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ReCell ADVANCED BATTERY RECYCLING

DIRECT RECYCLING OF END-OF-LIFE CATHODE MATERIAL THROUGH REDOX CHEMISTRY MEDIATORS

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ECS

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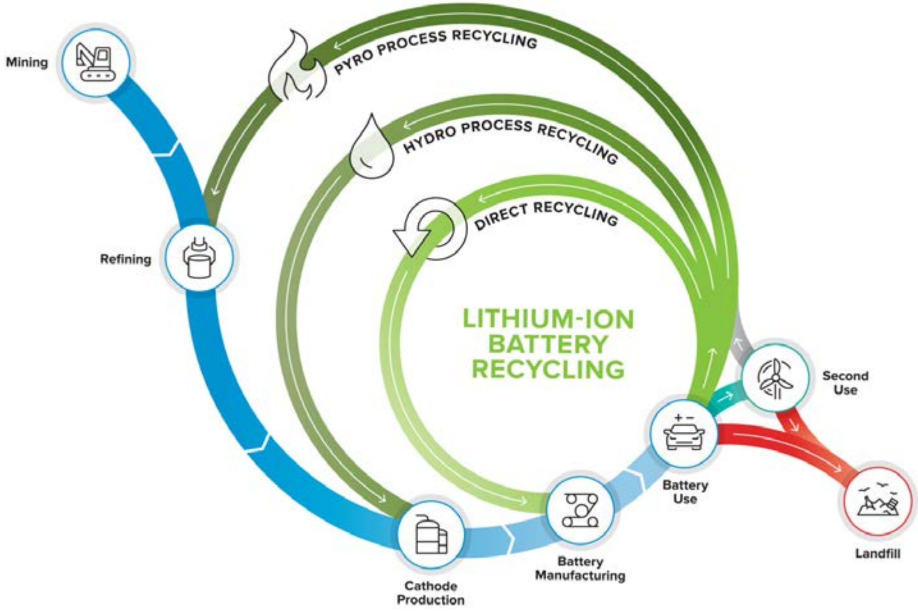
REDOX RELITHIATION RESEARCH OVERVIEW

LITHIUM-ION BATTERY RECYCLING OVERVIEW

Pyrometallurgy:
- High-temperature smelting → burning → separation
- Simple, mature technology; high CO_2 production and energy consumption; low recovery rates

Hydrometallurgy:
- Generally aqueous chemistries; involves chemical leaching (acid/base)
- Relatively mature technology; high recovery; less energy consumption; waste generation issues; remaining challenges with separation efficiency/cost

Direct:
- Recover active LIB components in relatively intact form; refurbish to match pristine performance and chemistry
- Still lab/pilot-scale technologies; least energy; least waste; remaining challenges with recovery, purity, performance



Gaines, L., et al., *Direct Recycling R&D at the ReCell Center.* Recycling, 2021. **6**(2): p. 31.

DIRECT RECYCLING OF END-OF-LIFE (EOL) BATTERIES

Direct:

- Recover active LIB components in relatively intact form; refurbish to match pristine performance and chemistry
- Still lab/pilot-scale technologies; least energy; least waste; remaining challenges with recovery, purity, performance

Redox mediator relithiation

Gaines, L., et al., *Direct Recycling R&D at the ReCell Center*. Recycling, 2021. **6**(2): p. 31.

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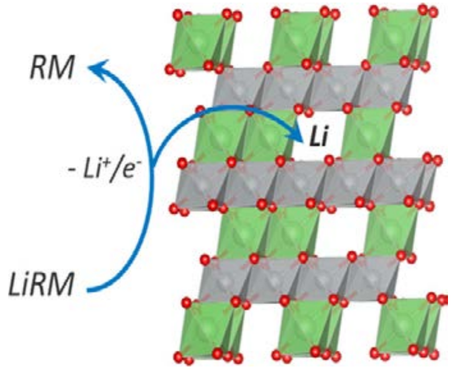
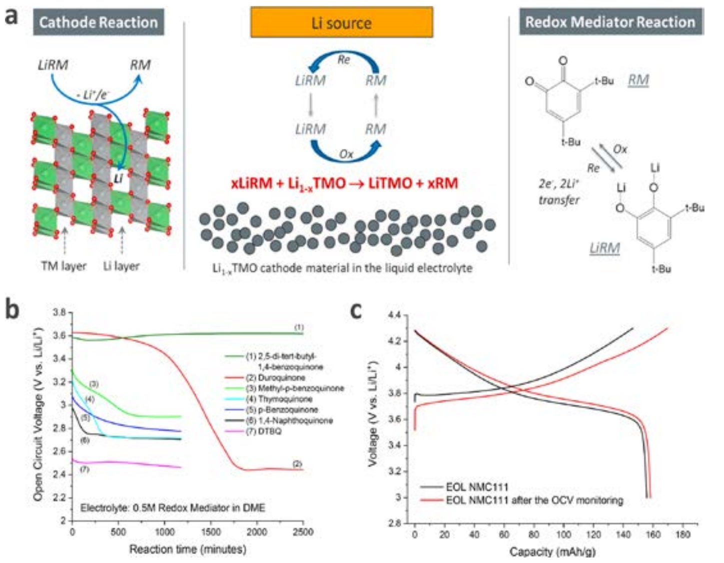
REDOX MEDIATOR RELITHIATION



Park, Kyusung, Jiuling Yu, Jaclyn Coyle, Qiang Dai, Sarah Frisco, Meng Zhou, and Anthony Burrell. 2021. 'Direct Cathode Recycling of End-Of-Life Li-Ion Batteries Enabled by Redox Mediation', *Acs Sustainable Chemistry & Engineering*, 9: 8214-21.

- **Redox Reaction:** Redox Mediator (RM) shuttles charges between lithium (Li) metal and End-Of-Life (EOL) cathode
  - The reduction of lithiated redox mediator (LiRM) on Li shows chemical changes of Li metal and RM
  - Hence, successful relithiation of EOL cathode material
- **Advantages:** low temperature reaction, rapid, degree of Li deficiency of the starting EOL cathode is not needed to design the reaction, good performance for chemically delithiated NMC 111
- **Areas to work on:** commercial EOL material not as fully relithiated, cost of redox mediator, reversibility of redox mediator, lithium source, impurities, pH control



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CHEMICALLY DELITHIATED EOL NMC111

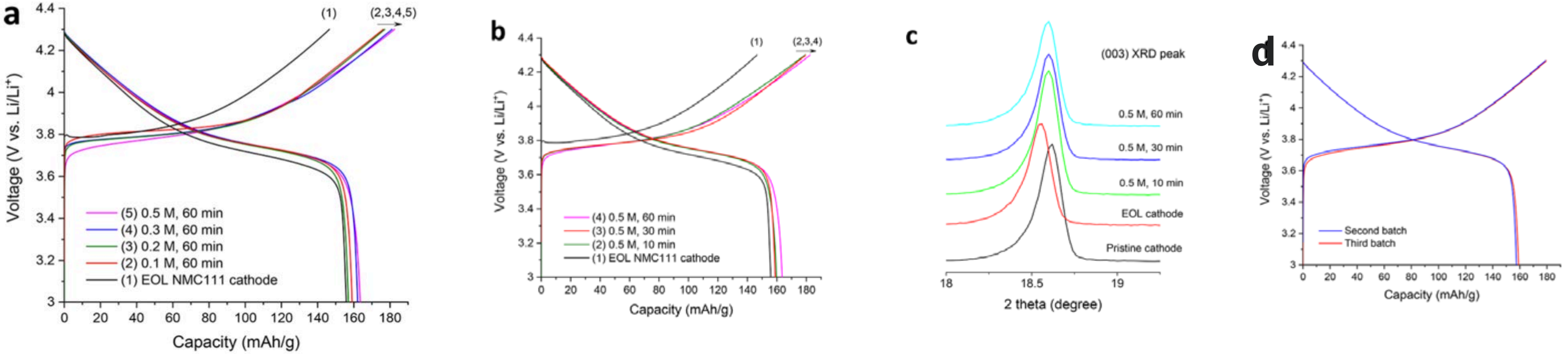
Chemically delithiated (CD) NMC111 W/ NO_2BF_4

- $LiMO_2$ + x $\mathbf{NO_2BF_4}$ (acetonitrile) → (*1hr, R.T.*) $Li_{1-x}MO_2$ + x NO_2 + x $LiBF_4$
- 20% Li loss was confirmed w/ ICP.

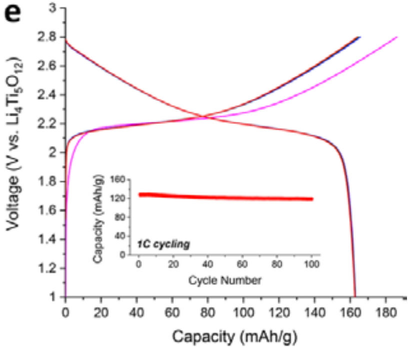
	Li	Ni	Mn	Co
Pristine NMC111	1.083	0.604	0.197	0.200
Chemically delithiated NMC111	0.843	0.610	0.189	0.201

CHEMICALLY DELITHIATED EOL NMC111

Successfully relithiated EOL material



- Chemically delithiated EOL NMC111 successfully relithiated at 0.5M for 60 minutes
- The XRD shows Li content restored based on the peak shift of the EOL NMC111, pristine NMC111 and relithiated EOL NMC111
- Redox mediator solvent was also reused for second and third batch of relithiation



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DIRECT RECYCLING OF CYCLED EOL BATTERIES

Existing Technical Efforts Under the ReCell Consortium:

(A) Pretreatment/Materials Processing
- Cell Preprocessing (shredding, separator removal)
- Low-Temperature Analysis (shredding safety)

(B) Active Material Separation
- Rare-Earth Magnetic Roll
- Froth Flotation
- Solvent-Based Gravity Separation

(C) Separation/Purification of Other Components
- Electrolyte Removal/Recovery
- Thermal Binder Removal
- Soxhlet Extraction (binder removal)
- Black Mass Purification (metallic impurity removal)

(D) Relithiation + Upcycling
- **Redox Chemistry Relithiation**
- Electrochemical Relithiation
- Hydrothermal Relithiation / Upcycling
- Ionothermal Relithiation / Upcycling
- Solid-State Relithiation / Upcycling
- Single-Crystal Upcycling

(E) Solvent-Based Process (ORNL)
- Multi-track pathway to delaminate, separate, and relithiate using a suite of solvents

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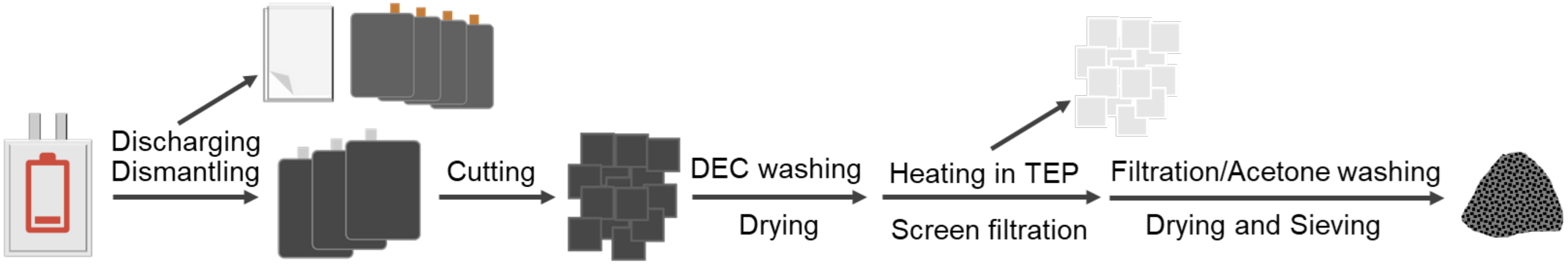
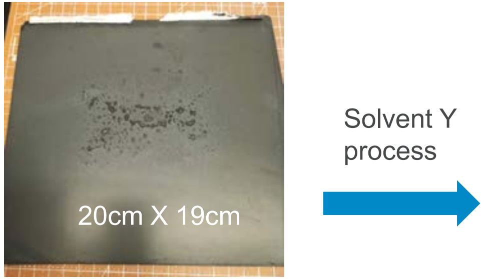
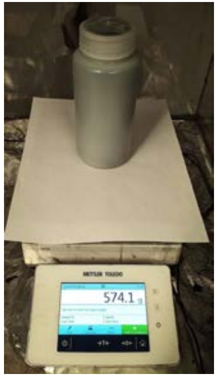
RELITHIATING CYCLED EOL NMC622 MATERIAL



- Commercial partner prepared pouch cells using pristine NMC622 material
- Cycled the cells to ~20% capacity fade
- Discharged the cells before dismantling
- Shred, Wash, Dry, Filter, Sieve, and Grind
- The recovered cathode powder through Solvent Y process is End-of-Life (EOL) NMC622 material



Recovered cathode



Kirwa, C. Coyle, J, et al., 'A Comparison of Relithiation Methods for the Direct Recycling of End-of-Life Lithium-ion Battery Cathode Materials.', *Acs Sustainable Chemistry & Engineering (submitted)*

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REDOX MEDIATOR RELITHIATION PROCESS

Lithiated Redox Mediator

Redox reaction

At 60℃ for 2hrs

Magnetic stirring at low temperature

Annealing

At 720℃ for 4hrs

Relithiated material

- Dissolve 2,5-di-tert-butylhydroquinone (DTBHQ) in 1,2-dimethoxyethane (DME)
- Add lithium metal strips to the solution and stir overnight
- Raise temperature to 60℃ and remove lithium metal strips
- Add Solvent Y EOL material and carry out the reaction for 2hrs at 60℃
- Filter the material after reaction
- Anneal at 720℃ for 2hrs

DURAN® GLS-80 stirred reactor

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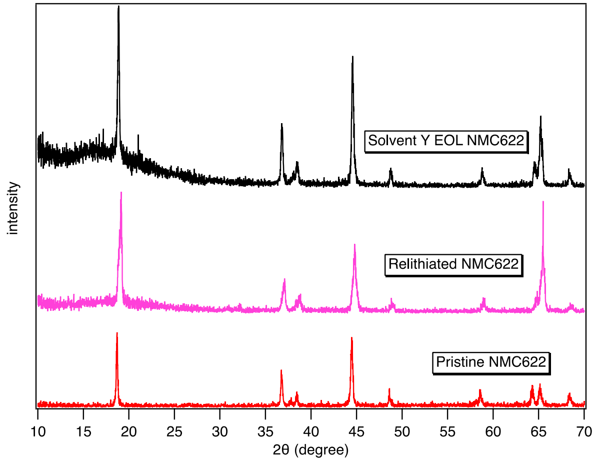
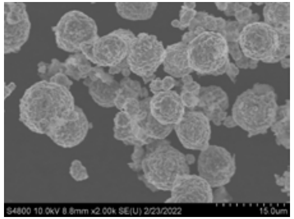
CHALLENGES RELITHIATING CYCLED EOL NMC622

SEM, XRD, and ICP-OES

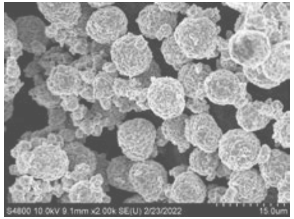
- Li ratio is recovered in the relithiated powder. It is comparable to the pristine material
- No impurity phases observed for the relithiated material
- The SEM morphology show no structural changes in the material



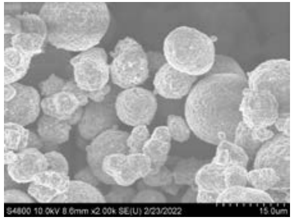
ICP Results	Li	Ni	Mn	Co
Solvent Y EOL NMC622	0.844	0.647	0.203	0.150
Relithiated NMC622	1.094	0.650	0.201	0.149
Pristine NMC622	1.055	0.606	0.192	0.202



Solvent Y EOL NMC622



Relithiated NMC622



Pristine NMC622

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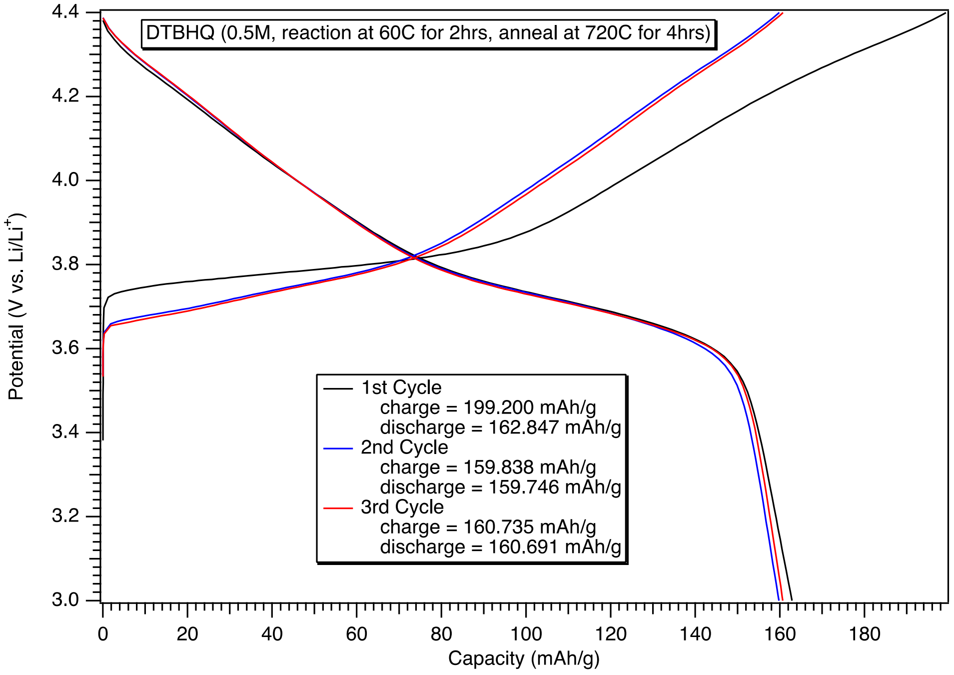
CHALLENGES RELITHIATING CYCLED EOL NMC622

Half cell performance on solvent y recovered NMC 622

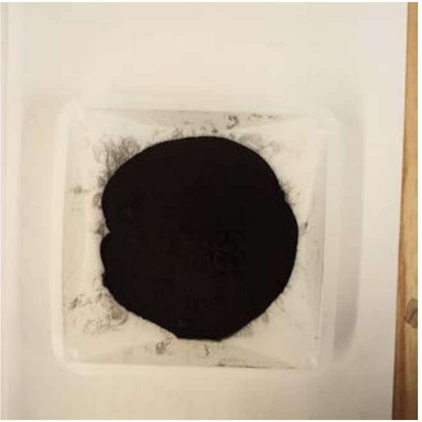
- Relithiated NMC622 reversible capacity is much lower than expected 179mAh/g reversible capacity of pristine NMC622
- LiF impurity affects relithiation of EOL materials
- Washing step is introduced to remove LiF and other surface impurities



RELITHIATING CYCLED EOL NMC622

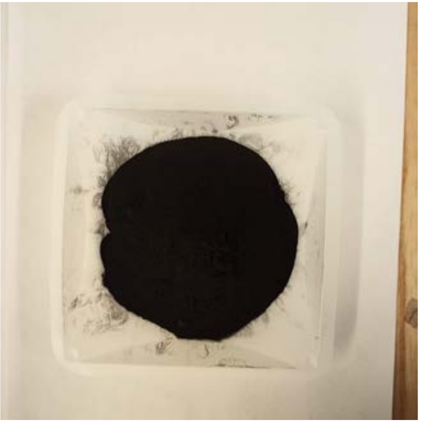
WASHING CYCLED EOL NMC622

Initial wash with basic solution



Cycled EOL NMC622

Recovered EOL cathode material through Solvent Y EOL Process



Washed EOL NMC622

Using a basic solution to wash EOL NMC622 powder

Relithiated Washed EOL NMC622

Restoring lithium content of the washed EOL NMC622 using redox mediator relithiation

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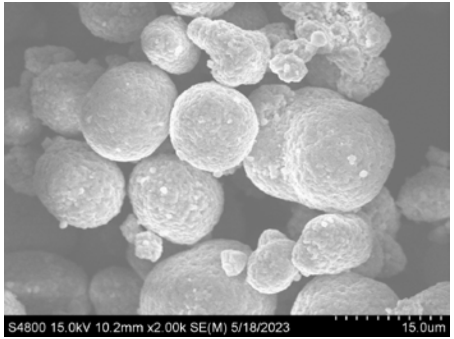
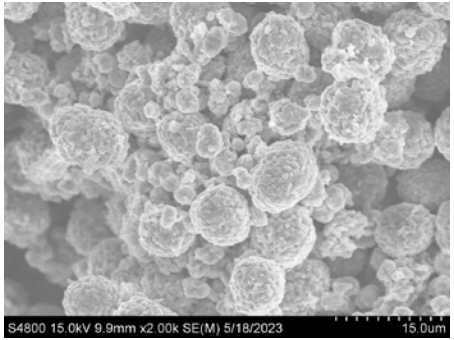
MATERIAL CHARACTERIZATION

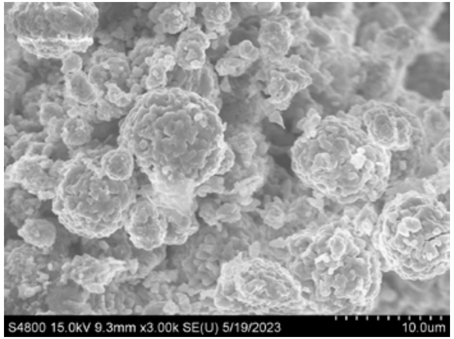
SEM and ICP-OES



pristine NMC622



EOL NMC622



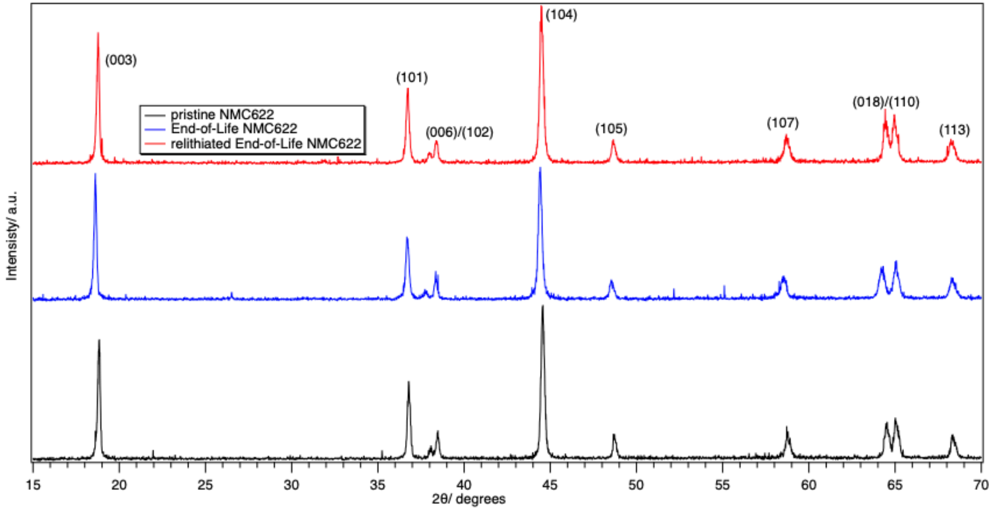
Relithiated EOL NMC622

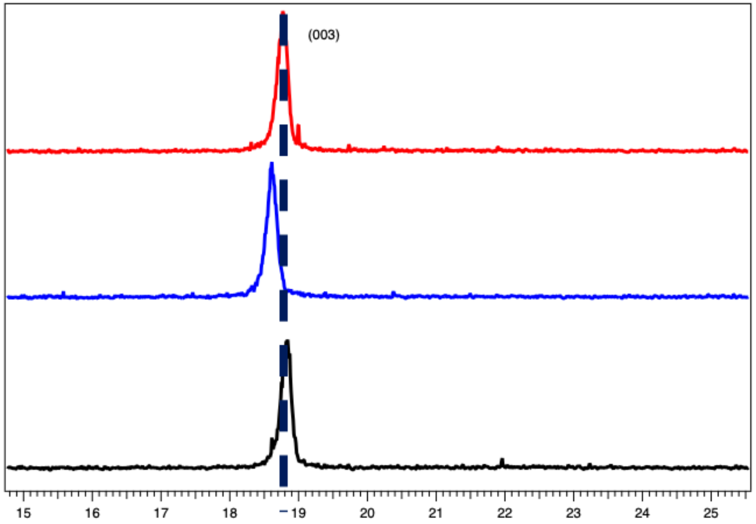
ICP Results	Li	Ni	Mn	Co
Pristine NMC622	0.961	0.616	0.189	0.196
EOL NMC622	0.767	0.649	0.200	0.151
Relithiated EOL NMC622	1.090	0.657	0.195	0.148

- Li ratio is recovered in the relithiated powder. It is comparable to the pristine material
- Well-preserved structure after relithiation and no damage observed after annealing

MATERIAL CHARACTERIZATION

XRD



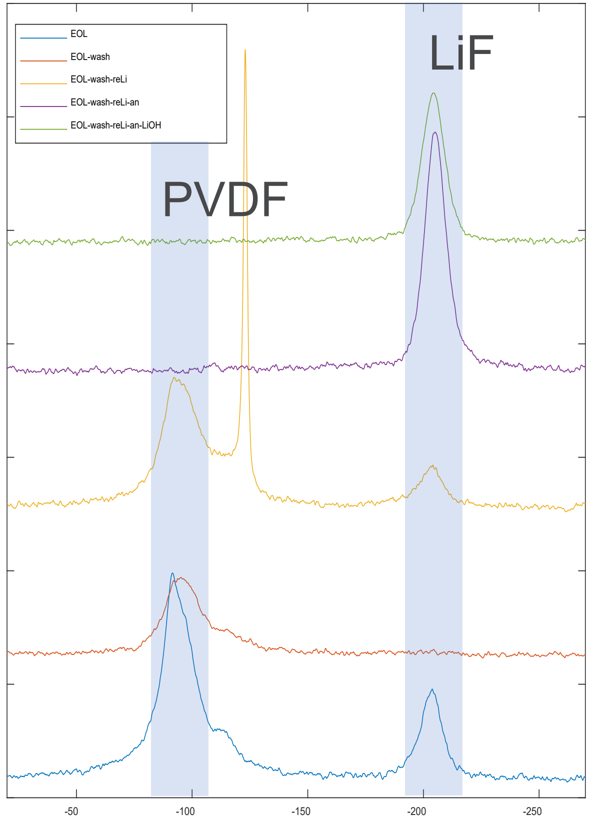


- Well-preserved structure after relithiation and no damage observed after annealing
- No impurity phases observed for the relithiated material

MATERIAL CHARACTERIZATION

Solid NMR analysis of ^{19}F in NMC622 powder

- Going from unwashed EOL (blue) → washed EOL (red)
  - ✓ Washing removes LiF peak
- Going from washed EOL (red) → relithiated washed EOL (yellow)
  - ✓ LiF peak reappears
- Going from relithiated washed EOL → annealed relithiated washed EOL (purple)
  - ✓ Annealing removes PVDF peak and increases LiF peak
  - ✓ Annealing with excess LiOH (green) does not add as much LiF as without the LiOH



Collaboration with
Fulya Dogan Key - Argonne National Laboratory, Chemistry Sciences and Engineering Division
Evelyna Wang - Argonne National Laboratory, Chemistry Sciences and Engineering Division

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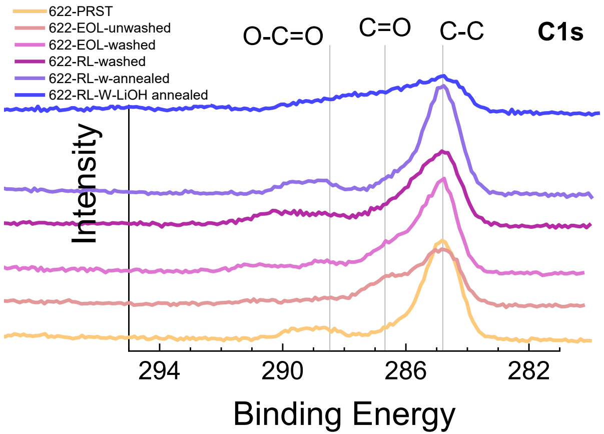
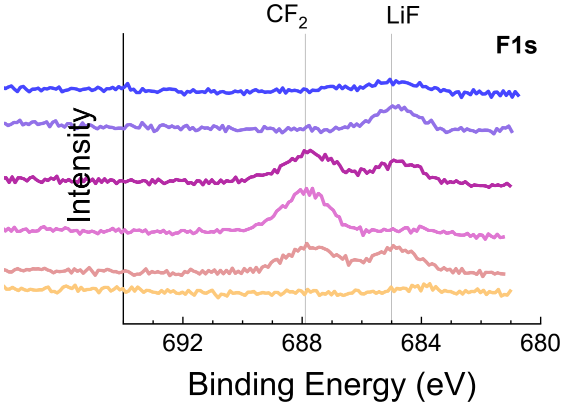
MATERIAL CHARACTERIZATION

XPS analysis of C1s and F1s regions

- SEI components: mainly Lithium ethylene decarbonate (LEDC, ~290eV) in C1s and LiF (~685 eV) in F1s. CF2 is from the PVDF binder.
- The organic component (LEDC) appears to have been effectively removed from the samples during the process.
- The CF_2 peaks vanished after the samples were annealed, whether with or without LiOH.
- Although the LiF peaks disappeared once the EOL samples were washed, they reappeared after the samples were relithiated.





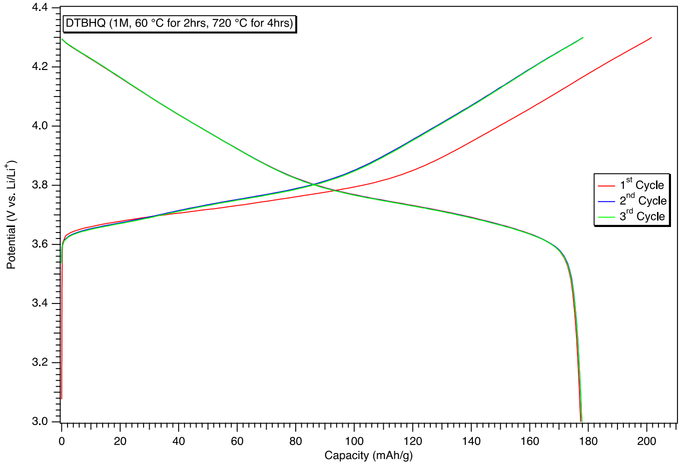
Collaboration with

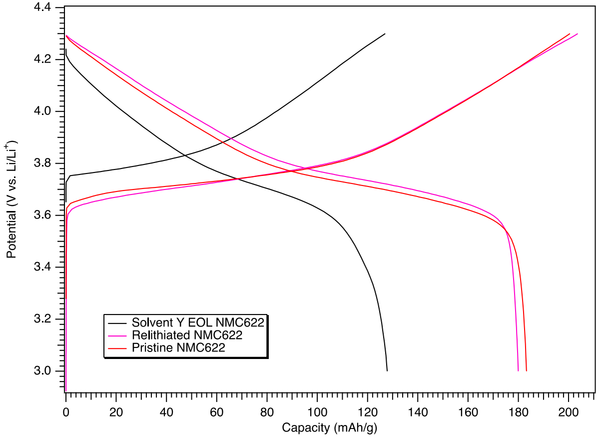
Seoung-Bum Son - Argonne National Laboratory, Post Test Facility

CHALLENGES RELITHIATING CYCLED EOL NMC622

Half cell performance on solvent y recovered NMC 622

- Relithiated NMC622 reversible capacity is comparable to capacity of pristine NMC622 after washing
- LiF impurity affects relithiation of EOL materials



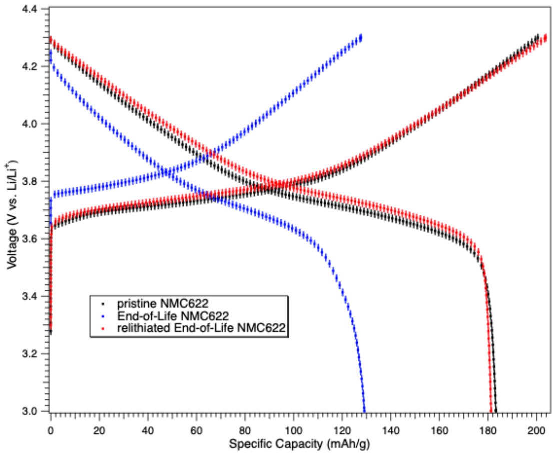


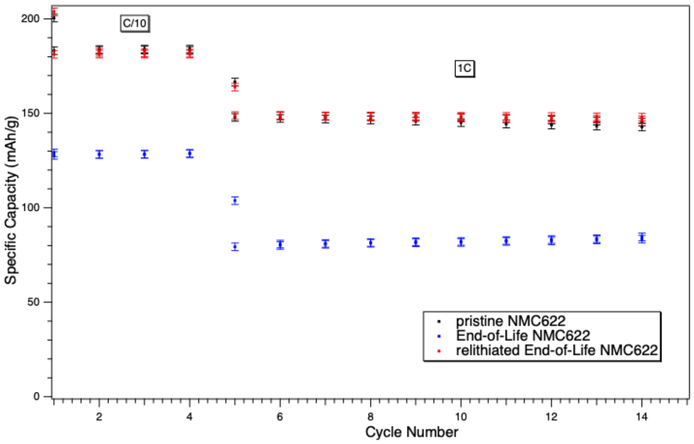
	Charge (mAh/g)	Discharge (mAh/g)
Pristine NMC622	200.48	183.23
Relithiated NMC622	126.99	127.82
Relithiated NMC622	203.65	179.97

ELECTROCHEMICAL ANALYSIS

Half cell performance on solvent y recovered NMC 622

- Relithiated NMC622 capacity is comparable to capacity of pristine NMC622





	1st charge (mAh/g)	1st discharge (mAh/g)	1st cycle efficiency (%)	2nd charge (mAh/g)	2nd discharge (mAh/g)	2nd cycle efficiency (%)
pristine NMC622	200.485	183.228	91.39	183.799	183.388	99.78
relithiated End-of-Life NMC622	203.765	181.264	88.96	182.262	181.370	99.51

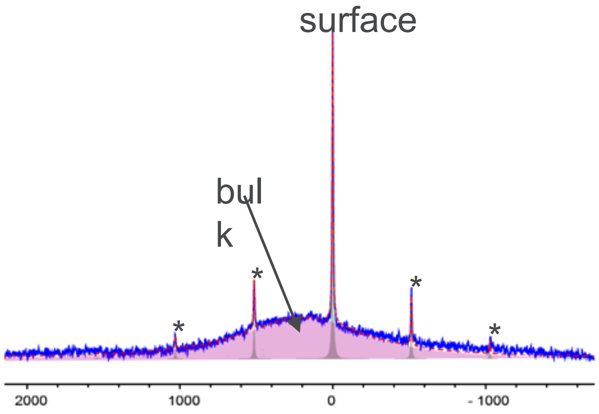
CONCLUSION

MATERIAL CHARACTERIZATION

Solid NMR analysis of ^{7}Li in NMC622 powder

Relative amounts of
surface vs bulk Li:

- Washing removes surface Li
- Relithiation introduces surface Li
- Annealing removes surface Li
- Annealing with LiOH adds some more surface Li



*denotes spinning side band

	surface	bulk
EOL	0.0849	0.9151
EOL-wash	0.0367	0.9633
EOL-wash-reLi	0.0838	0.9162
EOL-wash-reLi-an	0.0465	0.9535
EOL-wash-reLi-an-LiOH	0.0491	0.9509

Collaboration with
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Evelyna Wang - Argonne National Laboratory, Chemistry Sciences and Engineering Division

SUMMARY

- Pristine NMC622 powder was used as the baseline
- Solvent Y process was used to recover cycled EOL cathode powder (NMC622)
- Redox relithiation process was used to restore lithium content in the EOL cathode powder
- Relithiated powder had capacity during formation that was close to that of pristine material
- The material structure did not show obvious changes

FUTURE WORK

- Optimize washing step to remove impurities (LiF)
- Understand the bulk and surface amounts of Li (ongoing NMR tests)
- Improve the battery performance of the relithiated EOL NMC622 material

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QUESTION?

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