OTHER MATERIALS SEPARATION

Project ID: bat380

K. PUPEK
Argonne National Laboratory
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2019 DOE Vehicle Technologies Office
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
Argonne	*$2650k*
NREL	*$965k*
ORNL	*$550k*
UCSD	*$150k*
WPI	*$150k*
MTU	*$150k*

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 – OTHER MATERIAL RECOVERY

To maximize the potential of the recycling process all materials that can be recovered and reused in a battery must be looked at. This effort looks at the recovery processes and their products to drive toward a profitable recycling industry

- Electrolyte Component Recovery, A. Lipson (Argonne)
- Anode/Cathode Separation, E. Dahl (Argonne)
- Hydrothermal Delamination of Electrodes, I. Belharouak (ORNL)

ELECTROLYTE COMPONENT RECOVERY

- Electrolyte needs to be removed before other materials are reprocessed The electrolyte materials will breakdown in water or at high temperatures and impact the cathode material
- Electrolyte can be removed in different ways with different materials recovered. Initial processes were chosen for simplicity and potential for being profitable

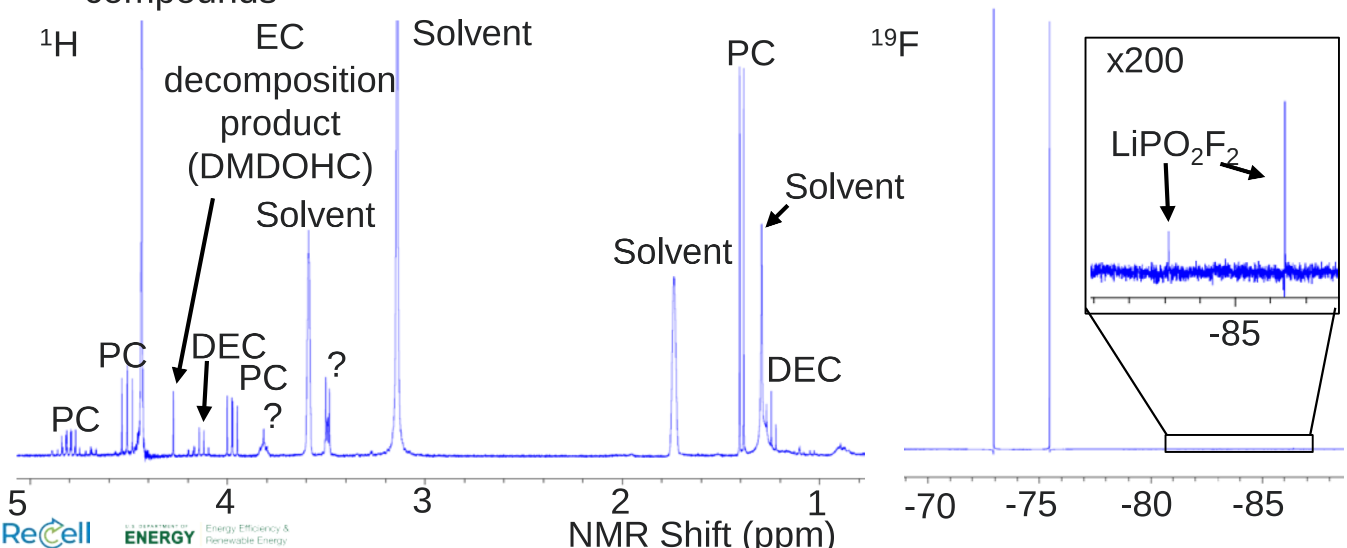
Process	Recovers $LiPF_6$	Recovers Volatile Organics	Recovers Ethylene Carbonate (EC)	Generates LiF	Chosen for Initial Study
Thermal Drying	No	Yes	No	No	No
Supercritical CO_2	No	Yes	Yes	No	No
Supercritical CO_2 + Cosolvent	Yes	Yes	Yes	No	No
Solvent Extraction	Yes	Yes	Yes	No	Yes
Water Washing	Yes/No	No	No	Yes	Yes

ReCell ADVANCED BATTERY RECYCLING

ELECTROLYTE COMPONENT RECOVERY

Analysis of Extracted Electrolyte (NMR)

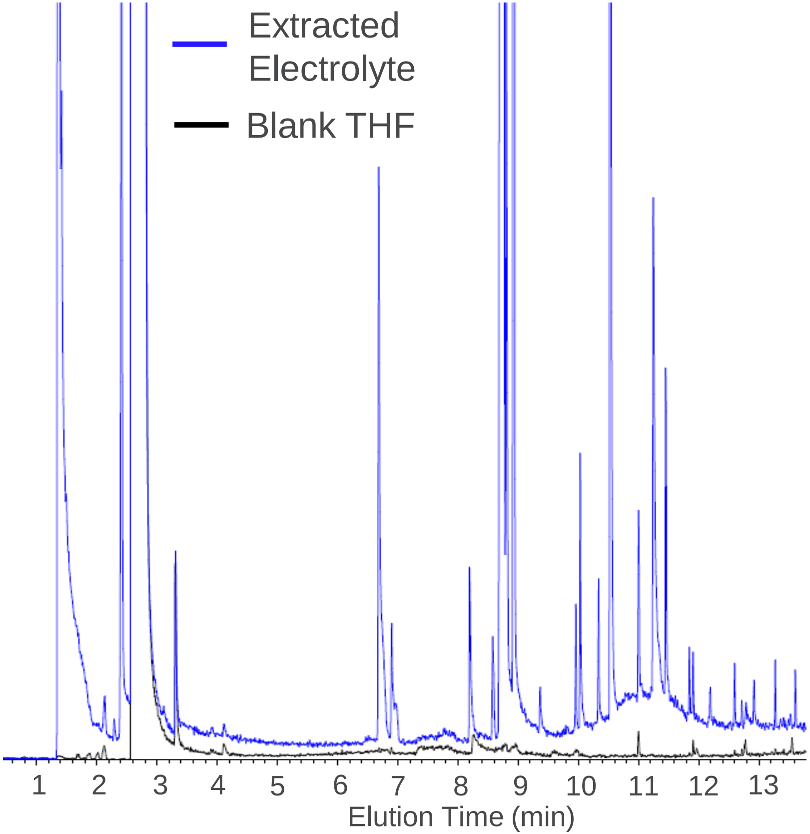
- Utilized cycled commercial battery electrodes to extract electrolyte from
- Solvents chosen were acetonitrile (ACN), dimethyl formamide (DMF), tetrahydrofuran (THF), and diethyl carbonate (DEC)
- All extracts contained similar components (showing THF)
  - Carbonates, EC decomposition product, small quantities of other unknown compounds



ELECTROLYTE COMPONENT RECOVERY

Analysis of Extracted Electrolyte (GC-MS)

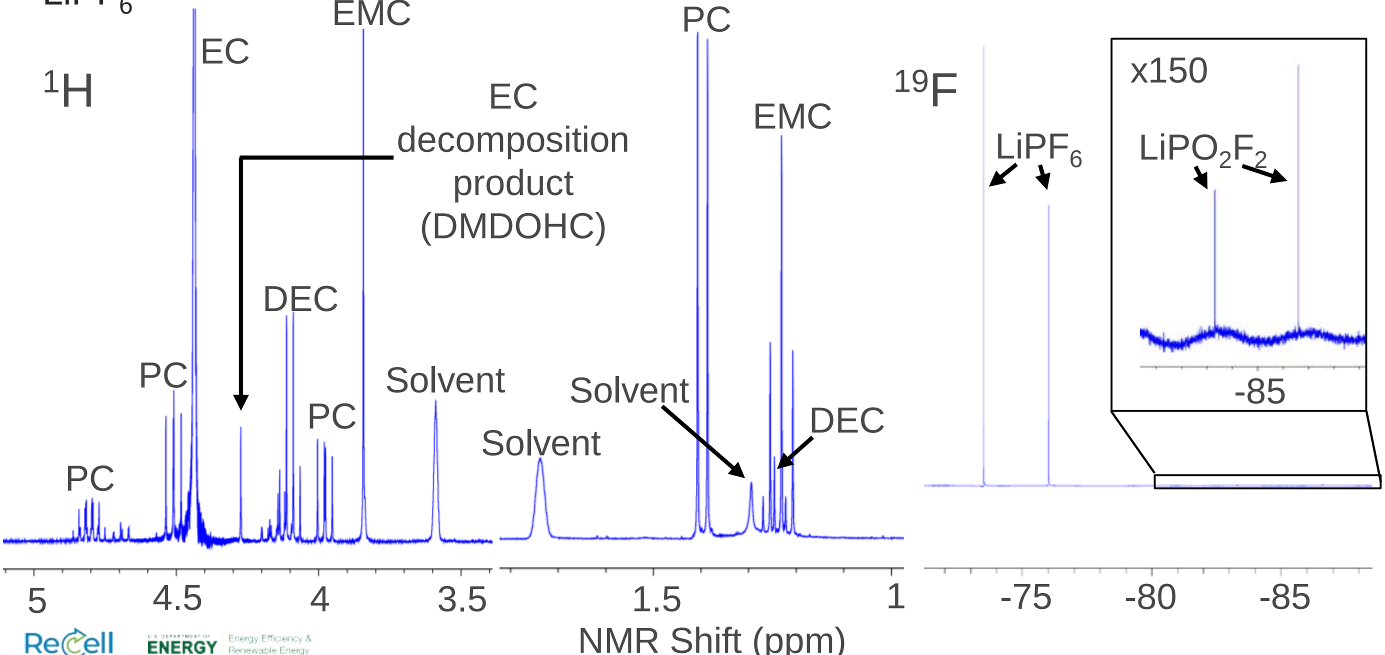
- THF peak at 2.607 min
- Most prominent THF + Cathode peaks
  - POF$_3$ at 1.360 min (25.996%)
  - EC at 8.758 min (31.670%)
  - PC at 8.932 min (8.058%)
  - Possible organosilicon compound at 10.534 min (8.999%)
- All other peaks > 0.5% have large molar masses, suggesting complex structures



ELECTROLYTE COMPONENT RECOVERY

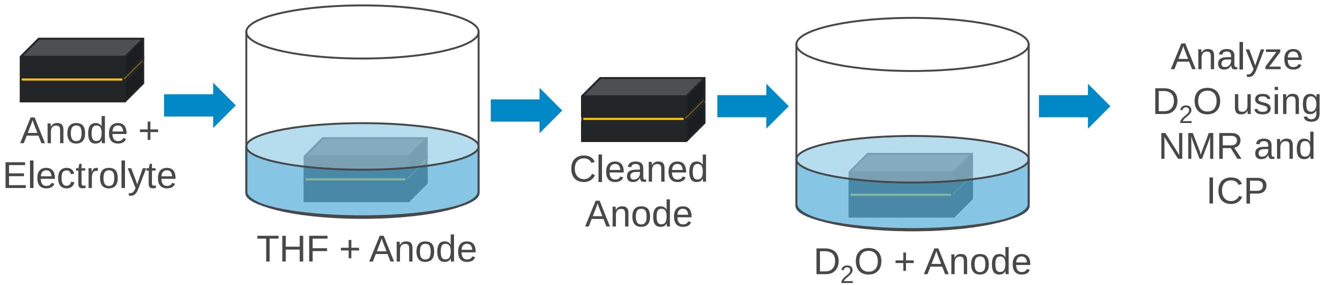
Analysis of Recrystallized Electrolyte (re-dissolved for NMR)

- Evaporating off the volatile solvents leaves behind fewer impurities. No obvious deleterious compounds remaining
- In DEC (shown) and DMF there was a similar amount of $LiPO_2F_2$ as the just-extracted electrolyte. ACN and THF showed substantial hydrolysis of the $LiPF_6$

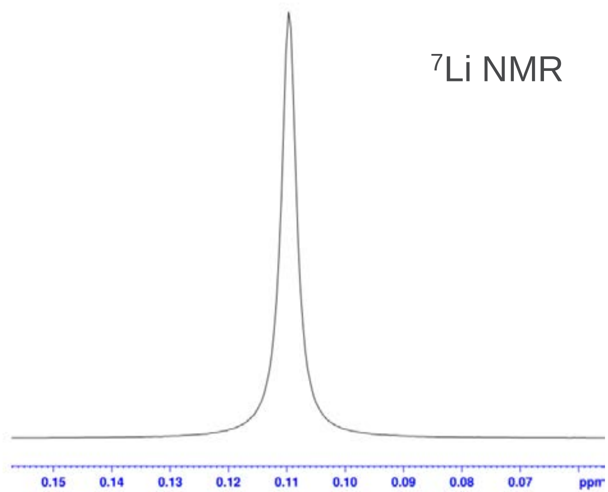


ELECTROLYTE COMPONENT RECOVERY

Possibilities for extracting additional Li from the anode



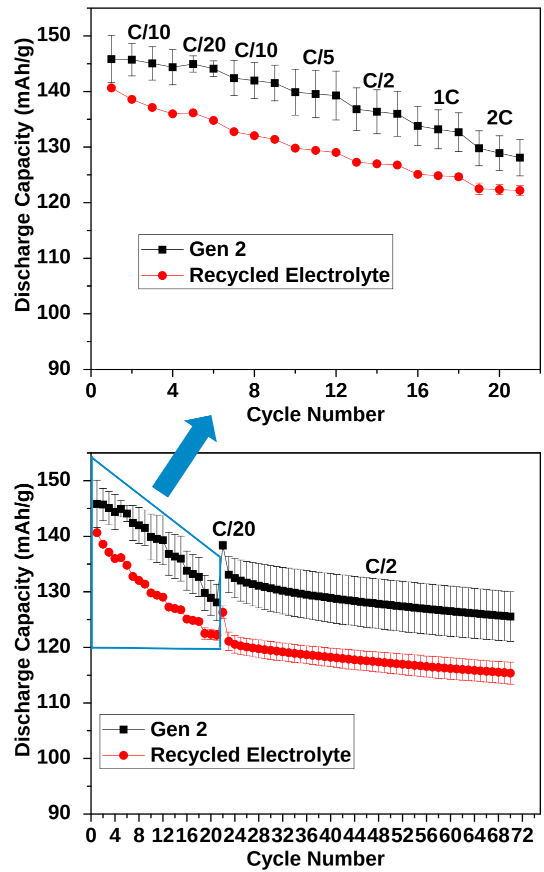
- Li appears to be a single species in the solution
  - Likely $LiCO_3$ or LiOD
- ICP indicates 2.2 wt.% Li in the anode that could be extracted by water
  - This corresponds to about 16% of the Li that was in the cathode



ELECTROLYTE COMPONENT RECOVERY

Electrochemical performance of recovered salt in full cell

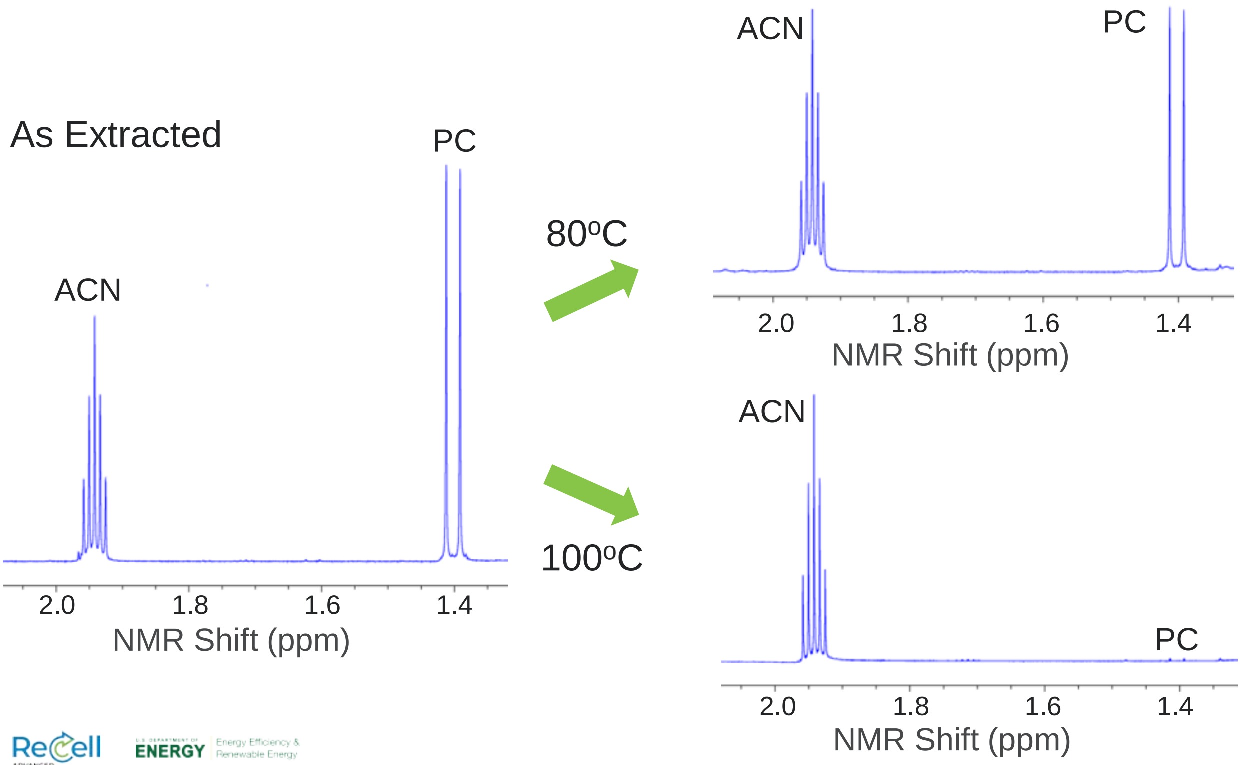
- Recycled electrolyte shows capacity fade in the initial cycles
  - This electrolyte contains PC, which requires additives to prevent degradation of the graphite anode
    - Insufficient additives likely remain to effectively mitigate this issue
  - PC either needs to be removed or additives added
- Rate performance is good despite capacity fade



ELECTROLYTE COMPONENT RECOVERY

Purification of $LiPF_6$

- Effectively removed PC using a vacuum oven at 100ºC
  - Real process will require a process without vacuum



ANODE/CATHODE SEPARATION

- Evaluate multiple methods of separation and purification
  - Screening, air classification, and magnetic separation
- Characterize real black mass from end of life cells
  - Identify contaminants
  - Identify and characterize materials requiring removal
- Create model black mass for experimental use
  - Start with simple binary mixtures
  - Increase complexity of mixtures as techniques are refined
- Economic evaluation of separation methods
- Down select most effective methods

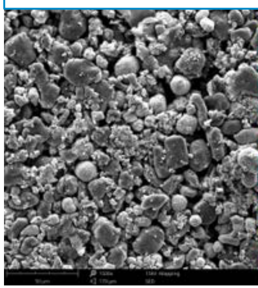
ANODE/CATHODE SEPARATION

Technical Accomplishments – Study of Black Mass

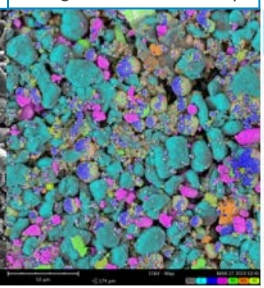
- Black mass from shredded, unsorted end of life lithium ion cells was analyzed using various methods
  - Multiple cathode chemistries were present
    - NMC, LMO, LFP, NCA, LCO
  - Abundance of 5-20 µm aluminum and copper particles were found

ICP-OES full Spectrum Scan							
Mg (0.1)	Ca (3.2)	Mn (13.8)	Fe (0.2)	Co (32.0)	Ni (28.8)	Cu (0.5)	Cd (0.4)

SEM

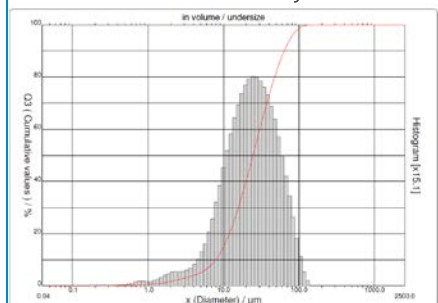


Merged Elemental Map



Atom	%
C	70.52%
O	16.01%
Co	4.09%
Ni	3.05%
Mn	2.27%
Fe	1.91%
Al	1.11%
Cu	1.04%

Particle Size Analysis

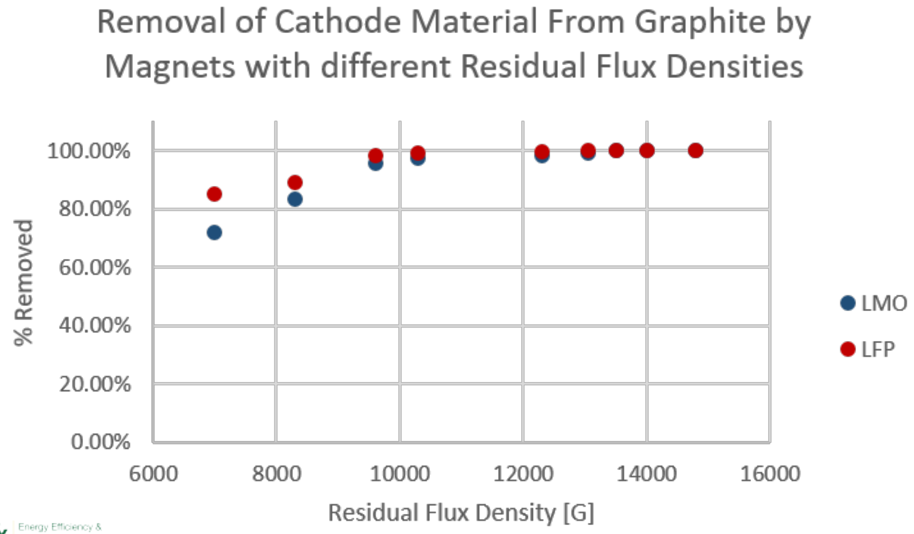


d50 : 24.54 µm	Average : 30.84 µm

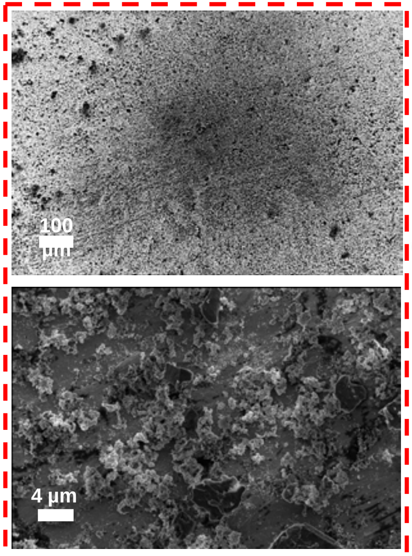
ANODE/CATHODE SEPARATION

Technical Accomplishments – Magnetic Separation

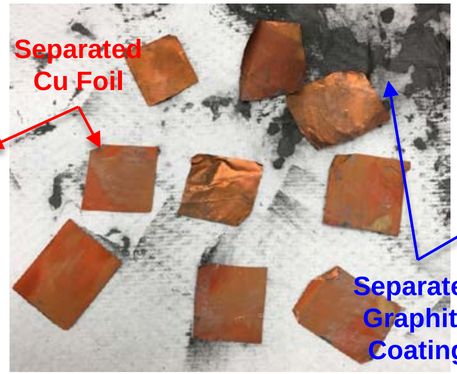
- Model black mass was created using 50/50 mixtures of LMO/graphite and LFP/graphite
- Test were conducted with various AlNiCo, SmCo and NdFeB magnets
- Separation quickly approaches 100% once neodymium based magnets are used.

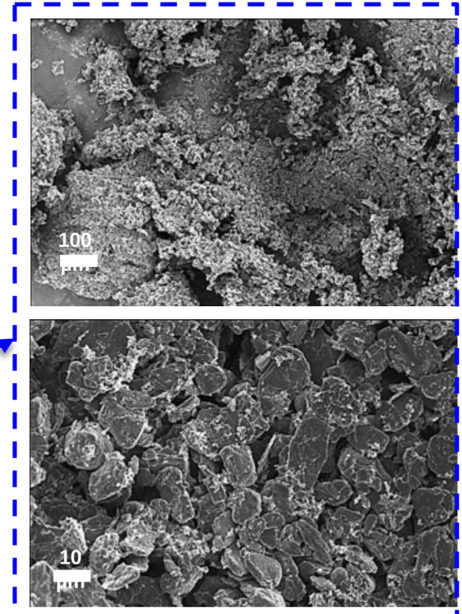


HYDROTHERMAL DELAMINATION OF ELECTRODES – ANODE



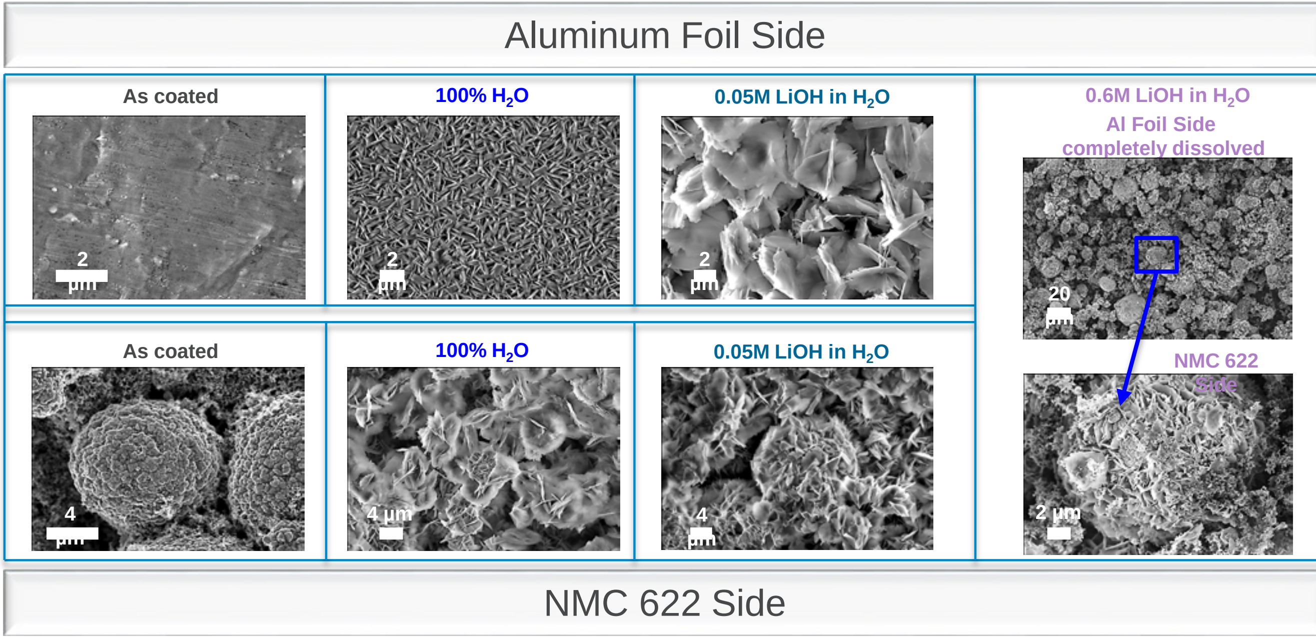
0.6g of Graphite coated on Cu foil in 20 mL H_2O (100% H_2O) at 170°C for 24h





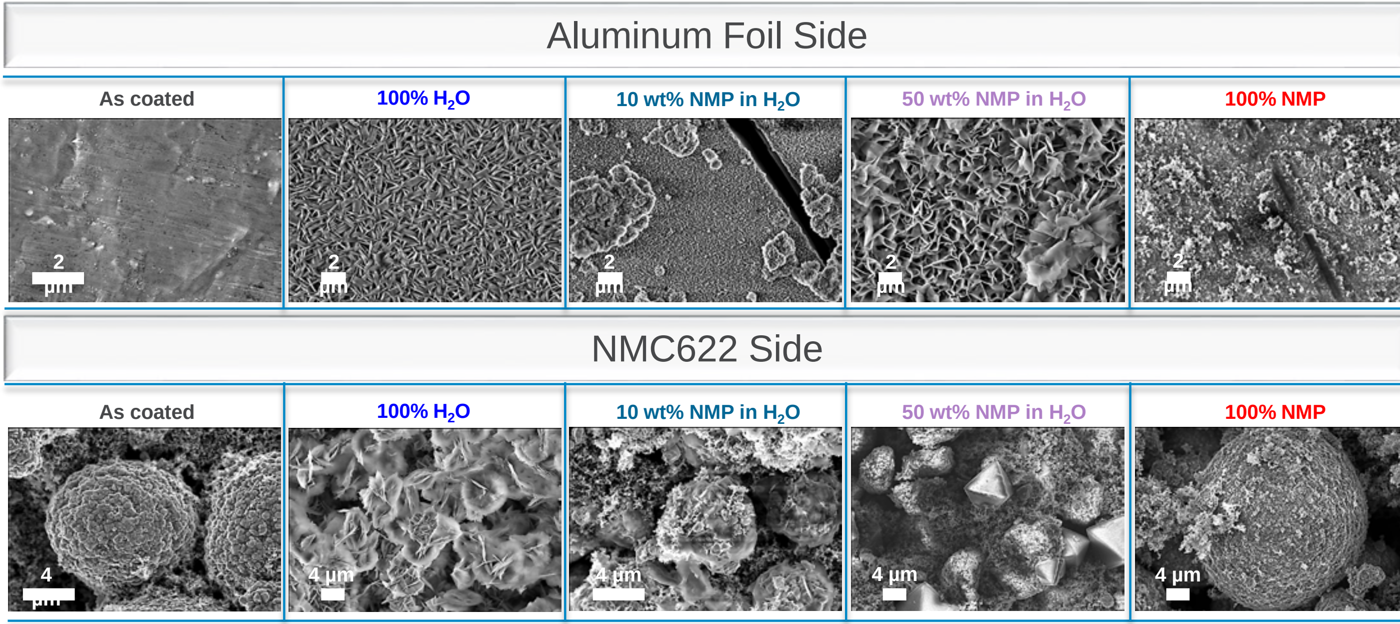
Separation and recovery of anode (graphite coating and copper) was easily achieved through the hydrothermal treatment in DI water at 170 °C for 24 hrs

HYDROTHERMAL DELAMINATION OF ELECTRODES – CATHODE



Black mass was recovered from NMC622 cathode and Al was dissolved in basic solution through hydrothermal treatment (170 ºC; 24h; 20 mL solvent; 0.6 g sample).

HYDROTHERMAL DELAMINATION OF ELECTRODES – CATHODE



Corrosion in aluminum was observed in hydrothermal treatment owing to the presence of mild base (LiOH) when treated with DI water – NMP mixture (170 ºC; 24h; 20 mL solvent; 0.6 g sample).

RESPONSE TO REVIEWERS

- **New Project FY19**

REMAINING CHALLENGES AND BARRIERS

- In an actual industrial setting the composition of the feedstock will likely vary from day to day and change over time as battery technology changes
- The recycling technology must be robust enough to accommodate variable feedstock
- The processes developed to separate and purify each particular component of the cell must be compatible one another.
- Current generation electrolytes are formulated as a complex mixture of salt(s), carbonate solvents and various additives
- In order to create a reusable product the output electrolyte or salt needs to be a consistent product (composition, concentration, purity, impurity profile)
- Pre-processing (shredding and/or thermal treatment) may convert $LiPF_6$ into several different Li species, useless or harmful, if used in a new electrolyte
- Direct recycling of graphite from end of life cells will require separating many materials to achieve high purity products.

FUTURE WORK

- Determine the necessary level of purification for each electrolyte component recovered
- Investigate other methods of electrolyte component removal and recycling (thermal treatment for removal of volatile organics, supercritical CO2)
- Feasibility of water washing (anode fraction) to improve recovery of Li
- Impact of pre-processing (shredding, thermal treatment) method on recoverable electrolyte components quantity and purity
- Feasibility of a simple magnetic separation of additional cathode materials
- Separation of model black mass components using multiple methods (density, size, magnetism, conductivity)
- Electrochemical testing of recovered components (electrolyte, graphite)
- Optimize process parameter for hydrothermal delamination (anode and cathode)
- Design and investigate continuous process for hydrothermal delamination.
- Cost modeling of the processes to determine potential of profitability

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

SUMMARY

- We used actual EV battery cells to study multiple aspects of electrolyte components extraction from cathode and anode, qualitative and quantitative depend on the solvent used.
- We used various analytical techniques to investigate chemistry and purity of recovered electrolyte components.
- Cells (coin cell format) were assembled and cycled to assess usability of recovered materials as a new electrolyte.
- A hydro/solvothermal process for electrode delamination was investigated. We demonstrated that delamination can be cleanly achieved without using any auxiliary chemicals.
- Black mass from shredded, unsorted end of life lithium ion cells was analyzed using various analytical techniques.
- Model mixture of cathode and anode powders were used to successfully separate the materials based on their magnetic properties.
- Data collected during the process development are being added to the EverBatt model

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