RECELL DIRECT CATHODE RECYCLING: RELITHIATION AND UPCYCLING

Project ID: bat465



JACK VAUGHEY
Argonne National Laboratory

2021 DOE Vehicle Technologies Office
Annual Merit Review
June 21-25, 2021

This presentation does not contain any proprietary, confidential, or otherwise restricted information

PROJECT OVERVIEW

Timeline

- Project start: October 2018
- Project end: September 2021
- Percent complete: ~90%

Budget

FY19	$4,615k
FY20	$5,150k
FY21	$4,915k

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

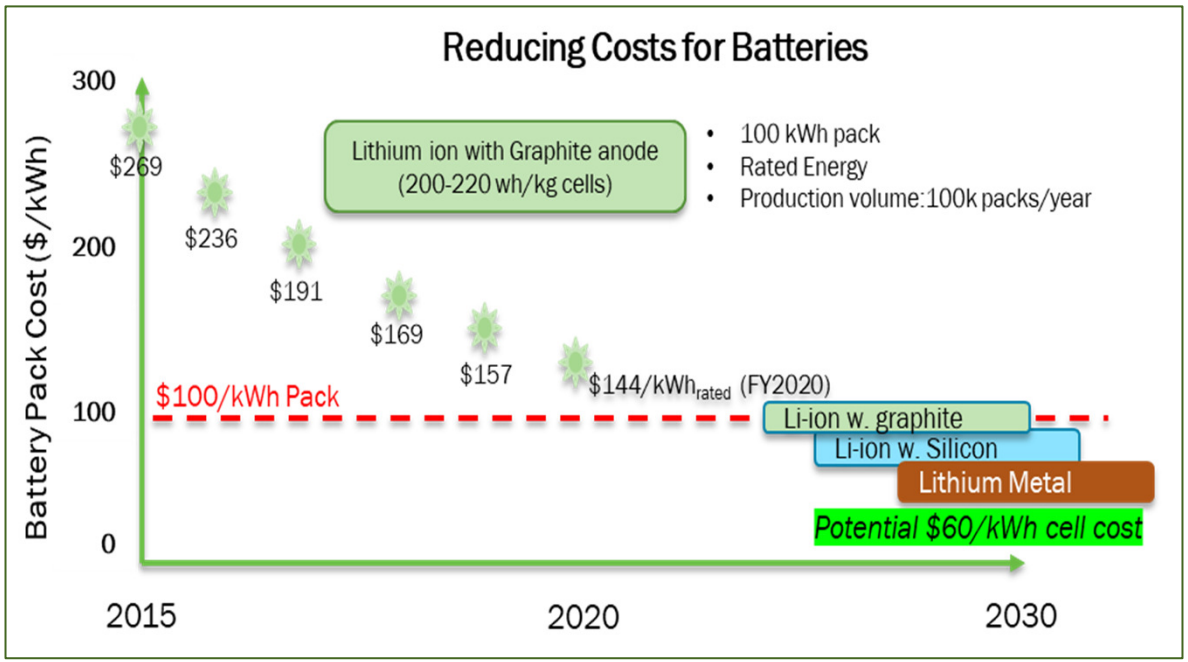
Partners

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

ReCell ADVANCED BATTERY RECYCLING

RELEVANCE

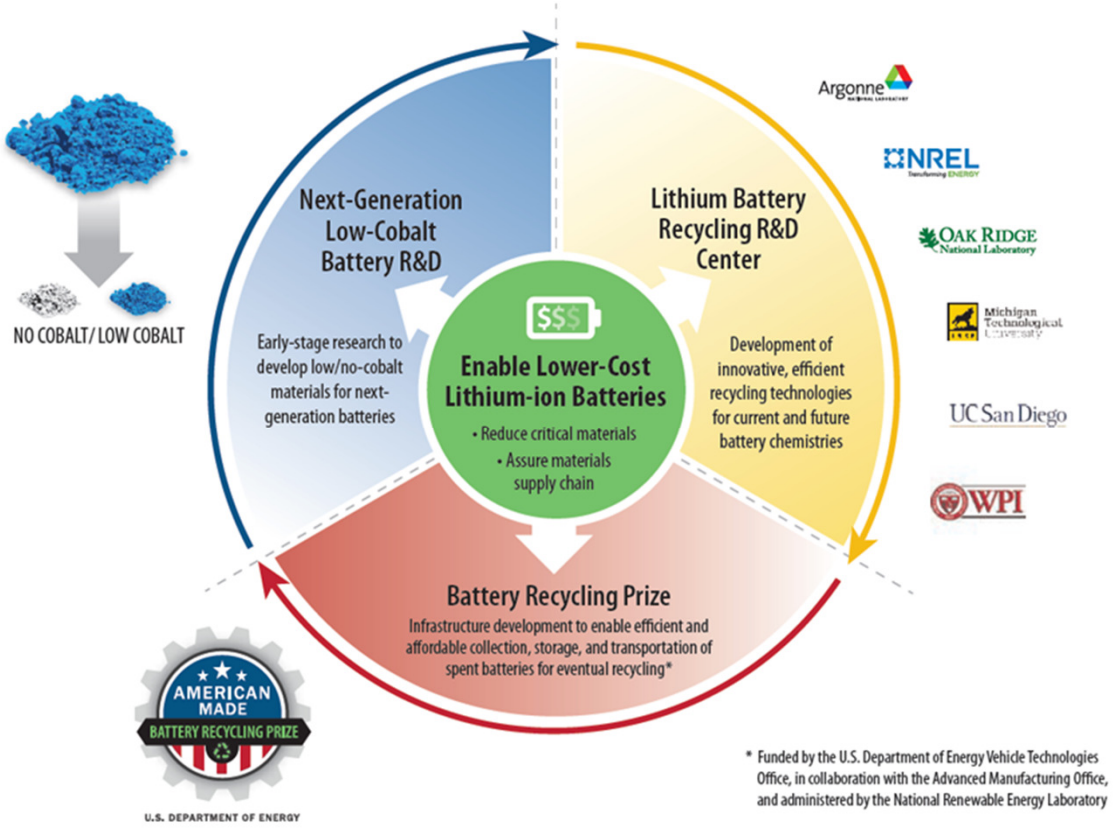
By 2025, reduce the cost of EV battery packs to less than $100/kWh with technologies that significantly reduce or eliminate the dependency on critical materials (such as cobalt) and utilize recycled material feedstocks.



ReCell
ADVANCED BATTERY RECYCLING

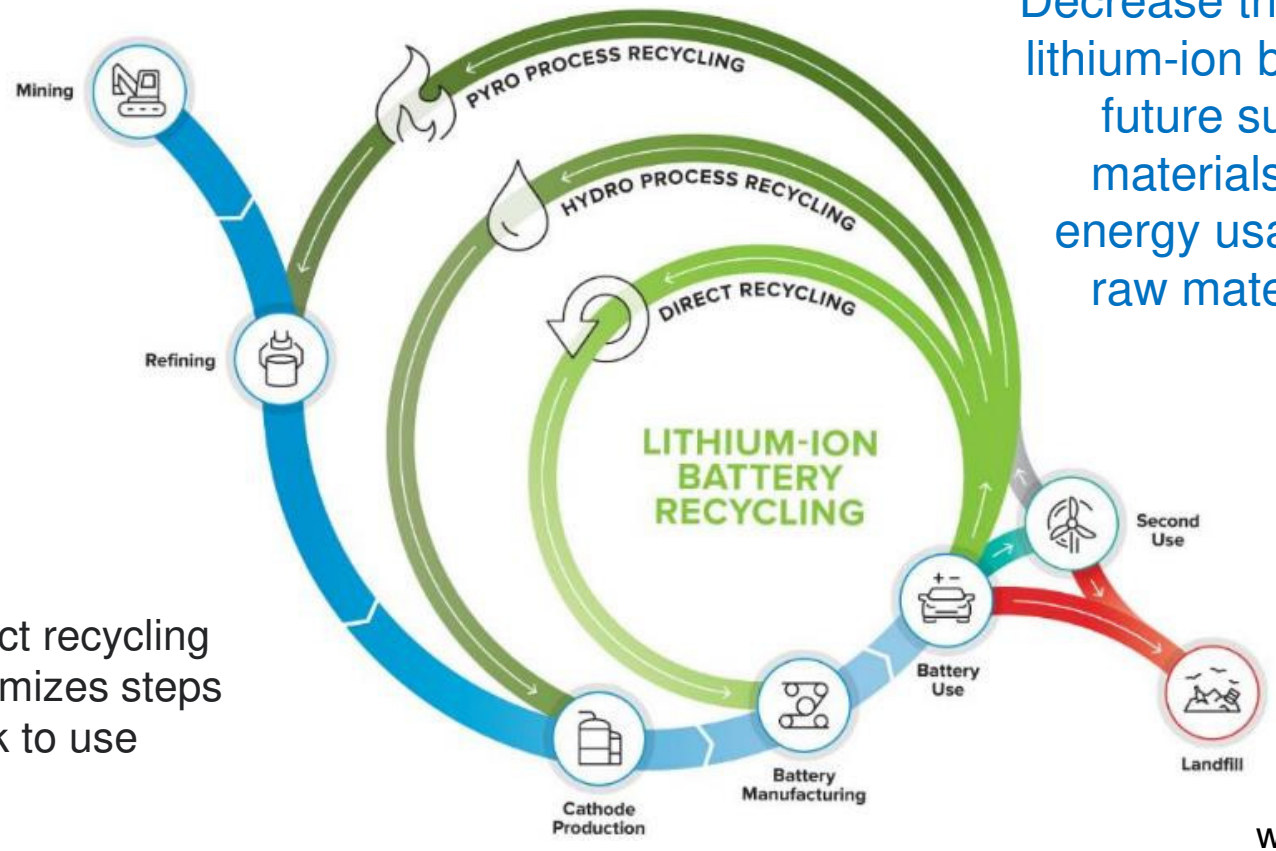
RELEVANCE

- Lower cost of batteries
- Enable lower environmental impacts
- Increase our country's energy security



ReCell ADVANCED BATTERY RECYCLING

APPROACH



Direct recycling minimizes steps back to use

ReCell's Mission:

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

www.ReCellCenter.org

ReCell ADVANCED BATTERY RECYCLING

APPROACH

Year 1 – Bench scale testing: Powder-to-Cell → Year 2 – Start to scale up unit operations → Year 3 – Finish scale up and show cell-to-cell recycling

- Binder Removal
- Cathode/ Cathode Separation
- Relithiation
- Cathode Upcycling
- Impurity Impact



DIRECT CATHODE RECYCLING

OTHER MATERIAL RECOVERY



- Cell Shredding
- Electrode Delamination
- Anode/ Cathode Separation
- Electrolyte Component Recovery

Cross Cutting Projects

- Cell Design for Rejuvenation



DESIGN FOR SUSTAINABILITY

MODELING AND ANALYSIS



- EverBatt (TEA/LCA)
- LIBRA (Supply Chain Modeling)

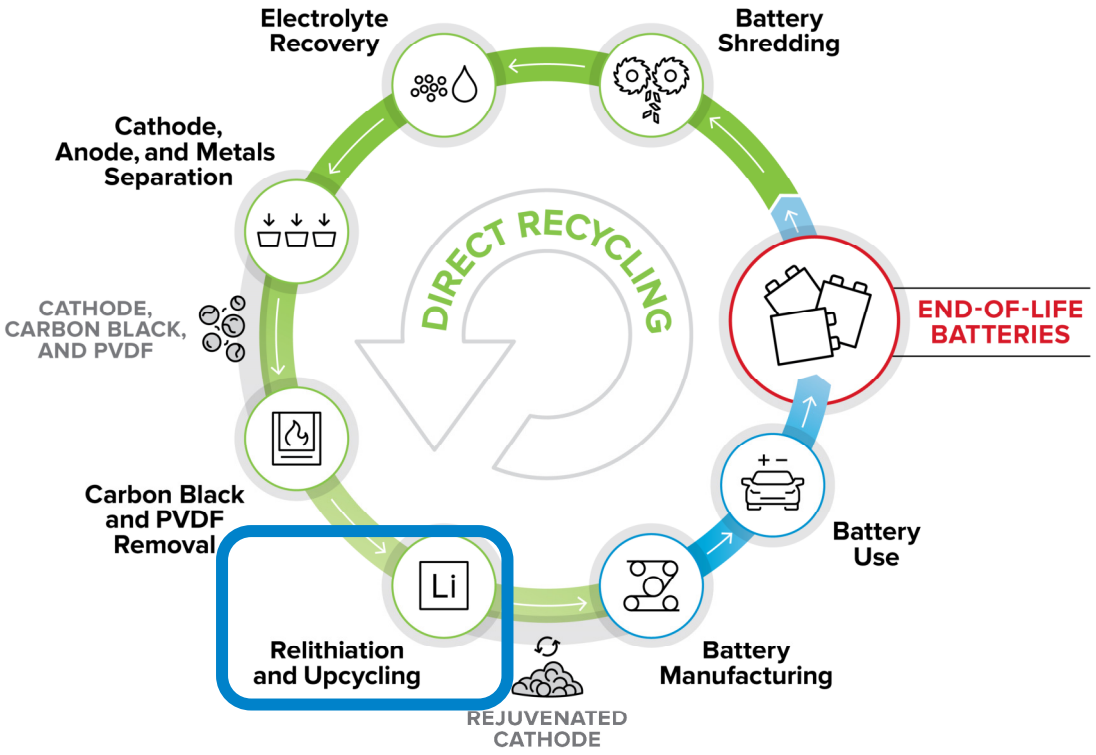
Program does not include battery dismantling, transportation, or 2nd use

ReCell ADVANCED BATTERY RECYCLING

APPROACH

- Multiple processes investigated to mitigate risk
- Continual review of new project ideas
- End projects that are not showing promise in cost and performance
- These processes can benefit other recycling processes

Typical Direct Recycling Process Flow



ReCell
ADVANCED BATTERY RECYCLING

MILESTONES

FY20 Q3	Complete	Down-select solvent(s) to separate black mass from current collector and optimize the process conditions to achieve >90% recovery of black mass
FY20 Q4	Complete	Demonstrate recovery of anode and cathode powders using the new pilot scale froth column
FY21 Q1	Complete	Preliminary report of sensitivity analysis of battery recycling in the LIBRA model focusing on outputs including the number of recycling plants built and the percentage of batteries recycled over time.
FY21 Q2	Complete	Demonstrate 30% graphene yield from spent anode using a Taylor Vortex Reactor
FY21 Q3	Ongoing	Final report on performance and cost modeling of directly recycled manufacturing scrap
FY21 Q4	Ongoing	Provide preliminary cost analysis, yield, and efficiency on the separation-relithiation conditions on NMC spent electrodes via solvent-based dual process

Each Individual project has its own milestones, though not listed here.

COVID-19 has reduced lab time and may cause delays in completing FY22 milestones

DIRECT CATHODE RECYCLING: RELITHIATION AND UPCYCLING

ReCell ADVANCED BATTERY RECYCLING

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

TECHNICAL ACCOMPLISHMENTS

End of Life Batteries

For transportation systems, End-of-Life (EOL) is the point where the loss in performance effects the users needs. This loss can be attributed to power fade, impedance rise, and interfacial breakdown with loss of active lithium to the SEI, parasitic side reactions, and formation of insoluble species.

This presentation reflects work and migration of effort by the ReCell team in the areas of

(1) **Relithiation** – restoring the lithium lost by the EOL cathode during normal use. Relithiation is needed for upcycling to remove cation defects and prevent nucleation of interfacial phases, i.e. spinel.

(2) **Upcycling** – reflects the reality that the cathodes of yesterday may not be the cathodes of tomorrow. Develop processes to convert NMC111 to the higher capacity NMC622.



TECHNICAL ACCOMPLISHMENTS

Relithiation to Upcycling

In FY21, we've shifted some of our teams focus from relithiation to upcycling (NMC111→ NMC622) with input from the EverBatt Team and Management.

Projects

- Thermal Relithiation → Thermal Upcycling
- Hydrothermal Relithiation → Hydrothermal Upcycling
- Ionothermal Relithiation → Ionothermal Upcycling
- Electrochemical Relithiation
- Redox Shuttle Relithiation

New FY21 Projects

- Solvent Based Dual Processing Relithiation
- Single Crystal Cathodes

ReCell ADVANCED BATTERY RECYCLING

TECHNICAL ACCOMPLISHMENTS

Thermal Relithiation and Upcycling Processes

Relithiation

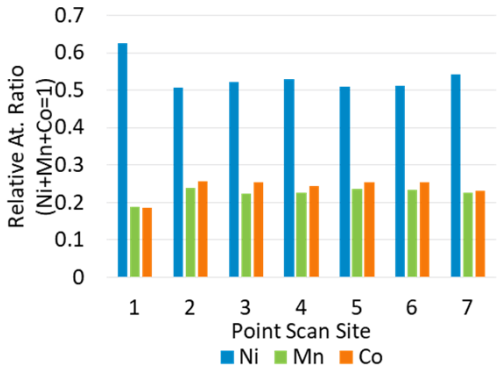
- A two stage annealing process (350 ºC, 650 ºC) with LiOH was optimized to maximize reversible capacity (vs pristine)
- EverBatt – limiting the amount of EtOH / kg NMC yields a product that is 1/3 cost of pyroprocessing

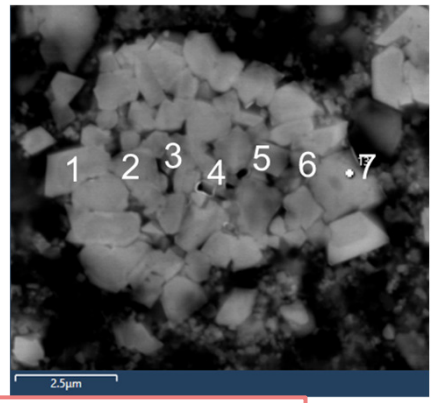
Sample	[Li]	[Ni]	[Mn]	[Co]	mAh/g
Pristine	1.092	0.321	0.352	0.328	162
Delithiated	0.943	0.330	0.330	0.339	141
EtOH mix	1.068	0.317	0.358	0.325	163
Solid mix	1.062	0.323	0.340	0.336	145

Upcycling

$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2 + Ni(SO_4) + LiOH \rightarrow LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$

- Needs oxidizing atmosphere
- XPS: Amount of Ni^{3+} increases with O_2 annealing
- Lower the temperature the better
- Lithium deficient mix yields NiO, $LiCoO_2$, or $Li(NiMn)O_2$.





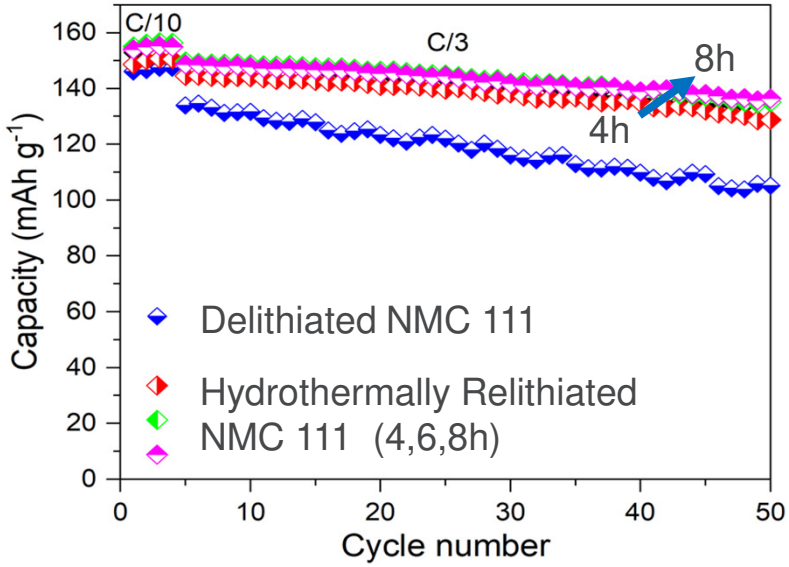
EDS: edges are slightly more Ni rich than the bulk

TECHNICAL ACCOMPLISHMENTS

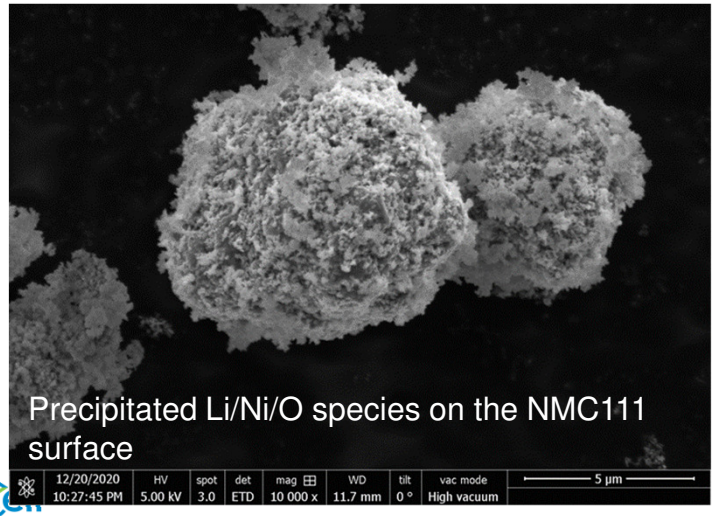
Hydrothermal Relithiation and Upcycling Processes

Relithiation

- Developed a low temperature hydrothermal *relithiation* process that uses an alkaline solution of a mixed KOH / LiOH solution
- Worked with the EverBatt team to identify possible savings in chemicals



Upcycling



Adapting hydrothermal relithiation process to use various Ni(II) salts which form the hydroxide.

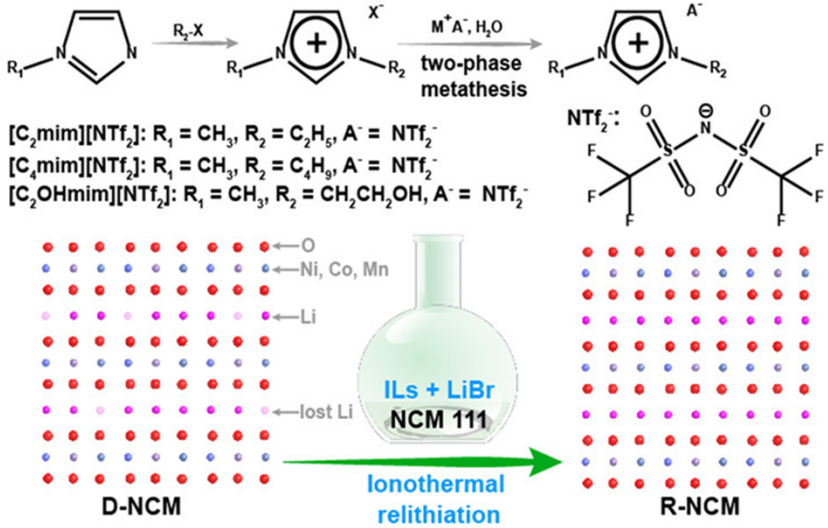
- Early results indicate that the process is sensitive to the Ni source the oxidizing power of the solution.

TECHNICAL ACCOMPLISHMENTS

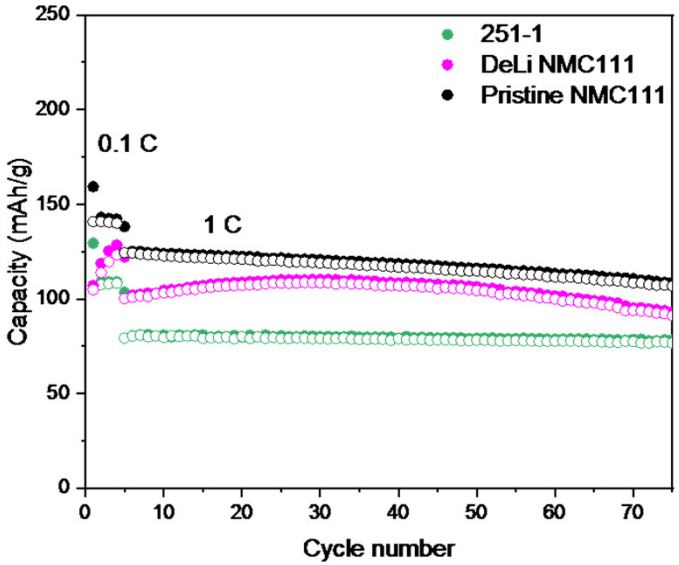
Ionothermal Relithiation and Upcycling Processes

Relithiation

- Identified ILs for controlling formation of solid-state materials with a minimal morphology changes.
- With EverBatt team, worked to identify ILs that can be readily recycled and reused after ionothermal relithiation.



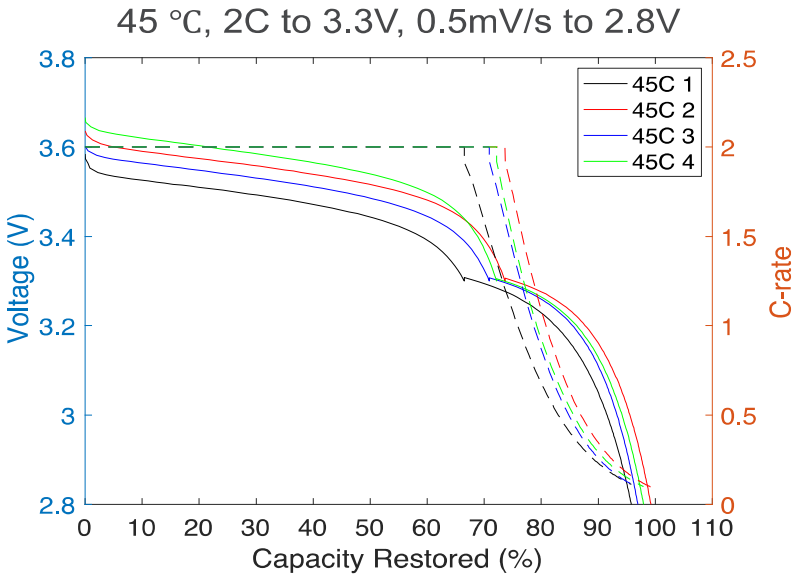
Upcycling



Adapting RTIL relithiation process. Solution is changed to add various NiX salts (X=SO_4^{-2}, Cl^-, OAc^-). Early results indicate that the process needs to be adapted to be more oxidizing towards the dissolved nickel.

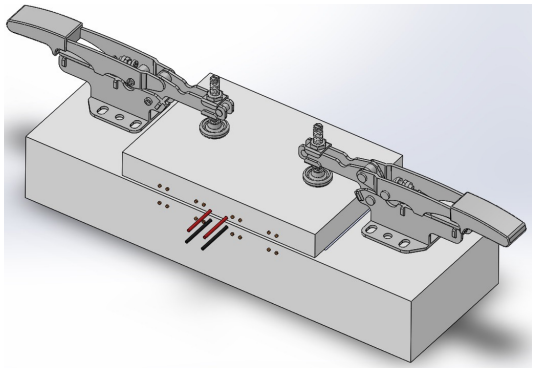
TECHNICAL ACCOMPLISHMENTS

Electrochemical Relithiation and Roll to Roll Model Development



NMC111 (@ C/10)	Charge (mAh/g)	Discharge (mAh/g)
1st Charge (C/10)	162.2	159.1
On Cycling	160.7	158.7

- Modeled the coupled lithium/vacancy diffusion in the chemically delithiated NMC 111 materials. Developed process that uses short cycling (~ 60 mAh/g) at 45 ºC to reduce impedance and restore performance (of pristine NMC 111).
- Identified process to relithiate the delithiated NMC 111 in less than 25 minutes comparable to pristine C/10 cycles



Reactor Redesign

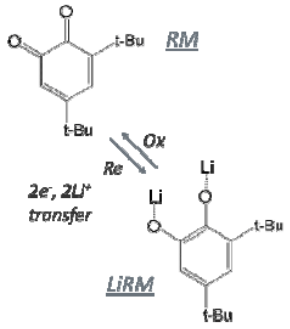
Enables elevated-temperature relithiation

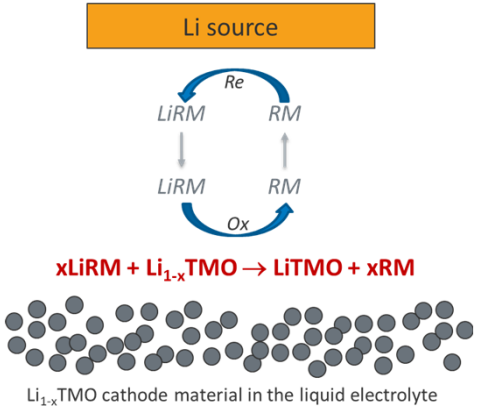
Prevents excessive electrolyte evaporation

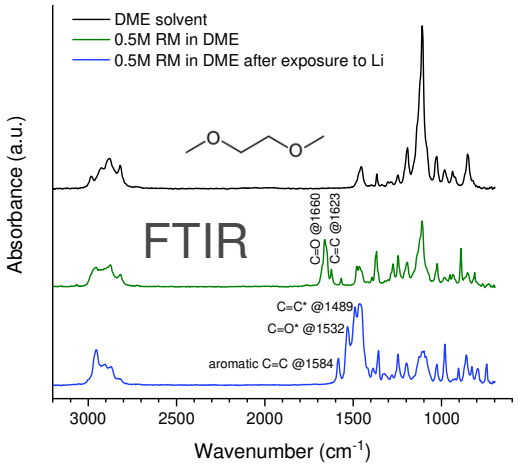
TECHNICAL ACCOMPLISHMENTS

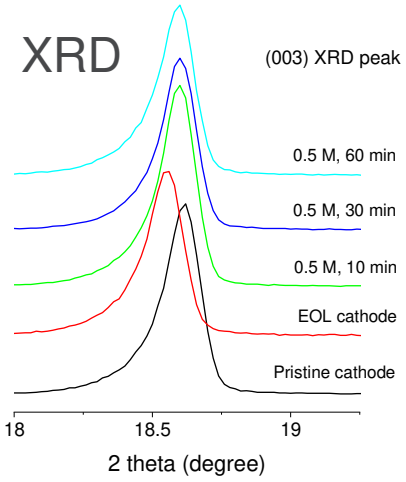
Redox Mediator (RM) Relithiation

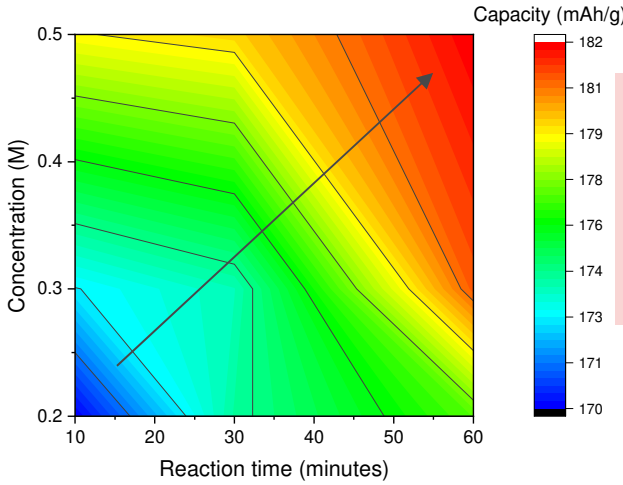
- Li metal reduces and lithiates quinone redox mediators that reduces the EOL cathode by transferring Li^+/e^- and restoring the Li concentrations.
  - Assessed - RM concentrations and reaction time: 0.5M RM electrolyte for 10 min to fully lithiate EOL NMC111
  - Assessing reusability of the RM electrolytes to reduce materials costs (w EverBatt)











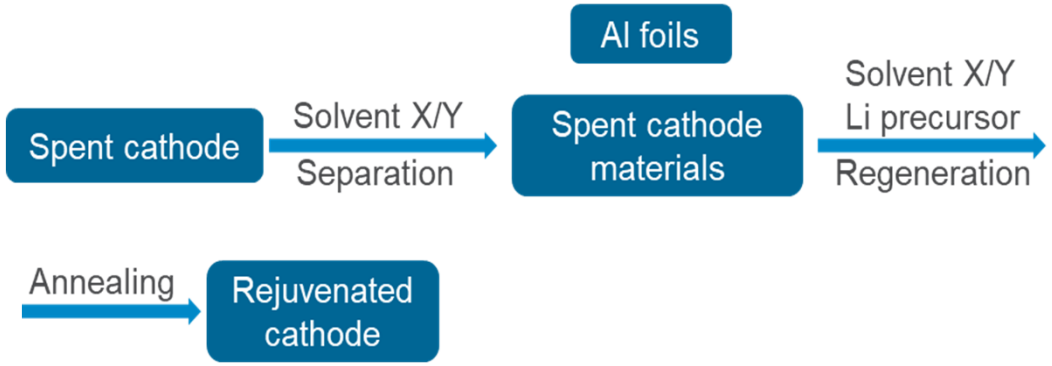
Capacity higher with increased time and Redox Mediator concentration.

TECHNICAL ACCOMPLISHMENTS

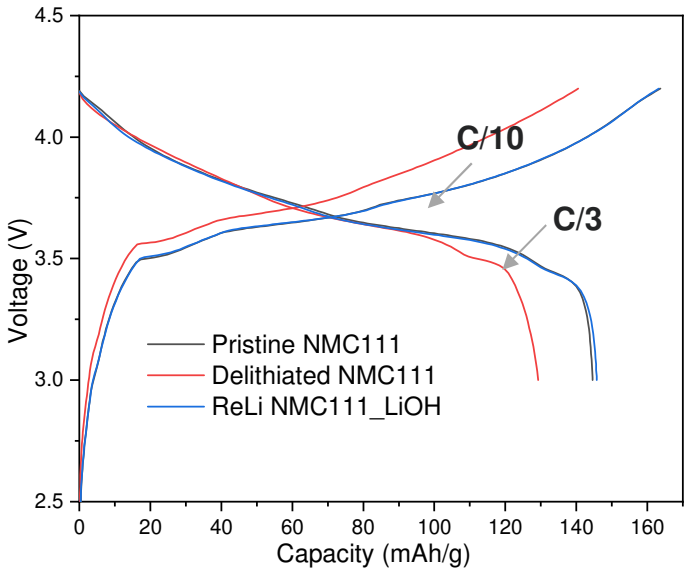
FY21 New Projects

Dual Solvent Relithiation Process

Goal: to develop a process that can separate cathode materials from Al foils and restore lithium content in the same solvent system



Full cell, 1st charge/discharge, C/10



Accomplishments:

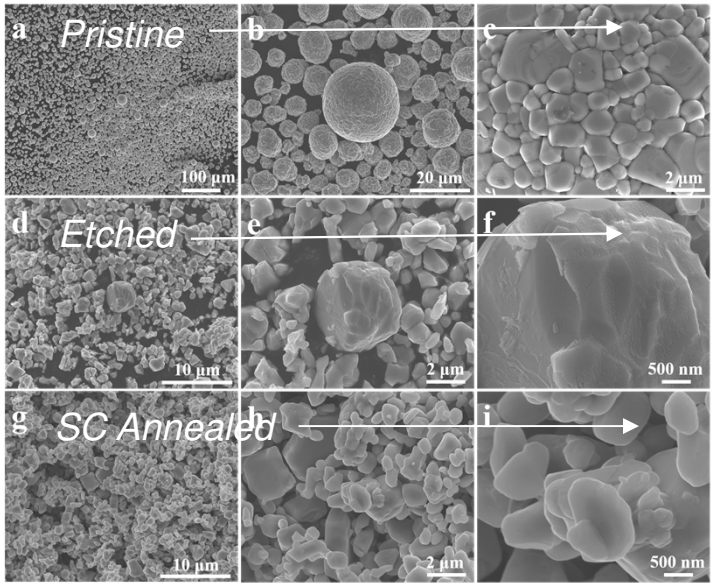
Identified a solvent, X, and lithium precursor that can regenerate spent cathode at a low temperature at ambient pressure, restoring electrochemical performance

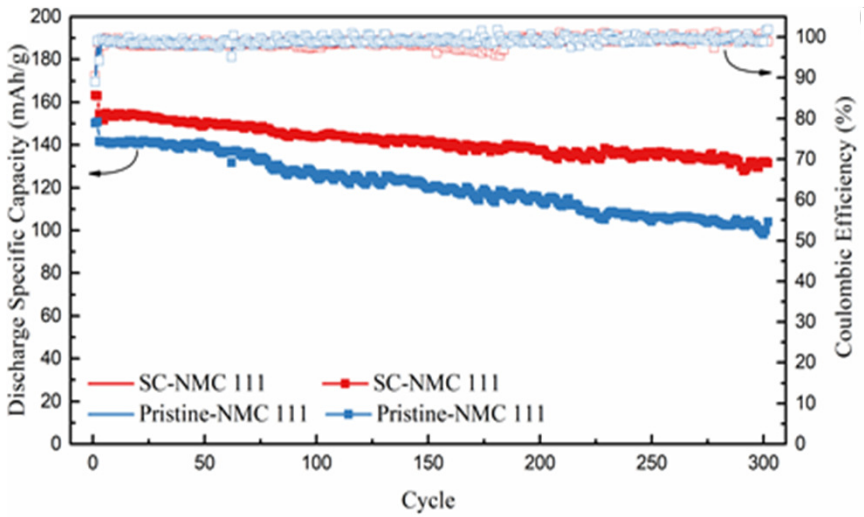
ReCell ADVANCED BATTERY RECYCLING

TECHNICAL ACCOMPLISHMENTS

FY21 New Projects

Single Crystal Cathode Upcycling





Half cell cycling at C/2; Single crystal NMC111 vs pristine NMC111

Process:

Etching disassociates the secondary particles into single crystal particles. The etched particles have rough surface and become smooth after heat-treatment with Li_2CO_3; any peak shift (due to delithiation on etching) is reversed. The annealing stage generates single-crystal NMC111 in a sub-micron size.

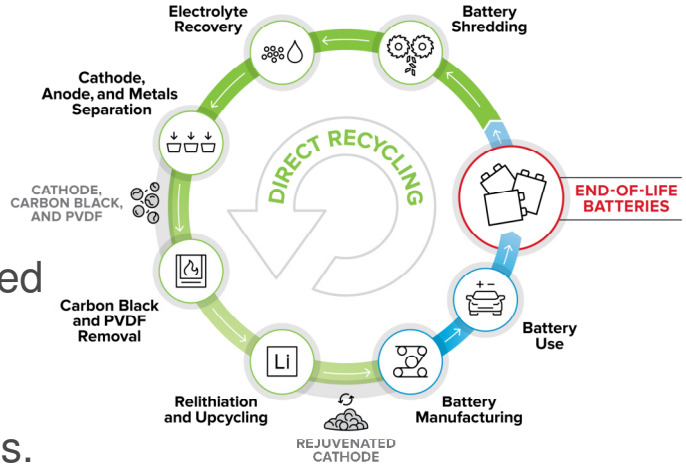
REMAINING CHALLENGES AND BARRIERS

Relithiation:

- Assessing and reducing costs (w Everbatt) on the various relithiation processes.
- Assess scale-up procedures and processes (w CAMP, MERF)

Upcycling:

- Identifying material processes and tools to determine upcycled sample homogeneity
- Feedstock consistency with various commercialized chemistries
- Interfacial phase formation that increases electrochemical impedance at the active interfaces.



ReCell ADVANCED BATTERY RECYCLING

PROPOSED FUTURE WORK

- Evaluate the proposed processes against commercially recovered (single phase) cathode materials
- With EverBatt team, identify cost basis of each process and identify areas of possible cost savings
- Work with CAMP/BMF to assess electrochemical properties of upcycled materials in larger cell formats.

ReCell ADVANCED BATTERY RECYCLING

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

SUMMARY

- In conjunction with the EverBatt team we have identified and acted on several observations and suggestions to lower the calculated costs of relithiated samples for the processes developed in FY19-20.
  - Materials costs ($/kg NMC) for the thermal relithiation process, once the amount of EtOH was reduced, have been calculated to be 1/3 that of pyroprocessing.
  - ORNL, NREL, and UCSD have identified significant savings by focusing on solvent re-use in their processes.
- At least one annealing step to crystallize the final re-lithiated product seems to be required to attain the best performance, except for the electrochemical process.
- Upcycling studies based on NMC 111 have identified pathways to create the desired Ni-rich stoichiometries (NMC 622) product. By EBSD the cations in the sample are homogeneous.
- Oxidizing synthetic conditions appear necessary to achieve a homogenous product.

RESPONSE TO REVIEWERS

Not reviewed last year

COLLABORATION AND ACKNOWLEDGEMENTS

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged –

Samm Gillard, Steven Boyd, and David Howell

Argonne NATIONAL LABORATORY

Michigan Technological University

NREL NATIONAL RENEWABLE ENERGY LABORATORY

WPI

OAK RIDGE National Laboratory

UC San Diego

ReCell ADVANCED BATTERY RECYCLING

Shabbir Ahmed (Argonne)
Yaocai Bai (ORNL)
Ilias Belharouak (ORNL)
Ira Bloom (Argonne)
Anthony Burrell (NREL)
Zheng Chen (UCSD)
Jaclyn Coyle (NREL)
Qiang Dai (Argonne)
Sheng Dai (ORNL)
Erik Dahl (Argonne)
Zhijia Du (ORNL)
Alison Dunlop (Argonne)
Jessica Durham (Argonne)
Kae Fink (NREL)
Tinu Folayan (MTU)
Linda Gaines (Argonne)
Daniel Inman (NREL)
Andy Jansen (Argonne)
Sergiy Kalnaus (ORNL)
Matt Keyser (NREL)
Greg Krumdick (Argonne)
Jianlin Li (ORNL)
Albert Lipson (Argonne)
Huimin Luo (ORNL)
Josh Major (NREL)
Margaret Mann (NREL)
Tony Montoya (Argonne)
Helio Moutinho (NREL)
Nitin Muralidharan (ORNL)
Andrew Norman (NREL)
Lei Pan (MTU)
Anand Parejiya (ORNL)
Kyusung Park (NREL)
Bryant Polzin (Argonne)
Kris Pupek (Argonne)
Vicky Putsche (NREL)
Seth Reed (Argonne)
Bradley Ross (Argonne)
Shriram Santhanagopalan (NREL)
Jeff Spangenberger (Argonne)
Venkat Srinivasan (Argonne)
Darlene Steward (NREL)
Nathaniel Sunderlin (NREL)
Jeff Tomerlin (NREL)
Steve Trask (Argonne)
Jack Vaughey (Argonne)
Yan Wang (WPI)
Olumide Winjobi (Argonne)
Zhenzhen Yang (Argonne)
Jiuling Yu (NREL)
Ruiting Zhan (MTU)

ReCell

ADVANCED
BATTERY RECYCLING

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

VEHICLE TECHNOLOGIES OFFICE

E-Mail: recell@anl.gov
Website: www.recellcenter.org