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Recycling and Recovery of Active Materials in Aged Commercial Lithium-Ion Batteries/Cells

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NAATBatt LITHIUM BATTERY RECYCLING WORKSHOP VII
August 7 – 9, 2024

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Introduction

The increasing use of lithium-ion batteries (LIBs) across various applications has raised concerns about their excessive accumulation at the end of life and the potential environmental impact of this accumulation.

UL is committed to **Building Resilience for a Sustainable Future**. As part of this commitment, the Electrochemical Safety Research Institute (ESRI) at UL Research Institutes is dedicated to investigating the recycling of LIBs to deliver an effective and sustainable solution.

- To address LIBs end-of-life management safety
- To mitigate the shortage of valuable transition metals for global sustainability
- To alleviate the negative impact globally
- To potentially conserve the natural resources

https://ul.org/library/safety-recycling-lithium-ion-batteries

https://progress.ul.org/#science-for-a-safer-world

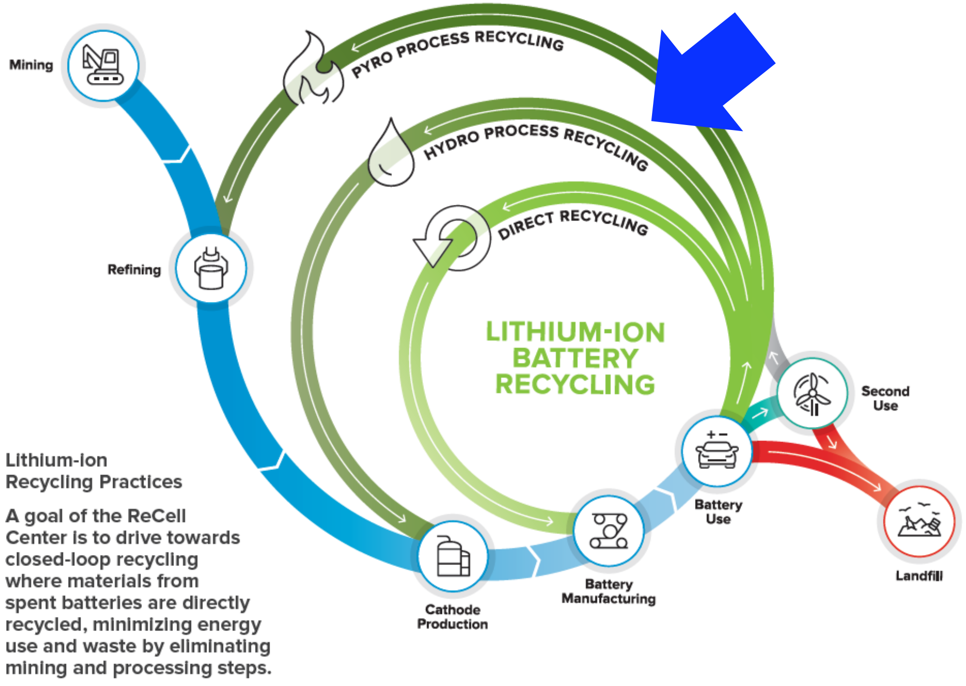
Research Objectives

ESRI initiated a collaborative effort with Professor Pulickel M. Ajayan and his team at Rice University on understanding and optimizing the recycling and recovery processes, focusing on an efficient and environmentally friendly hydrometallurgical pathway for recovering cathode materials.

RICE — Team — UL Research Institutes

Approaches:

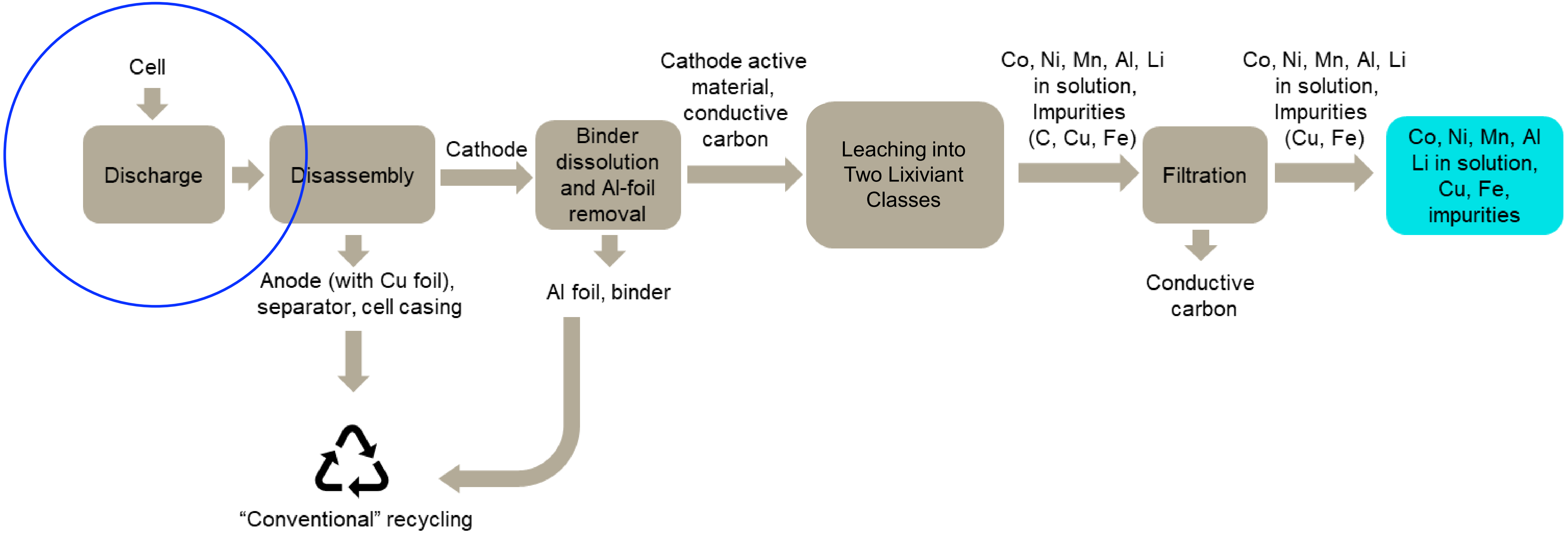
1. The Study of Cell Discharge in Salt Solutions
2. The Study of Hydrometallurgical Leaching with Two Lixiviant Classes.
3. Optimization of Cathode Materials Precipitation Pathways



https://recellcenter.org/research/

Processes:

Hydrometallurgical recycling of lithium-ion batteries: Pre-treatment and leaching.

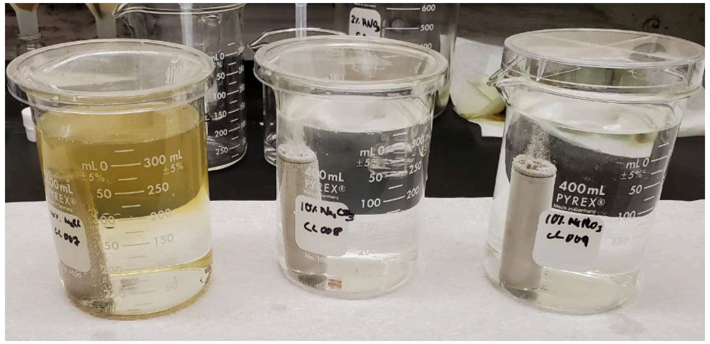


1. *The Study of Cell Discharge in Salt Solutions*

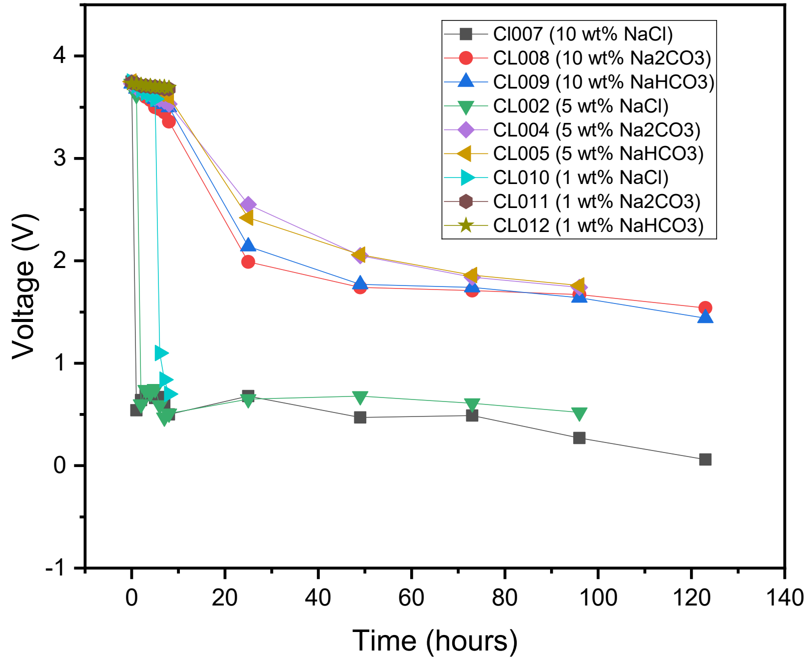
→ Cells were discharged by immersing them in various concentrations of salt solutions instead of using battery recyclers, followed by cell composition determination.

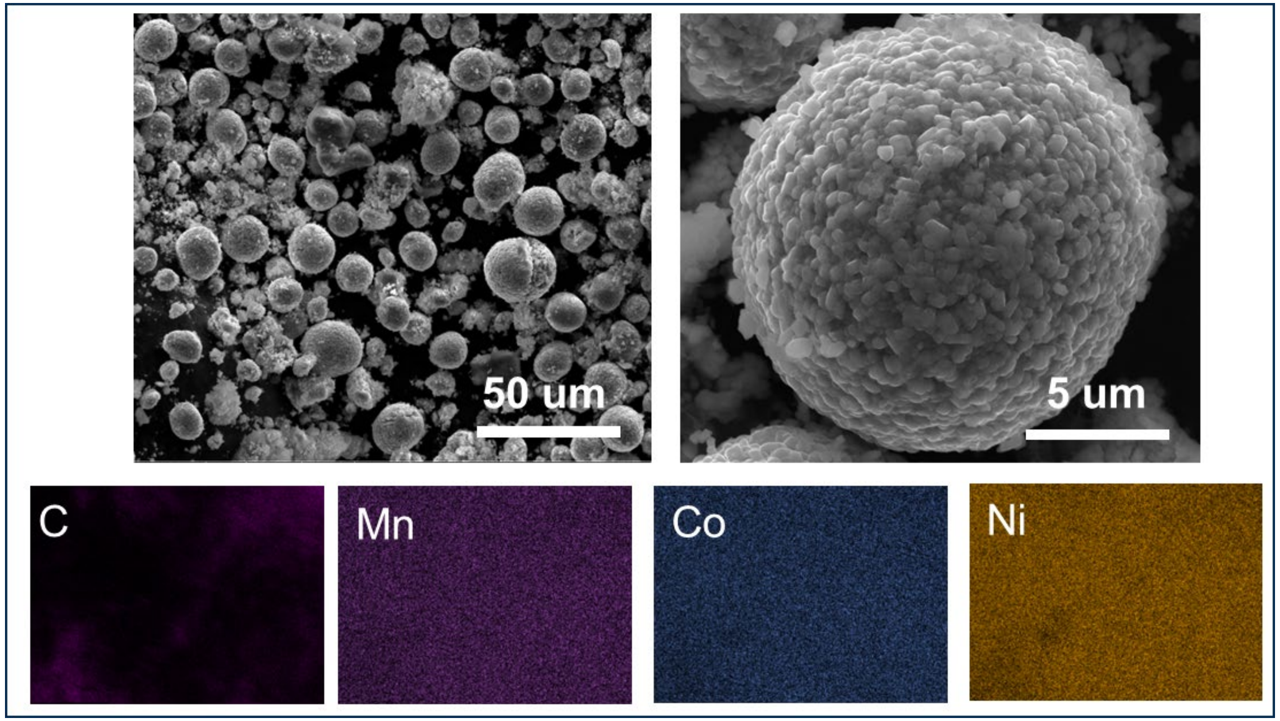
1. The Study of Cell Discharge in Salt Solutions – Cylindrical cells

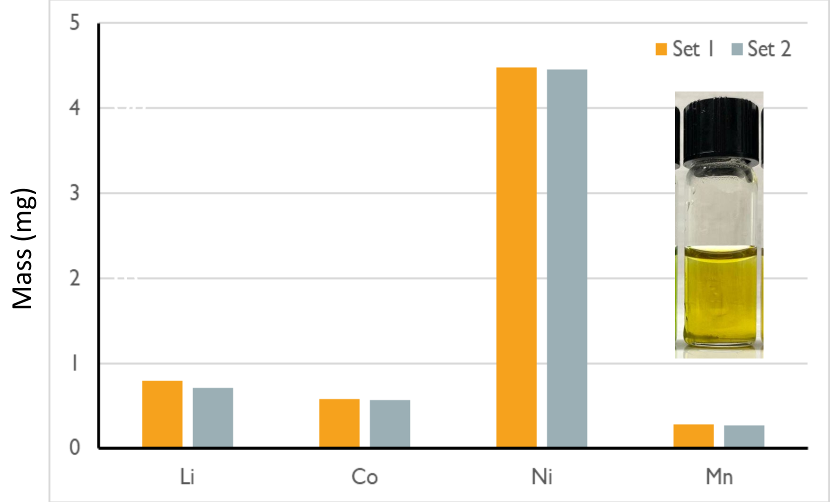
- *To determine the commercial cylindrical cells' composition*



Cylindrical cell samples were discharged by immersing them in various salt solutions. The reaction was followed by measuring the drop in voltage over time. Results show that in 8h, all cells immersed in NaCl salt solutions *(1%, 5%, 10% wt.)* were discharged below 1V, and within 48h, all cells with *Na_2CO_3 and $NaHCO_3$ salt solutions (1%, 5%, 10% wt.)* were below 2.5V.



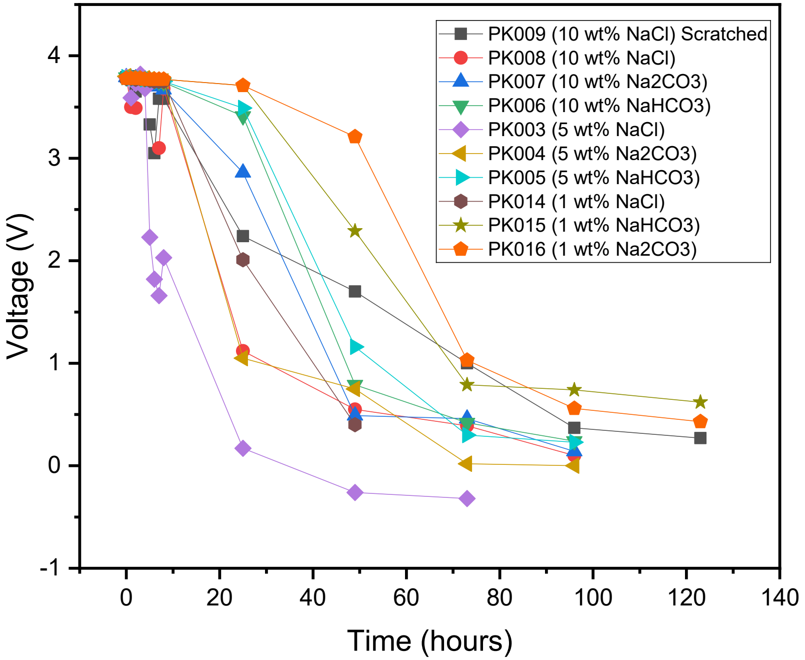




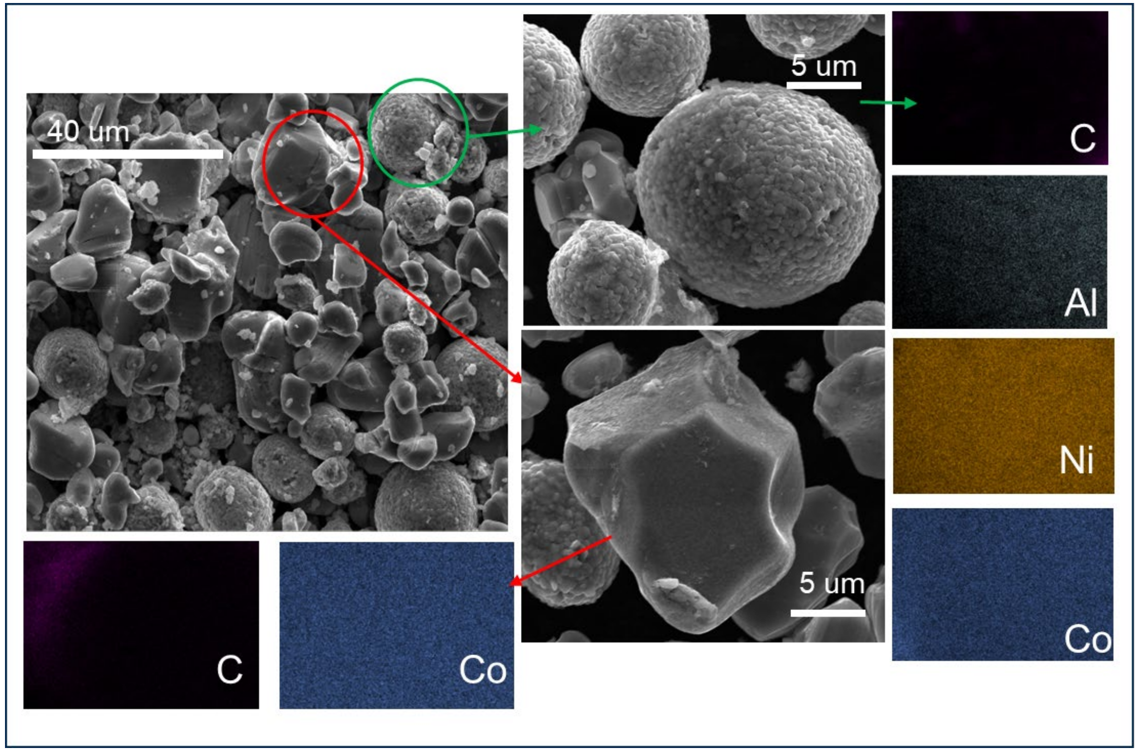
The pouch cell composition was determined to be a single type of cathode chemistry by FESEM and ICP-OES → NMC

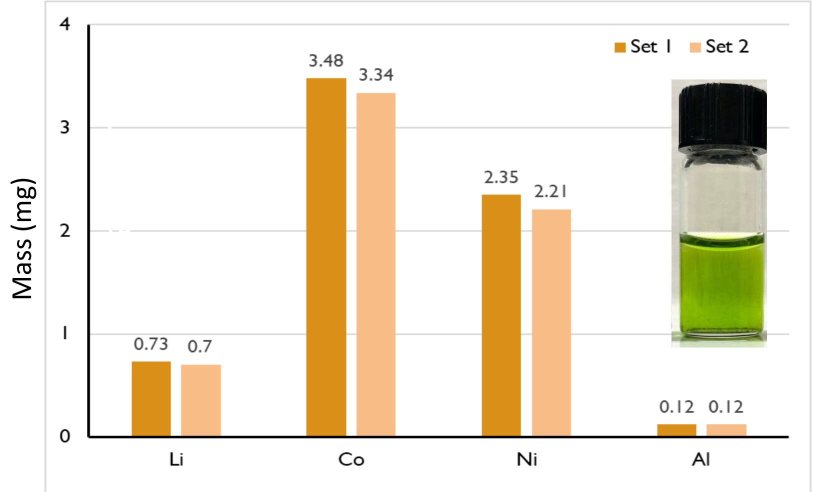
1. The Study of Cell Discharge in Salt Solutions – Pouch Cells

- *To determine the commercial pouch cells' composition*



Pouch cell samples were discharged by immersing them in various salt solutions. The reaction was followed by measuring the drop in voltage over time. Only one sample with surface scratching. Results show that after 48h, all cells were discharged below 2.5V, except *Sample PK016 (1 wt.% Na_2CO_3)* and the surface scratching does not speed up the discharge process.

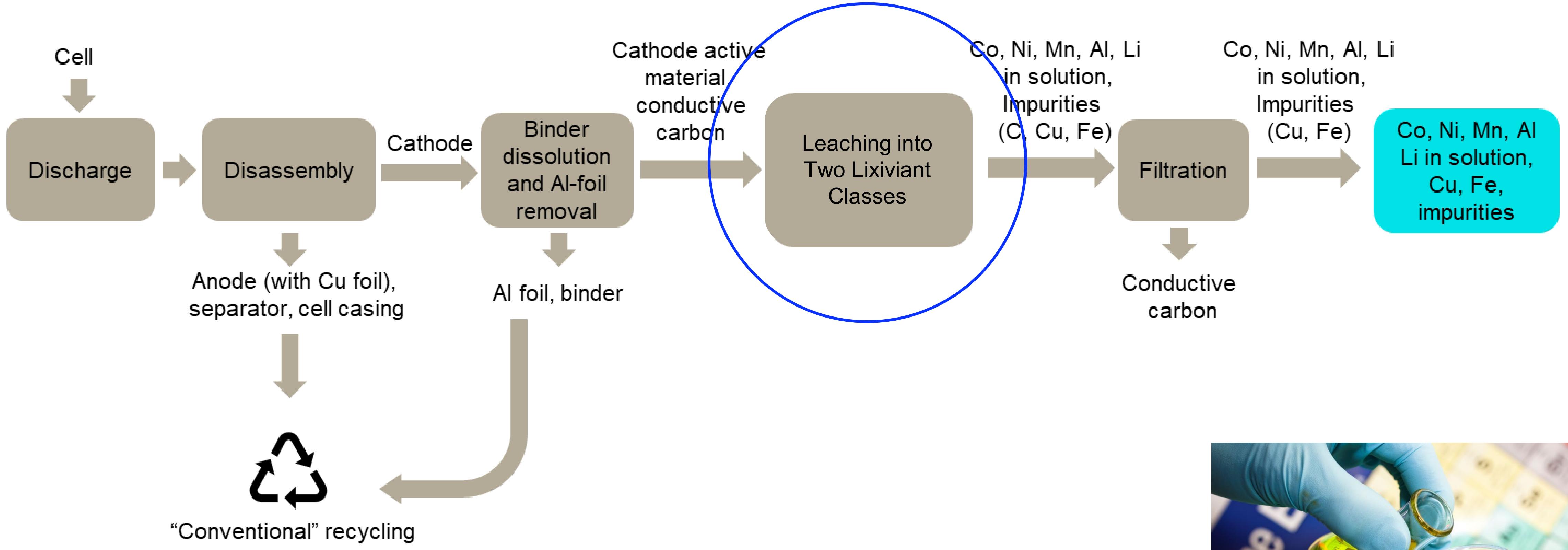




The pouch cell composition was determined to be two types of cathode chemistries by Rietveld refinement of PXRD pattern, FESEM, and ICP-OES → LCO and NCA

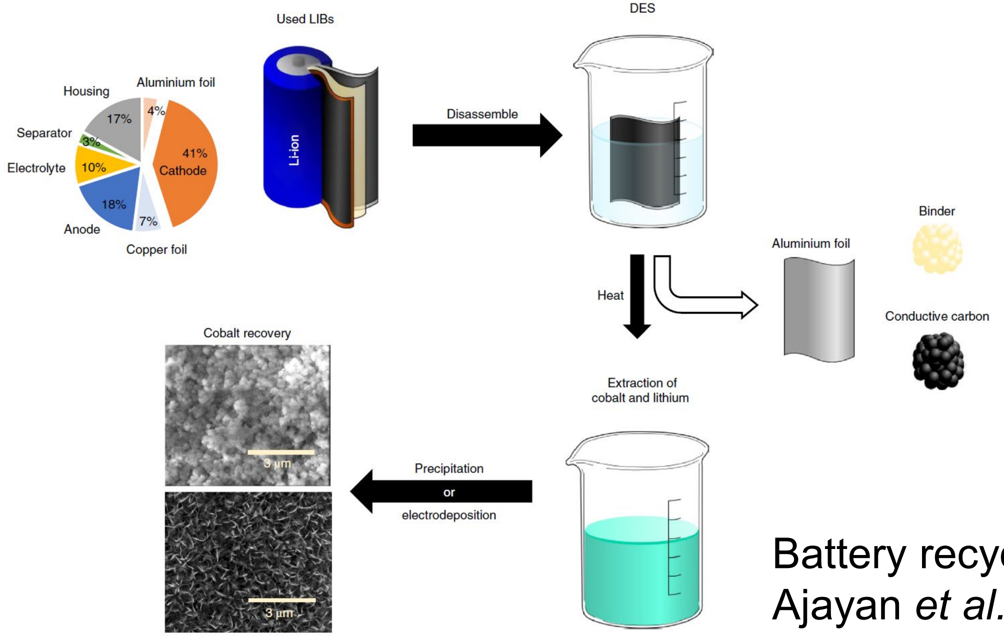
Processes:

Hydrometallurgical recycling of lithium-ion batteries: Pre-treatment and leaching.



2. *The Study of Hydrometallurgical Leaching with Two Lixiviant Classes*
   → To compare and optimize the leaching efficacies using inorganic acids and deep eutectic solvents (DES) with a "greener" approach

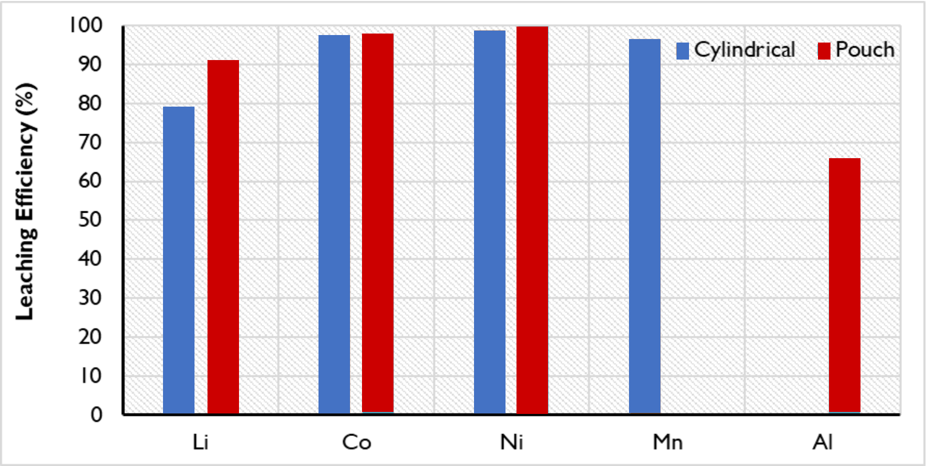
2. The Study of Hydrometallurgical Leaching with Two Lixiviant Classes



Results were compared between a traditional hydrometallurgical leaching process, which utilizes inorganic acids, and an alternative approach using a safer solvent blend designated as a "deep eutectic solvent" (DES), a development from Ajayan's team at Rice University. (Patent no.: US11,591,670 B2)

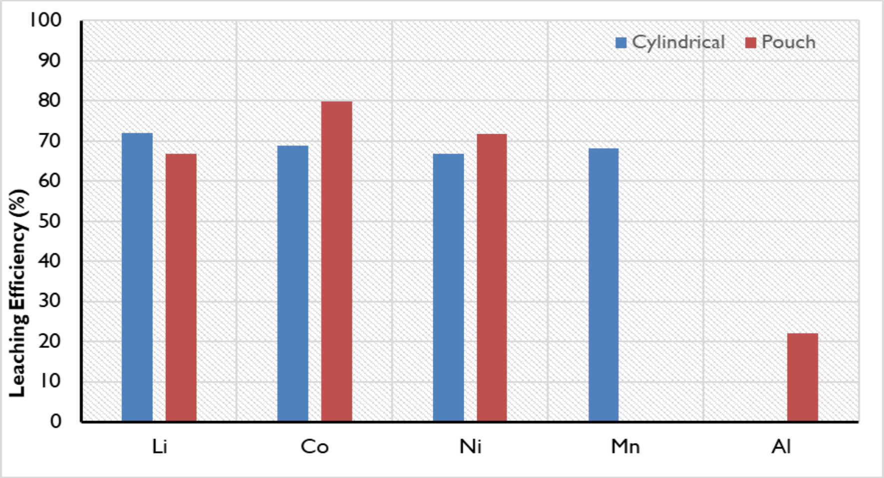
Battery recycling using DES
Ajayan *et al.*,2019

Leaching in inorganic acids



The leaching process with inorganic acids achieves over 90% efficiency for most elements analyzed by ICP-OES.

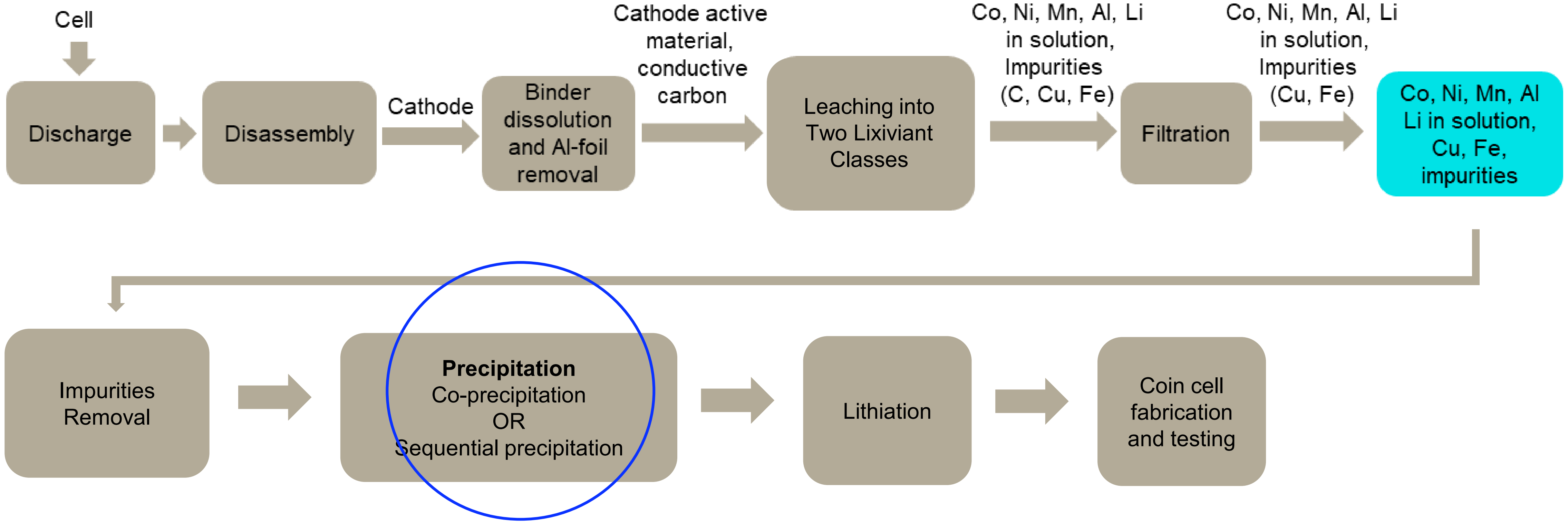
Leaching in DES



The leaching process with DES demonstrates lower efficiency; however, the efficiency increases significantly after optimizing the DES formulation.

Processes:

Hydrometallurgical recycling of lithium-ion batteries: Pre-treatment and leaching.



3. *Optimization of Cathode Materials Precipitation Pathways*

→ Co-precipitation and sequential precipitation were conducted to separate the valuable transition metals.

Co-precipitation: using a single-chemistry cathode

Sequential precipitation: utilizing a blended chemistries system

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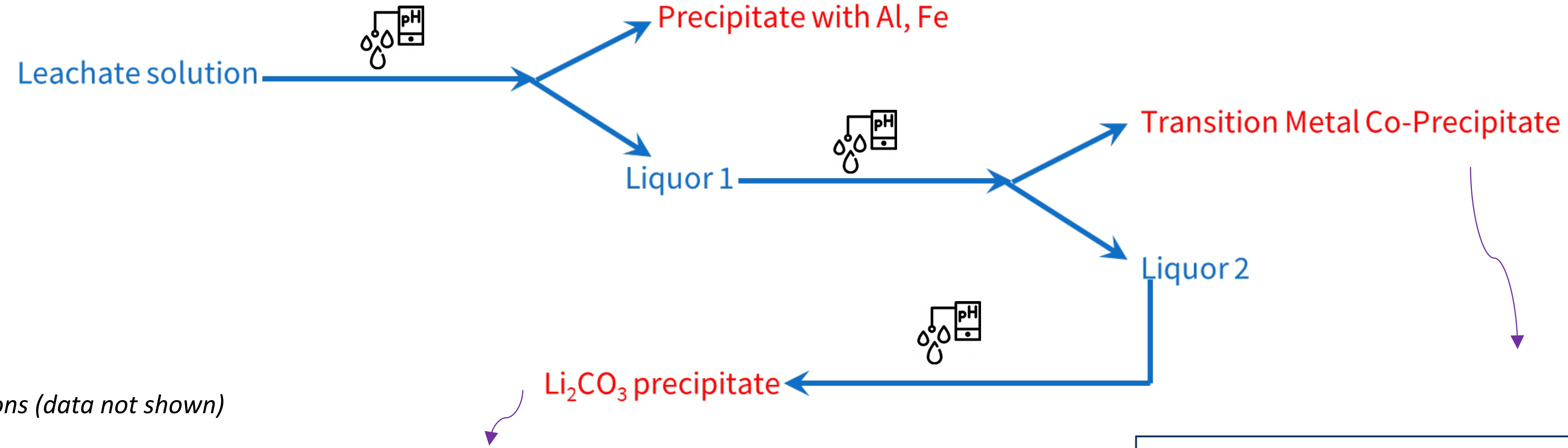
3. Optimization of Cathode Materials Precipitation Pathways

Co-precipitation



Lithiation and heat treatment reactions (data not shown)

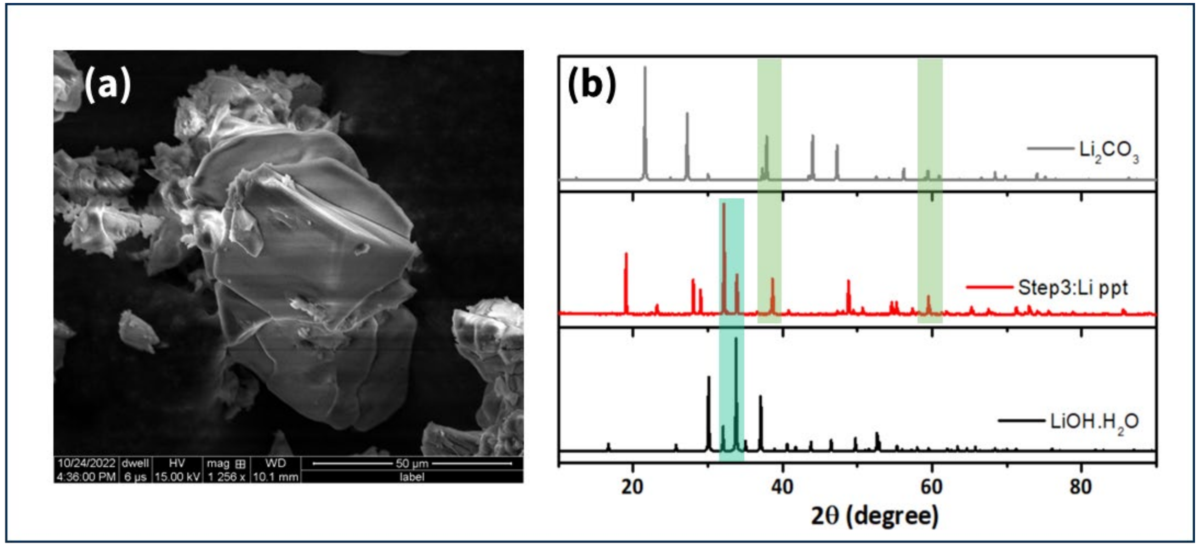


Figure 24 **(a)** SEM of the Li precipitate. **(b)** PXRD patterns of the precipitate.

Table 1: Precipitation percentages of different metals from the leachate

Element	Precipitation%
Co	98.9
Ni	97.6
Mn	94.3

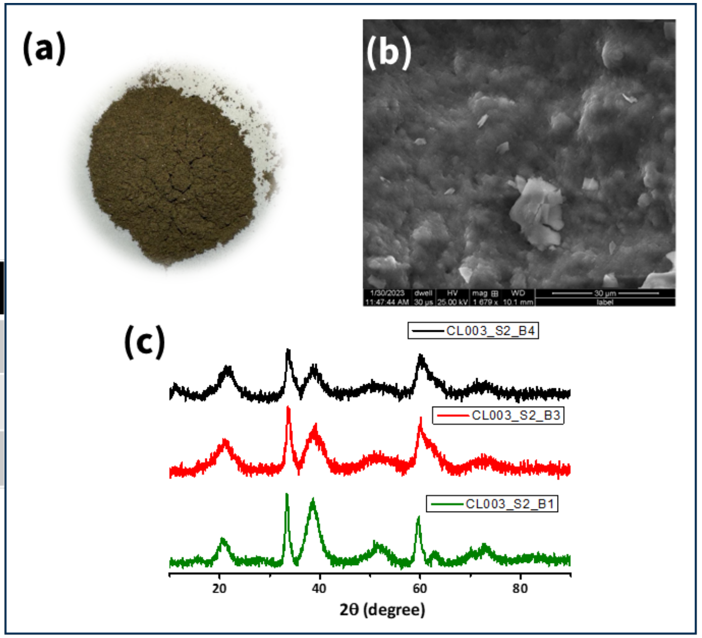
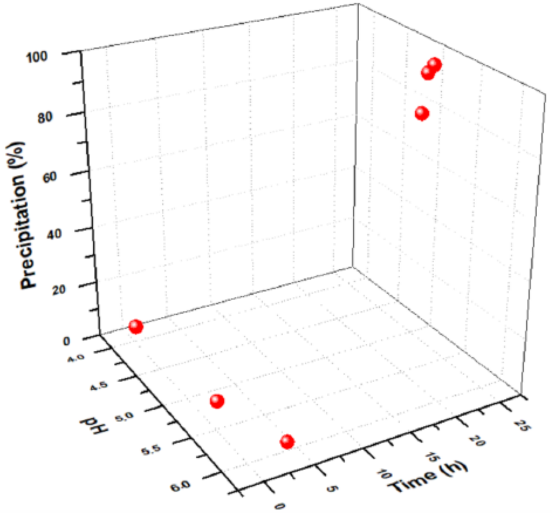


Figure 23 **(a)** Photograph of the precipitate. **(b)** SEM image of the precipitate. **(c)** PXRD patterns of the precipitates.

→ Co-precipitation is more suitable for single cathode chemistry, as it attempts to maintain the stoichiometry of the recovered cathode materials before lithiation.

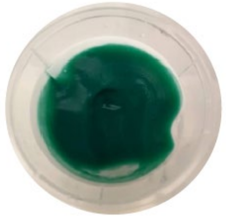
Sequential precipitation



Al precipitate (%) conditioned at different pH over time (h).

STEP 1: Al Removal Leachate Solution → $Al(OH)_3$ precipitate (ppt) + Filtrate 1

STEP 2: Ni Removal → Filtrate 2 + Ni-DMG ppt



A mixture of Co and Ni precipitates was detected by ICP while adjusting the pH.

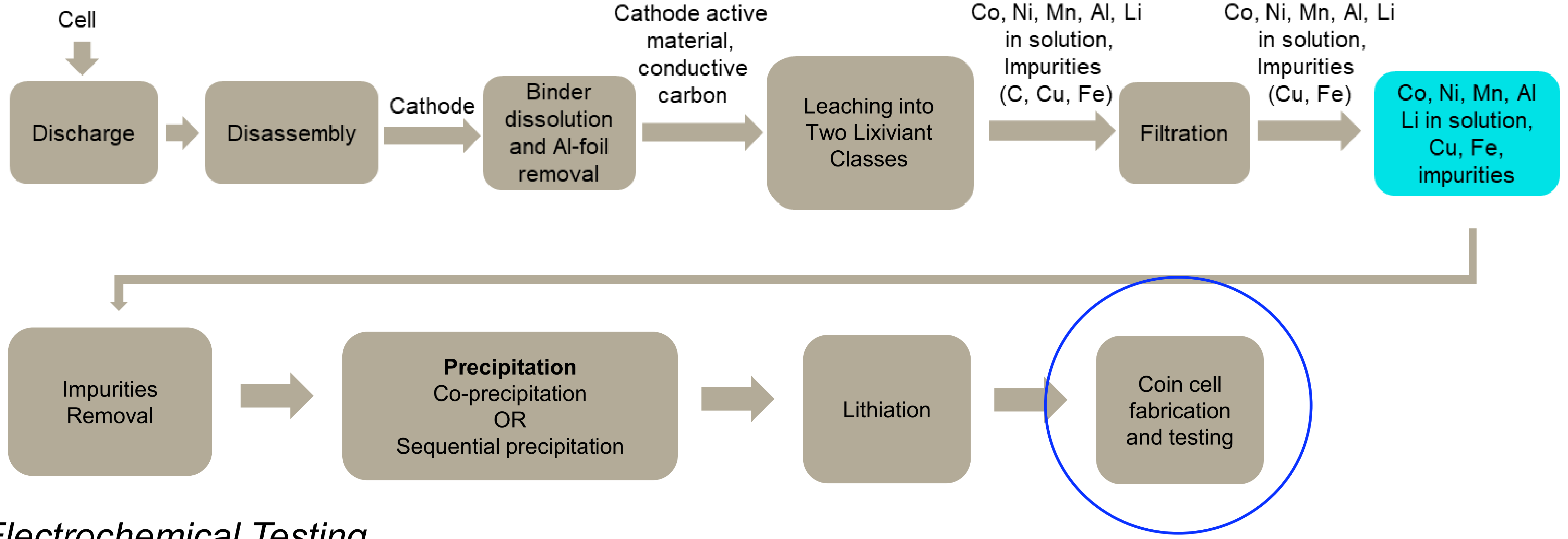
STEP 3: Co Removal → Filtrate 3 + $Co(OH)_2$ ppt

STEP 4: Li Removal → Filtrate 4 + Li_2CO_3 ppt

→ The sequential precipitation reaction is better suited for blended cathode chemistries to separate individual metals for recycling.

II. Processes:

Hydrometallurgical recycling of lithium-ion batteries: Pre-treatment and leaching.



Electrochemical Testing

→ Closing the loop by lithiating the recycled cathode materials, followed by fabricating coin cells for performance evaluation. (preliminary results not shown.)

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Research Findings

1. *The Study of Cell Discharge in Salt Solutions*

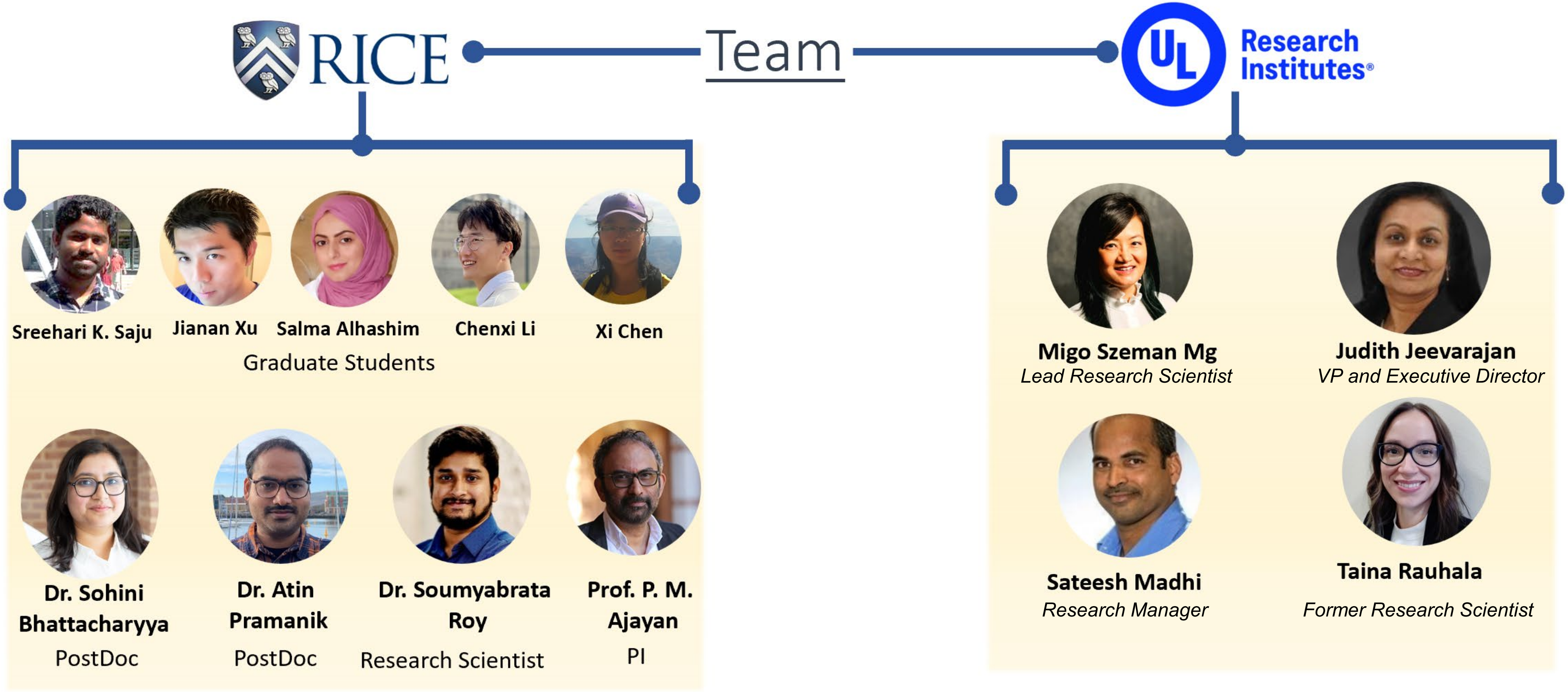
   - Discharge methods for two different Li-ion cell formats were established using salt solutions with specific combinations and concentrations.

2. *The Study of Hydrometallurgical Leaching with Two Lixiviant Classes*

   - An optimized protocol and lixiviant concentration for efficient leaching of cathode materials using inorganic acids was established, enabling more effective and sustainable extraction.
   - DES combinations were explored as a sustainable and eco-friendly alternative for effectively leaching cathode materials.

3. *Optimization of Cathode Materials Precipitation Pathways*

   - An optimized procedure for co-precipitation from an inorganic acid leach solution has been developed.
   - In a sequential precipitation process, it is possible to achieve 99% precipitation of aluminum, and the separation of Co and Ni needs further optimization.



Manuscript under preparation

In addition …

Besides our collaborative research effort, **UL | ESRI** is also involved in public safety campaigns and initiatives to proactively raise public awareness and advocate the importance of battery recycling through knowledge sharing and education.

UL ESRI
PUBLIC SAFETY CAMPAIGNS AND INITIATIVES

Be Nice To Your Device

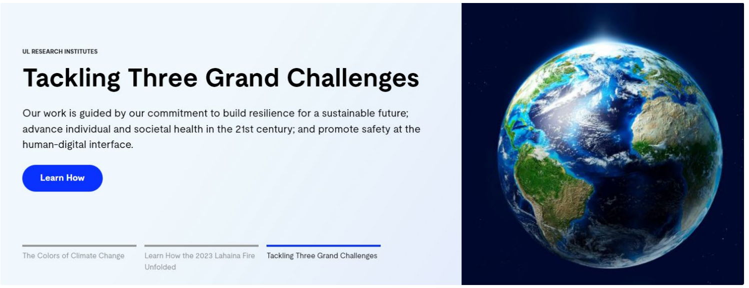
https://benicetoyourdevice.org/

Summer Internship 2024 Direct Recycling

Conference & Publication

UL Research Institutes

Thank you



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