U.S. DEPARTMENT OF ENERGY'S (DOE)
VEHICLE TECHNOLOGIES OFFICE (VTO)
2020 ANNUAL MERIT REVIEW (AMR)

ReCell ADVANCED BATTERY RECYCLING

DIRECT CATHODE RECYCLING: RELITHIATION AND UPCYCLING

RECELL CENTER FOR ADVANCED BATTERY RECYCLING

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bat465
Virtual Poster
June 1-4, 2020

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

PROJECT OVERVIEW

Timeline

- Project start: October 2018
- Project end: September 2021
- Percent complete: ~50%

Budget

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

Barriers

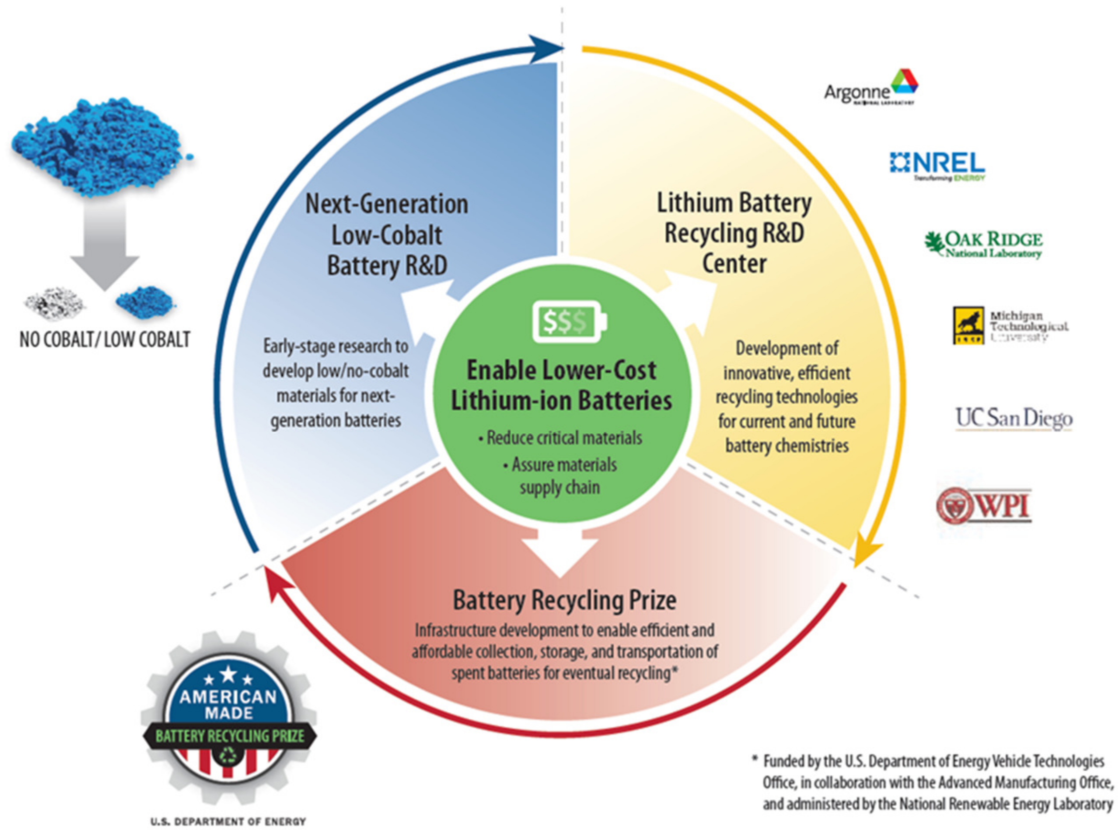
- Recycling and Sustainability
  - Cost to recycle is currently 5-15% of battery cost
  - Material shortage (Li, Co, and Ni)
  - Varying chemistries result in variable backend value

Partners

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

RELEVANCE

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



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

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

PROGRAM MILESTONES

FY19 Q1 Complete Establish the battery recycling center's mission and include its targets and goals

FY19 Q2 Complete Provide an initial progress report on roll-to-roll relithiation

FY19 Q3 Complete Provide an initial progress report on design for recycle initiative

FY19 Q4 Complete Establish the ReCell Center's Battery Recycling Laboratory and Scale-up Facility

FY20 Q1 Complete Electron Backscatter Diffraction data comparison of various chemically delithiated NMC-111 versus pristine NMC-111

FY20 Q2 Complete All five relithiation processes added to EverBatt at lab scale and production scale

FY20 Q3 Ongoing 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 Ongoing Demonstrate recovery of anode and cathode powders using the new pilot scale froth column

Each Individual project has its own milestones that are not listed here.

COVID-19 has reduced lab time and may cause delays in completing FY20 milestones

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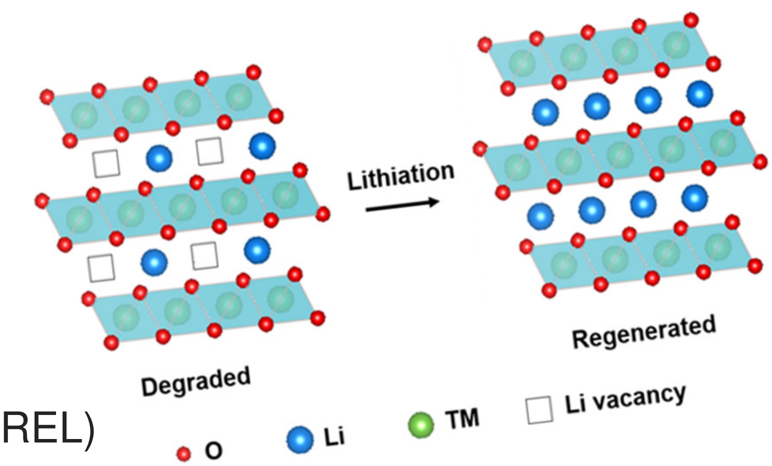
APPROACH – DIRECT CATHODE RECYCLING

Relithiation and Upcycling

Several phenomena contribute to the gradual drop 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.

- **Relithiation**
  - Electrochemical – J. Coyle, X. Li (NREL)
  - Solid State – J. Vaughey (Argonne)
  - Hydrothermal – Z. Chen (UCSD)
  - Ionothermal – S. Dai (ORNL)
  - Redox Mediated – K. Park (NREL)
  - Roll to Roll Processing – N. Sunderlein (NREL)
- **Upcycling**
  - Compositional Change– J. Vaughey (Argonne)



CATHODE RELITHIATION

Examining Multiple Processes to Assess Costs

Industrially, the batteries coming into a recycling center (now) are either fully reduced (pyroprocessing) or dissolved (hydroprocessing) to isolate the desired components

ReCell seeks to develop and evaluate a Direct Recycling process that allows maintenance of material structures for common EV cathodes.

MODEL CATHODES

Baseline Materials

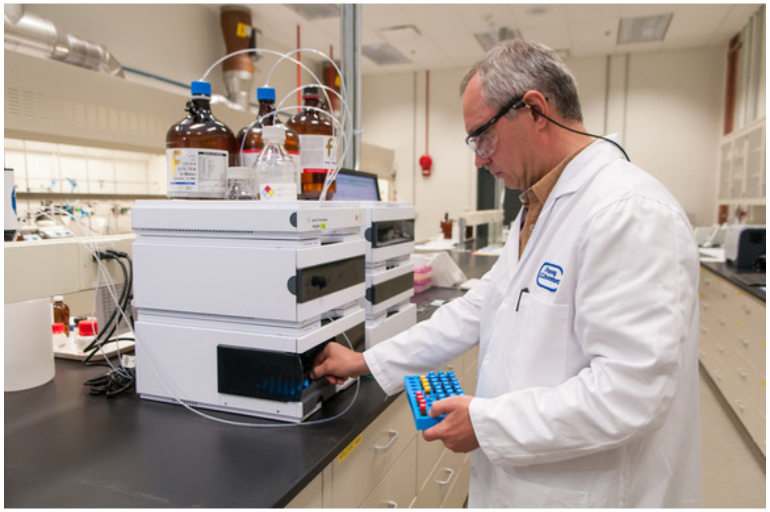
- **Materials** - MERF (@ANL) scaled up several kilos of a baseline delithiated NMC111 commercial material. It was distributed program wide and used to establish protocols and new spectroscopic techniques.

- **Analysis** –

(1) ICP and GDOES were used to establish metal ratios and lithium content.

(2) Electrochemical cycling analysis was used to assess impedance (surface damage), cycle-able lithium, and performance

(3) X-Ray diffraction was used to determine impurity phases and structural changes

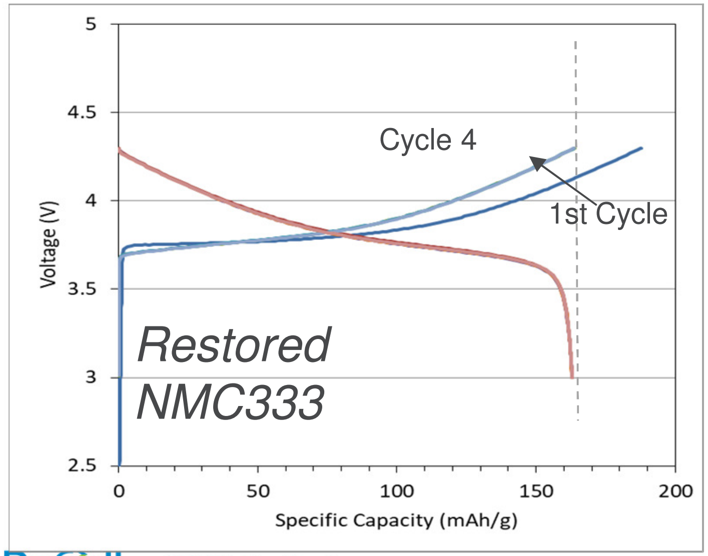


CATHODE RELITHIATION

Solid State Relithiation

Year two:

- Best results: coating the 10% delithiated NMC with LiOH; calcining to 650 ℃ in air (10h),
- Analysis: Recovery of NMC333 fully lithiated sample verified by XRD; Changes in Li content are measured using GDOE Spectroscopy
- Electrochemical performance was tested in half-cell configuration with capacity recovery

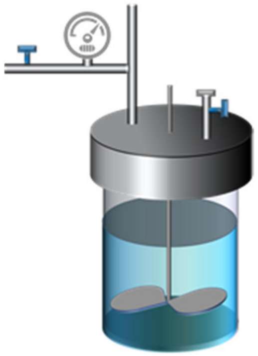


In year one we:

- Screened numerous Li salts for decomposition best temperature range and effectiveness
- Developed a fast GDOES technique to determine cation stoichiometry
- Developed TGA as a method to attain gross lithium content of received samples.

CATHODE RELITHIATION

Hydrothermal



Year two:

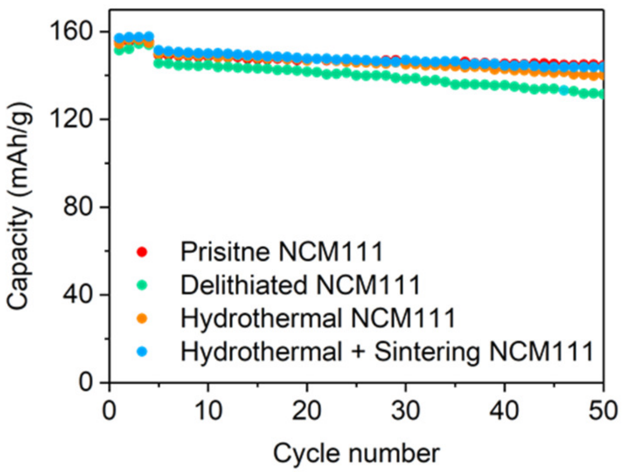
- Best results: Hydrothermal relithiation at 220°C for 4h followed by sintering at 850°C for 4h was the optimal regeneration condition
- Optimization: 4M LiOH could be replaced with 0.1M LiOH + 3.9M KOH the same structure and electrochemical performance were achieved

The hydrothermal relithiation mechanism was determined

$$xLi^{+}(aq) + xOH^{-}(aq)] + Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$$

$$\xrightarrow{220^{o}C\ 2h} LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 + x/2H_2O + x/2O_2$$

$$\xrightarrow{850^{o}C\ 4h} LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$$



In year one we:

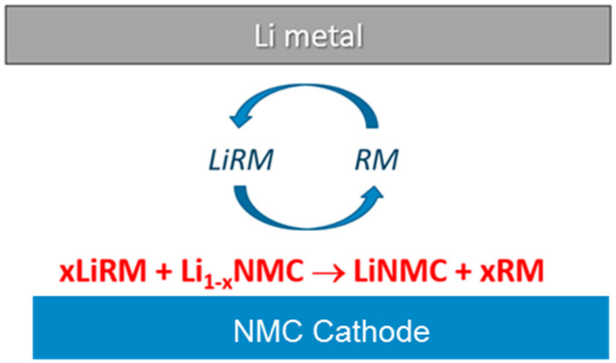
- Optimized LiOH concentration and reaction temperature
- Worked with EverBatt to identify high cost processes.
- Identified best temperature range to anneal post-processing samples.

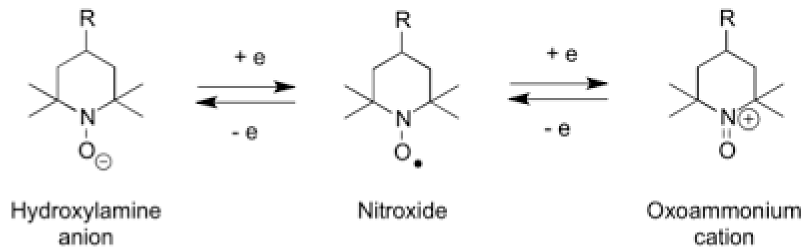
CATHODE RELITHIATION

Redox Relithiation

New Project FY19

Redox mediators are soluble organic molecules that can be oxidized and reduced at voltages common for commercial cathodes. By tuning the system, the RM molecule oxidizes the lithium-deficient cathode to a preset voltage and restores the material. It is reduced at the anode.





Accomplishments:

- Screened 10+ redox mediators and identified a working redox mediator for cathode relithiation
- Demonstrated the redox mediator concept
- Designed several reactors for powder processing and demonstrated relithiation of End-of-Life cathode powder

Initial Results are Very Promising

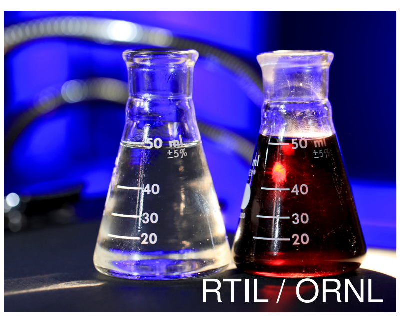
Capacity (mAh/g)	Redox Relithiation	Chem Delith	Pristine
1st Ch	**175**	146	184
1st Disch	**160**	156	162

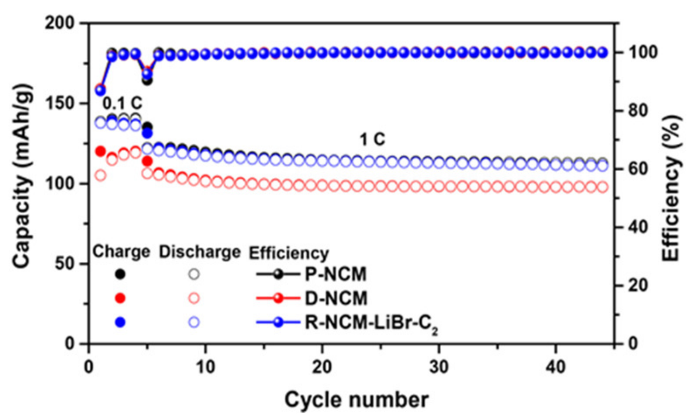
CATHODE RELITHIATION

Ionothermal

Year Two:

- ➢ Mechanistic studies of the full reaction have identified more cost-effective processes
- ➢ The cost was estimated to be \$21.62/Kg by EverBatt, comparable to conventional recycling technologies.
- ➢ Scale-up from 5 g to 25 g was achieved.
- ➢ Ionic liquid recovery and reuse was demonstrated



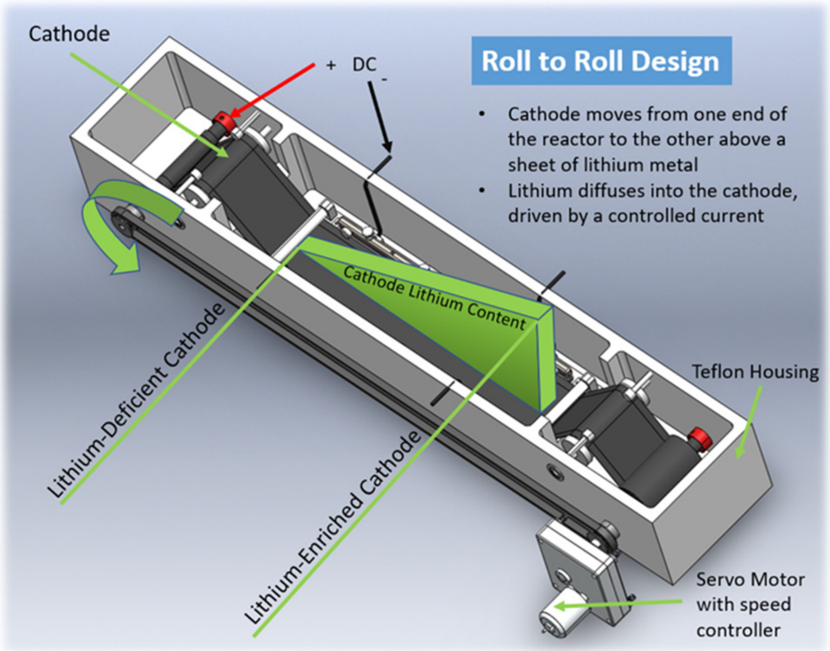


Year One:

- Successful relithiation via ionothermal synthesis based on ionic liquids was demonstrated.
- Screening of several salt/RTIL combinations to identify optimum combinations.
- Temperatures for relithiation refined.

CATHODE RELITHIATION

Electrochemical / Roll to Roll



Year Two:

- Determined the resistance of aged materials is dependent on the sample history
- Developed staged relithiation protocol to ensure optimal lithium ion vacancy distribution
- Optimized the Roll to Roll reactor design for minimum, invariant contact resistance
- Relithiated artificially-aged, commercial cathodes to >95% of their original capacities

Cell Production Using:	Virgin cathode material	Relithiated cathodes
Cell cost ($)	27.86	22.75
Cathode cost ($)	10.93	5.82
Cell cost/kwh ($)	165.85	135.42

CATHODE RELITHIATION

Processes

Thermal	Hydrothermal	Redox Mediator	Ionothermal	Electrochemical
• Need average lithium content	• Lithium supplied by LiOH / water solution	• Lithium supplied by anode of an electrochemical cell	• Lithium supplied by Li salt in an ionic liquid	• Lithium supplied by anode of an electrochemical cell
• two stage heating process	• Moderate heating step • One stage heating process	• Room temperature	• Moderate heating step • One stage heating process	• *Roll to Roll process under development* • Room temperature

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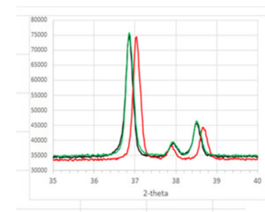
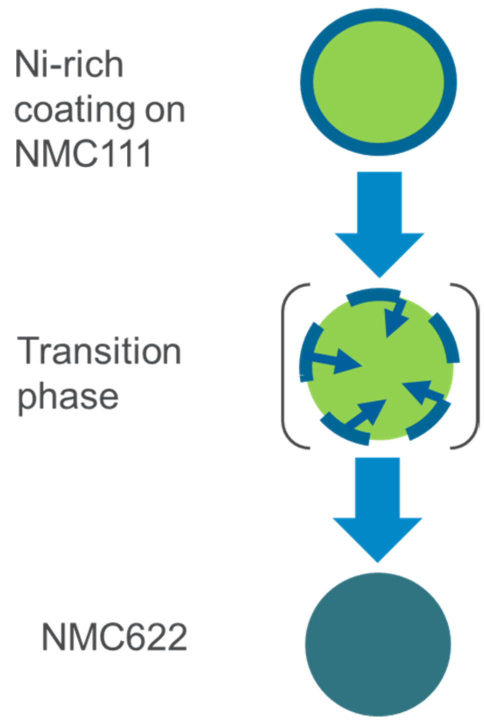
CATHODE UPCYCLING

Process Development for Altering Cathode Stoichiometry



Year Two:

- Evaluated different nickel salts as Ni/O sources; precipitated coatings with LiOH. Salt anion can be source of impurities.
- Targeted overall Ni composition increase was confirmed by GDOES.
- Depending on atmosphere - XRD shows the presence of either NiO or $LiNiO_2$ secondary phases



Year One:

- Identified importance of relithiation on altered surface chemistry
- Developed a methodology to add a homogeneous Ni/O coating
- Variation of annealing atmosphere was investigated.

ACCOMPLISHMENTS AND RESULTS

- Developed and evaluated numerous relithiation methods that vary time, temperature, processing steps, and chemicals and collaborated with the EverBatt team to model each to seek out areas of improvement.

- Scale-up studies of each of these processes are currently underway

- Cathode upcycling to Ni-rich materials has been limited by phase homogeneity within the desired stoichiometric range due to rocksalt formation at the surface.

For more information please see our quarterly reports at www.recellcenter.org.

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RECELL RECYCLING TOWN HALL

FRIDAY, JUNE 5, 2020 FROM 1:00 TO 3:00 (CENTRAL)

To continue the discussion the ReCell team will hold an interactive town hall meeting.

Please join us at the BlueJeans session shown below and ask questions through Slido

Take a picture of this slide

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