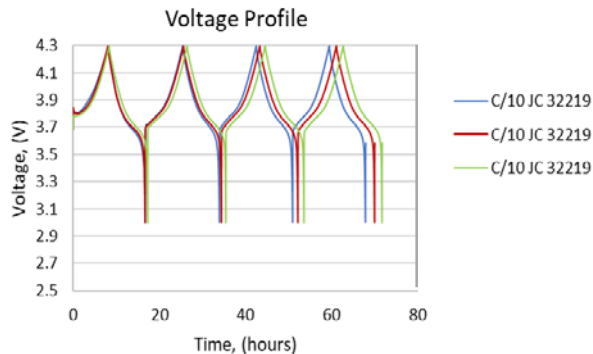
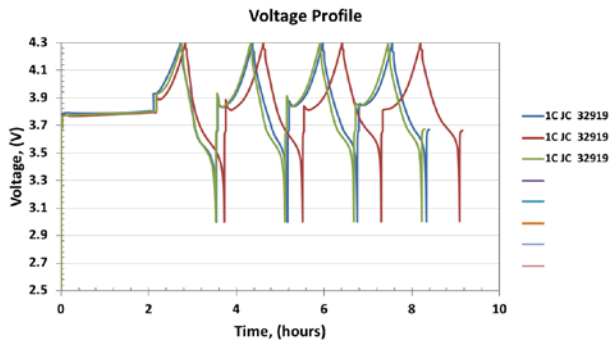
Adding 4 wt.% LiOH·H<sub>2</sub>O shows  
similar rate performance and  
capacities to the pristine material

# CATHODE RELITHIATION – ELECTROCHEMICAL

## Half cell with delithiated baseline NMC111 cathode

Formation Protocol at 25°C, 3.0-4.3 V:  
4 Cycles of 1C Charge, 1C Discharge

Formation Protocol at 25°C, 3.0-4.3 V:  
4 Cycles of C/10 Charge, 1C Discharge



NMC 111 Chemically Delithiated Averages	1 <sup>st</sup> Cycle Charge (mAh/g)	1 <sup>st</sup> Cycle Discharge (mAh/g)	1 <sup>st</sup> Cycle Efficiency	Reversible ( 3 <sup>rd</sup> ) Cycle Charge (mAh/g)	Reversible (3 <sup>rd</sup> ) Cycle Discharge (mAh/g)
1C 4x NREL (3 cells)	134	127	95%	128	126
C/10 4x NREL (3 cells)	144	141	98%	143	141

# CATHODE RELITHIATION – ELECTROCHEMICAL

## Full cell with electrochemically relithiated NMC111 electrode

Aging Protocol at 25°C, 3.0-4.2V:

Pristine NMC 111/TODA graphite

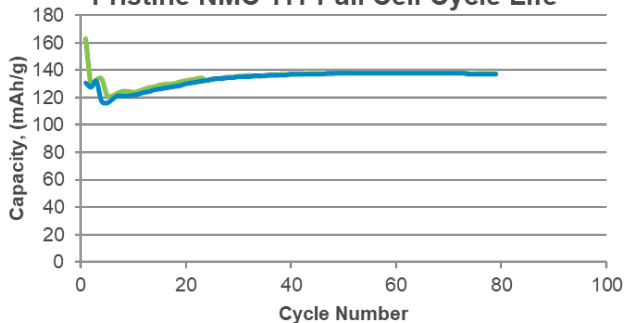
4 Cycles of C/10 Formation, C/3 Discharge/Charge

Relithiated Cathode Protocol at 25°C, 3.0-4.2V:

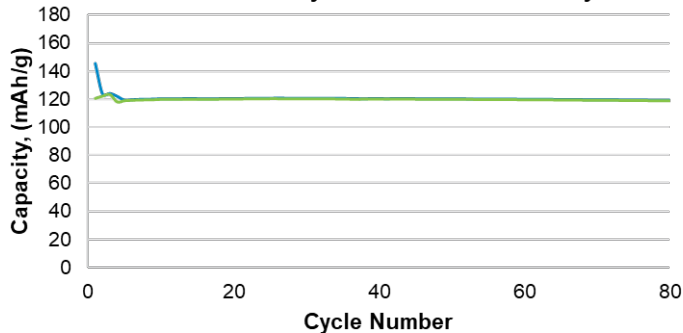
Relithiated Chemically Delithiated NMC111 (C/10 rate 4x)/ TODA graphite

Aging: 4 Cycles of C/10 Formation, C/3 Discharge/Charge

**Pristine NMC 111 Full Cell Cycle Life**



**Electrochemically Relithiated NMC 111 Cycle Life**



1st cycle "C" Capacity	162.6	mAh/g
1st cycle "D" Capacity	131.0	mAh/g
1st cycle efficiency	80.6	%
Reversible "C" capacity	129.0	mAh/g
Irrversible capacity loss	33.5	mAh/g
% Capacity loss	20.6	%

1st cycle "C" Capacity	145.5	mAh/g
1st cycle "D" Capacity	120.5	mAh/g
1st cycle efficiency	82.9	%
Reversible "C" capacity	120.1	mAh/g
Irrversible capacity loss	25.4	mAh/g
% Capacity loss	17.5	%

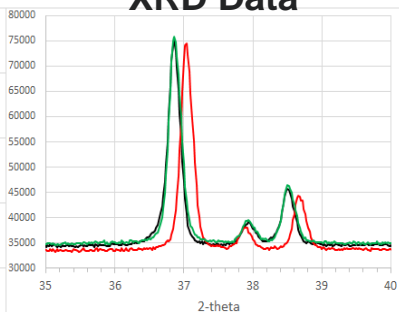
# CATHODE RELITHIATION – SOLID STATE

Delithiated baseline NMC111 samples were re-lithiated using a variety of lithium salts based on thermal stability of TGA measurements. Relithiation confirmed by XRD and GDOES elemental analysis.

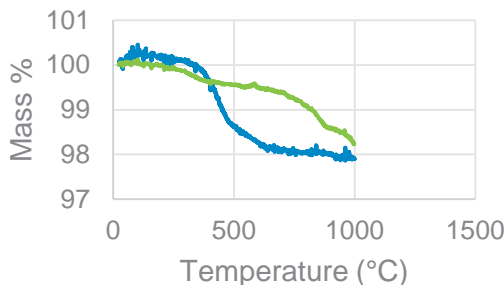
	$I_{003}/I_{104}$	$I_{003}/I_{104}$ (Post anneal)
Pristine NMC 111	1.29	1.27
Delithiated NMC 111	1.26	1.04
NMC Relithiated (LiOH H <sub>2</sub> O)	1.20	1.13
NMC Relithiated (Li <sub>2</sub> CO <sub>3</sub> )	1.33	1.35
NMC Relithiated (LiOH)	1.24	1.27

Heating samples may disorder the Li/Ni sites increasing cell impedance. The 003/104 ratio is used as a measure of this mixing.

**XRD Data**



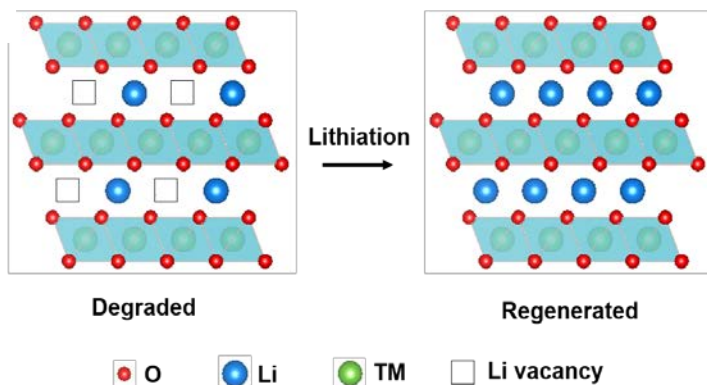
**TGA Stability**



Delithiated baseline showed significant site mixing on annealing

# CATHODE RELITHIATION – HYDROTHERMAL

Hydrothermal relithiation was first performed on chemically delithiated NMC111 cathodes and the composition of different cathode particles was quantified using inductively coupled plasma mass spectrometry (ICP-MS) measurements.

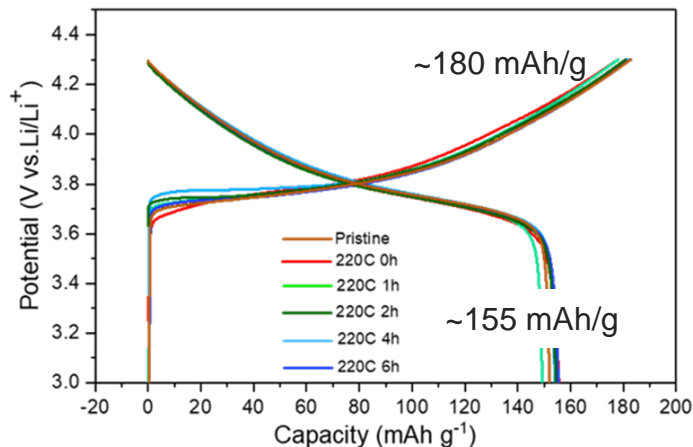
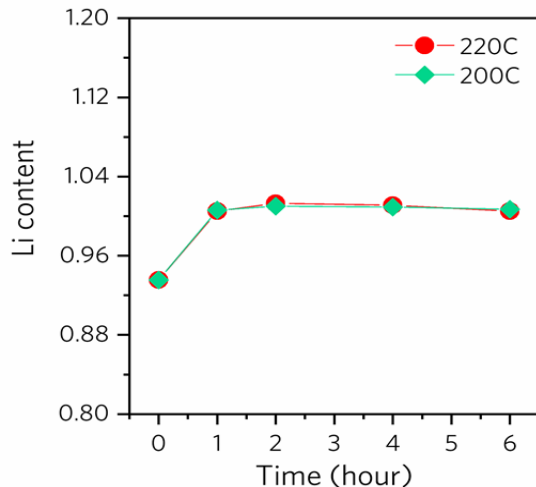


	Charge capacity	Discharge capacity	1 <sup>st</sup> columbic efficiency
Pristine	182	152	83.5%
220C 0h	177	155	87.5%
220C 1h	177	149	84.1%
220C 2h	180	154	85.5%
220C 4h	181	154	85.1%
220C 6h	182	156	84.3%

Electrochemical Cycling: Pristine vs relithiated (using LiOH) as the Li<sup>+</sup> source at 220 °C for various times.

# CHEMICAL RELITHIATION - HYDROTHERMAL

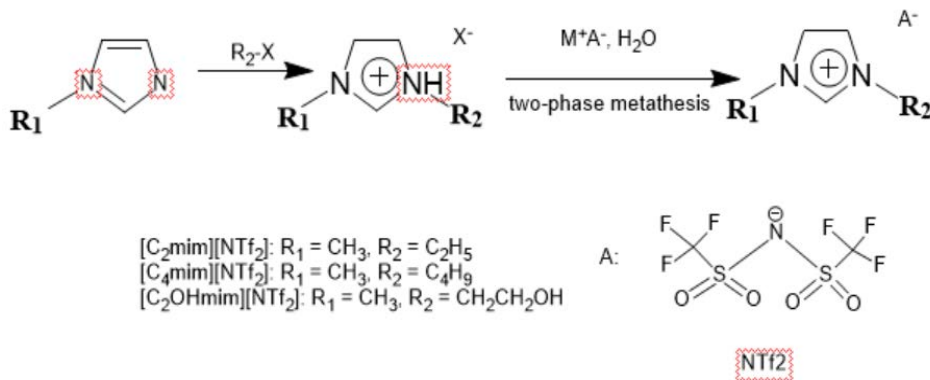
Lithium content vs time



- Chemically delithiated NMC111 particles can reach  $>1.00$  Li in about 1 hr (by ICP pristine NMC111  $\sim 1.07$  Li).
- Over 6 hrs the ratio (by ICP) varied possibly due to proton exchange, this is being investigated.

Electrochemical evaluation of relithiated particles. *Initial* cycling at C/10 based on an areal mass loading of  $> 10 \text{ mg/cm}^2$ .

# CHEMICAL RELITHIATION - IONOTHERMAL



Develop a relithiation strategy based on a salt dissolved in an ionic liquid used in the range 200-250 C

Ionic liquid	Lithiated reagent	Temp.	Mass Recovered (%)	IL recovered(%)	TGA final (%)
$[\text{C}_2\text{mim}][\text{NTf}_2]$	LiCl	250°C	22.8	92.0	97.73
	LiOAc	250°C	89.0	76.9	98.56
	LiCl	200°C	95.7	93.2	98.32
	LiOAc	225°C	81.7	73.0	98.17
$[\text{C}_4\text{mim}][\text{NTf}_2]$	LiCl	225°C	93.0	92.5	98.55
$[\text{C}_2\text{OHmim}][\text{NTf}_2]$	LiCl	250°C	78.4	90.4	96.76
	LiCl	200°C	82.8	92.7	99.06

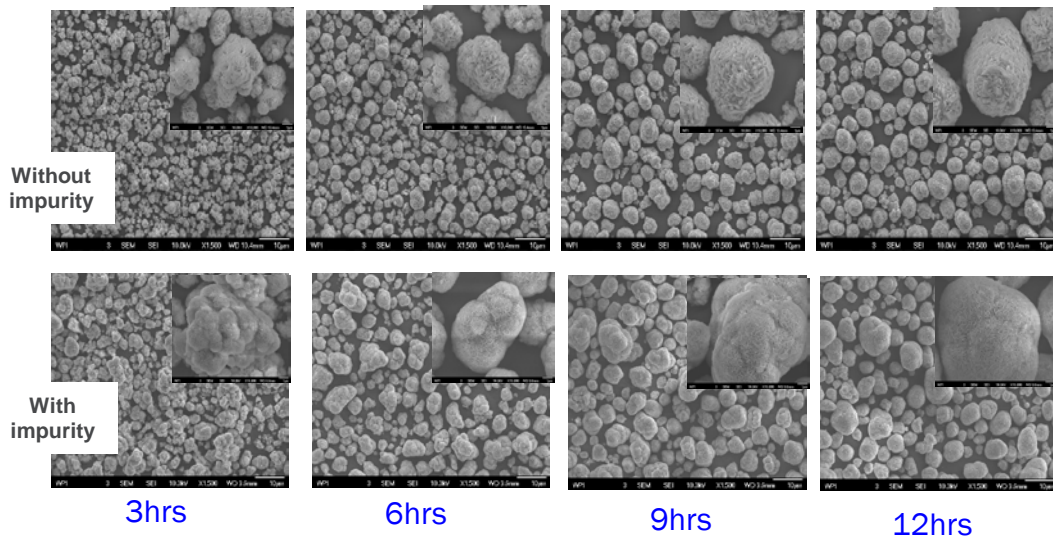
**Conclusion:**  
Relithiation using ILs was accomplished on test samples with recovery of lattice (XRD) and IL.

Dai, et al., ORNL



# CHEMICAL RELITHIATION - IMPURITIES

Reforming cathode materials recovered from complex mixtures allows for the introduction of impurities from the process. Some of the more common metals (materials) observed are Cu ,Al,  $\text{Al}_2\text{O}_3$ , carbon, and binder materials.



Hours	Tap density (g/mL)
3 hrs	1.03
6 hrs	1.40
9 hrs	1.88
12 hrs	2.02

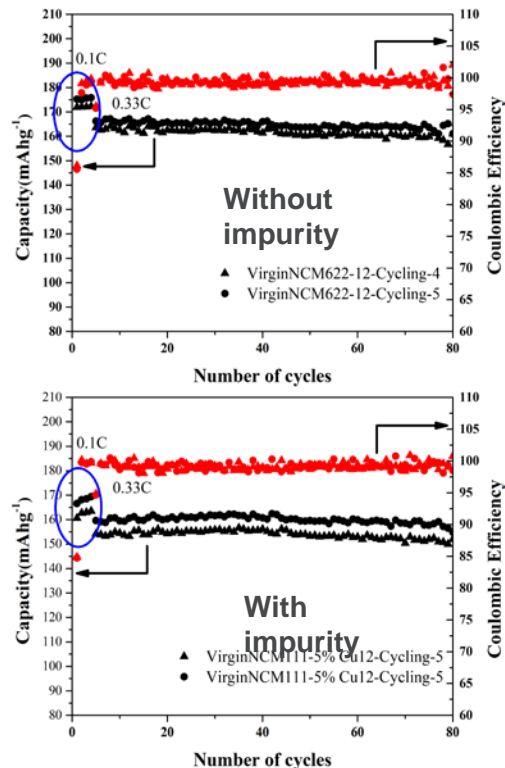
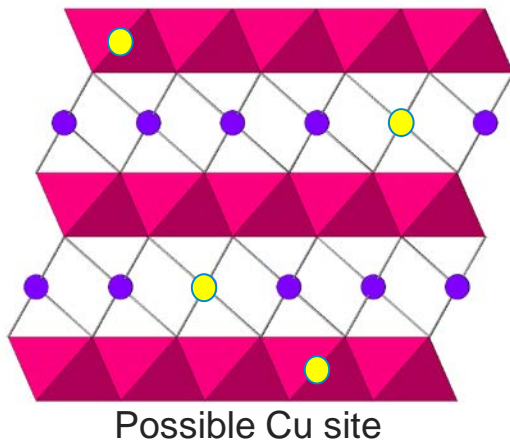
  

Hours	Tap density (g/mL)
3 hrs	0.79
6 hrs	1.16
9 hrs	1.31
12 hrs	1.45

Direct synthesis of 5% Cu substituted NMC samples. The differences in particle morphology was manifested in tap density measurements.

# CHEMICAL RELITHIATION - IMPURITIES

NMC622 with 5% Cu was synthesized and evaluated. Due to the chemistry of Cu it can technically go to both cation sites. Li-site substitution hinders rate, TM site substitution diminishes capacity.



NMC622 with 5% Cu shows lower specific capacity and fades slightly faster than control powder.

# RESPONSE TO REVIEWERS

- **New Project FY19**

# REMAINING CHALLENGES AND BARRIERS

- Developing a process to separate similar NMC materials in a cost effective manner
- Assess the role lithium deficient cathodes with different thermal stabilities behave in the black mass isolation process (vs fully lithiated cathodes)
- Evaluate if residual carbon from the lamination or binder removal process can act as a reducing agent (under heat) and irreversibly change the oxide content of the delithiated cathode
- Scaling: how homogeneous is the delithiated cathode as a function of lithium content and time?
- Scaling: does surface damage from chemical delithiation, black mass isolation, or long term cycling have an effect on the relithiation process

# FUTURE WORK

- Generate additional baseline cathode powders with higher amounts of delithiation to support the efforts of the cathode rejuvenation researchers.
- Generate additional baseline cathode powder mixtures that reflect the use of mixed powder cathode composites in the marketplace. Evaluate the role of non-homogeneous lithium contents
- Separation of cathodes by a variety of properties has been demonstrated. Optimization of surface properties is underway to improve the separation of layered cathodes from one another.
- Relithiation has been established by several methods. Evaluate the mechanism of relithiation versus methodology, notably ion exchange, thermal oxidation, and electrochemical.
- The presence of impurities is critical to recycling costs and material quality. Materials identified within black mass, if not separated, may be accidentally incorporated into the product. We will develop diagnostic tools and processes to detect these low weight percent additions that may be detrimental to performance.

***Any proposed future work is subject to change based on funding levels***

# SUMMARY

- We have investigated multiple methods of the chemical rejuvenation process for relithiating recovered cathodes. A model NMC111 system has been created and dispersed upon request to team members.
- Four different relithiation studies are under evaluation and each has been shown to be effective in terms of capacity retention. Specific issues are under study including the cation site mixing, impedance changes, impurity impacts and economic considerations.
- Material separation studies have been undertaken using methods that rely on unrelated phenomena. Froth separation studies, which utilize surface properties, have been used to separate LFP from layered oxides. Surfactant addition with control of pH has shown preliminary success in separating layered oxides. Initial magnetism based separation studies have shown separation of spinel from layered cathodes
- Binder removal has been accomplished by thermal treatment of samples. Slower burnout rates and addition of extra LiOH as a fluoride getterer have been found to give the best electrochemical performance.

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