

# Recycling EV waste: A materials challenge and industrial opportunity?

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ReLiB – Short loop recycling

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# Critical elements required for batteries



Production of key elements required for battery manufacture (such as Lithium and Cobalt) are limited to a small number of countries.

With the electric car revolution and move towards renewable technology, competition for such resources will inevitably increase.

Co is expensive and 60% of production is currently concentrated in the DRC (mining linked with human rights abuses).<sup>1</sup>

In addition, if current demand continues to rise, models predict that **known reserves of Co and Li will be considerably depleted by 2050**.<sup>2</sup>

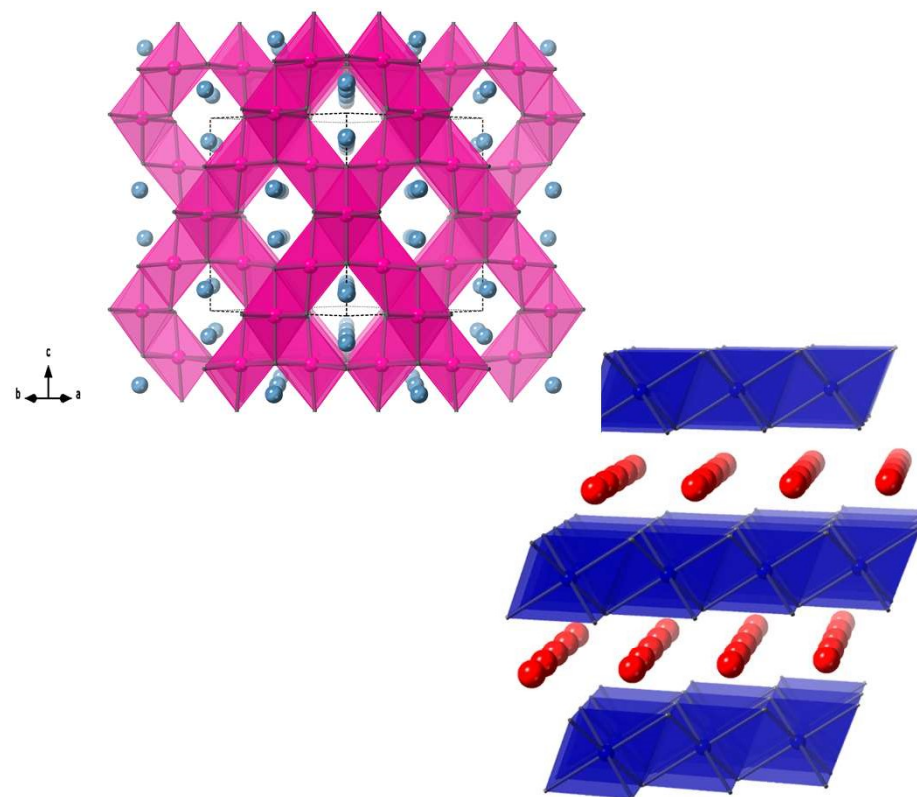
Given the rise in electric vehicles:

- Vital need to develop strategies to recycle of spent batteries
- Opportunity for UK to take a lead in this area → new UK industries

1. [https://wapo.st/2mjkbfk?tid=ss\\_mail&utm\\_term=.8870e57e6160](https://wapo.st/2mjkbfk?tid=ss_mail&utm_term=.8870e57e6160) (accessed 30/10/18)
2. A. Pehlken, S. Albach, T. Vogt, Is there a resource constraint related to lithium ion batteries in cars?, Int. J. Life Cycle Assess. 22 (2017) 40–53.

## Cathodes (present, near-future and future)

- Current on-road EVs: cathodes contain a mixture of **Li-Mn-O(spinel)** and **NMC (layered oxide)**.
- Most car manufacturers focusing on utilising **NMC/NCA** ( $\text{LiNi}_x\text{Mn}/\text{Al}_y\text{Co}_z\text{O}_2$ ), for future EVs (similar properties of  $\text{LiCoO}_2$  but at a much reduced cost).
- Ultimate aim is to move towards compositions containing less Co such as **NMC622** or **811**.



# Challenges of short loop recycling

## *Delivering a cost effective process*

- Current on road EVs Mn rich cathodes:- low resale value
- Greater impetus to recycle **low value** cathodes by recovering the materials and **converting to high value next generation cathodes** (e.g. Spinel → NMC)
- Subsequent repurposing treatments **must be economically justifiable** (avoiding high temperature heat treatments etc.)

## *Gap in characterization of spent batteries*

- Vital need for studies of EV batteries at various SOH (state of health): Identifying any changes that have occurred/contaminants (eg. F) will aid in developing regeneration methodologies.

# The binder problem

- Flawed assumption that the binder is inert. However, previous research in our group has shown that **PVDF is a powerful low temperature fluorination agent (200-400°C)**.
- Although the temperature required for fluorination is much higher than what batteries would normally be exposed to, batteries cycled over many years and/or mistreated may create conditions for substitution to occur.
- Even if fluorination has not occurred during cycling, **fluorine incorporation is likely to be a problem during regeneration**
- Fluorine and oxygen are notoriously difficult to distinguish using common characterization methods.



Journal of Fluorine Chemistry 117 (2002) 43–45



www.elsevier.com/locate/jfluchem

## Poly(vinylidene fluoride) as a reagent for the synthesis of $K_2NiF_4$ -related inorganic oxide fluorides

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### Abstract

In this paper we report an improved route to the synthesis of  $K_2NiF_4$ -related inorganic oxide fluorides, such as  $Sr_2TiO_3F_2$  and  $Ca_2CuO_2F_2$  using low-temperature fluorination of precursor oxides with poly(vinylidene fluoride). Use of this fluorinating agent results in high quality samples, without  $SrF_2$  or  $CaF_2$  or other impurities, which are commonly seen for alternative fluorination routes.

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**Keywords:** Poly(vinylidene fluoride);  $K_2NiF_4$ ; Inorganic oxide fluoride; Low-temperature fluorination

### RSC Advances

#### PAPER

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Chem. Sci., 2012, 3, 4763

### Direct regeneration of cathode materials from spent lithium iron phosphate batteries using a solid phase sintering method

X. Song,<sup>†</sup> T. Hu,<sup>†</sup> C. Liang,<sup>†</sup> H. L. Long,<sup>†</sup> L. Zhou,<sup>†</sup> W. Song,<sup>†</sup> L. You,<sup>†</sup> Z. S. and J. W. Liu<sup>‡</sup>

A direct regeneration of cathode materials from spent  $LiFePO_4$  batteries using a solid phase sintering method has been proposed in this article. The spent battery is firstly dismantled to separate the anode and cathode, and then the cathode plate is soaked in DMAC organic solvent to separate the materials and Al foil at optimal conditions of 30 min at 50 °C and solid liquid ratio of 1:1. SEM and TEM results of the spent  $LiFePO_4$  after separation show that there are some impurities and irregular morphologies with many agglomerations. The spent materials are sintered at appropriate temperatures with doping of new  $LiFePO_4$  at different ratios. Battery capacity regenerated  $LiFePO_4$  can reach over 120 mAh g<sup>-1</sup> at 0.1C discharge conditions, especially highest value of 144 mAh g<sup>-1</sup> with a doping ratio of 3:7 at 700 °C. The rate capabilities performance of batteries made from regenerated  $LiFePO_4$  with doping at 600 °C and generally better than those at 800 °C. All the performances of batteries made from regenerating with pure phase and uniform morphology can meet the basic requirements for reuse.

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### Short communication

### Recovery and heat treatment of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode scrap material for lithium ion battery

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### HIGHLIGHTS

- Solvent method with impregnation (SM) is used to recover  $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$  scrap materials.
- The discharge capacity and the cycle life are close to the original  $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ .
- The recovery method is low cost, high purity, high recovery rate and environment friendly.
- Acetylene black and Al foil can be recovered at the same time with this method.

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### ABSTRACT

Solvent method and solvent method are used to recover  $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$  scrap materials, and the effects of recovery methods and heat treatment on the electrochemical performances for Li-ion battery are investigated in detail. Among these recovered scrap materials, the cathode treated with solvent method display the best electrochemical performances, the discharge capacity and the cycle life are close to that of the original  $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$  raw material. Particle size distribution, tap density and recovery rate of scrap materials are also investigated. In addition, acetylene black and Al foil can be recovered at the same time with solvent method.

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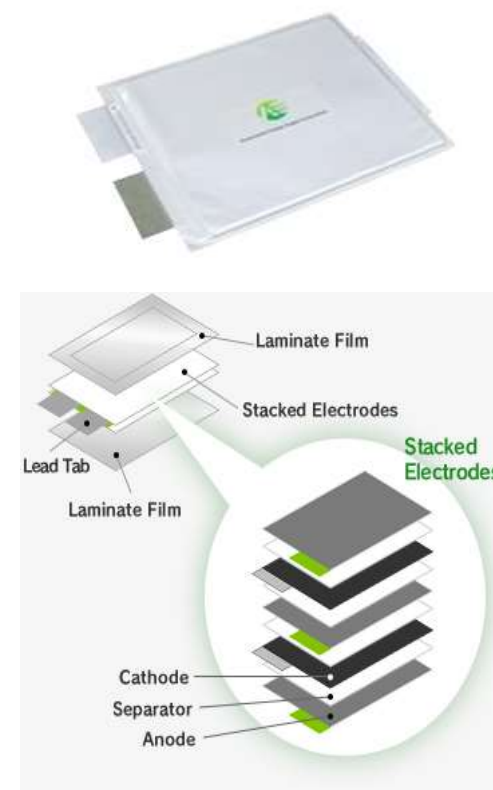
diamond

# Tackling the characterization gap

## Diamond proposal

*Investigations of failure mechanisms in real Li ion battery pouch cells and its implications on recycling*

- In depth study looking at batteries in **various SOH** (Pristine, QA failed and end of life). To date, most studies tend to focus on catastrophic failure whereas this study will aim to identify potential issues with batteries entering the recycling chain. This should aid in **improving the efficiency of any subsequent regeneration experiments.** (March 2019)





# Current short loop methods

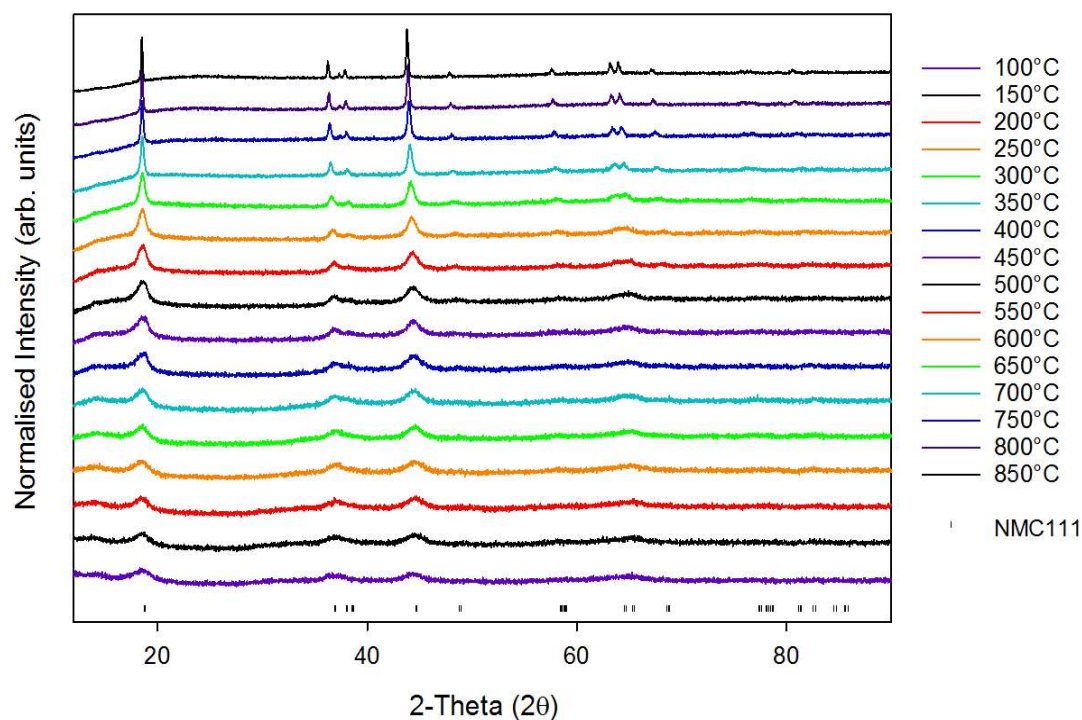
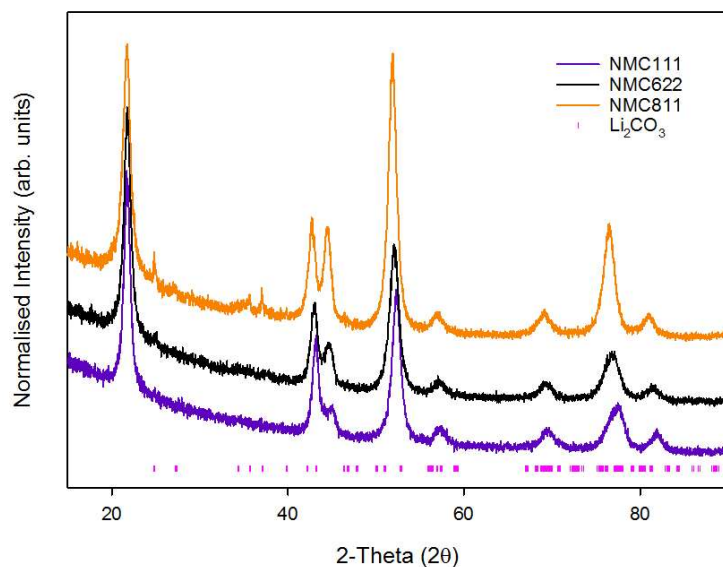


# Developing low T regeneration routes

In order to investigate potential regeneration routes, regeneration studies performed using solutions that would be typical for a standard leaching procedure → newly developed ReLiB project methodologies

Able to synthesize NMC at an intermediate (550°C) and low (100°C) temperatures

Joint ISIS/diamond proposal submitted to study changes in structure of NMC (synthesised at 100°C) with increasing temperature.



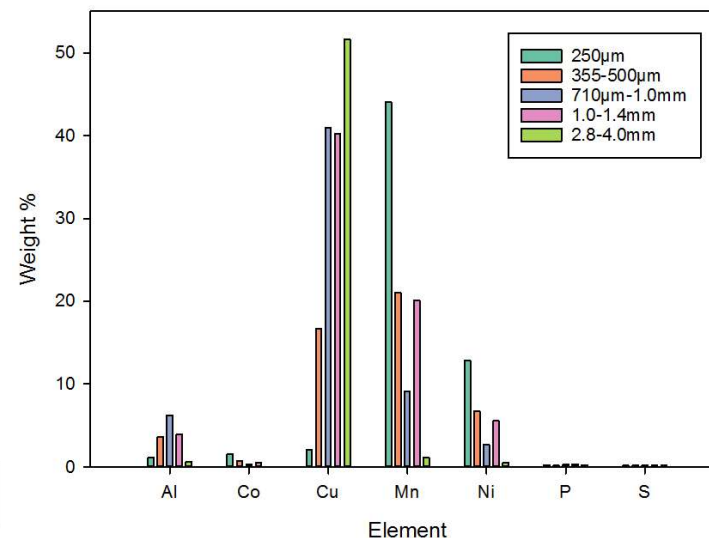
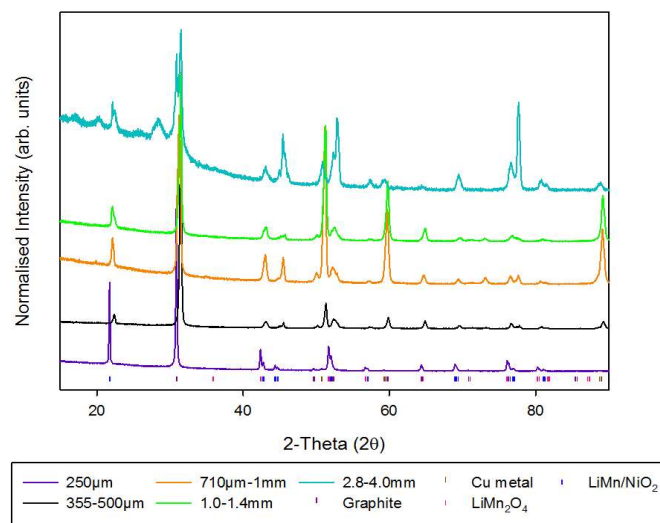


# Characterisation of shredded/manually separated battery components

- Cryogenically shredded – the battery is dipped in liquid nitrogen before being shredded. The recovered material is then fed through a number of sieves to aid separation.
- Manually dismantled – current collector sheets coated in electrode

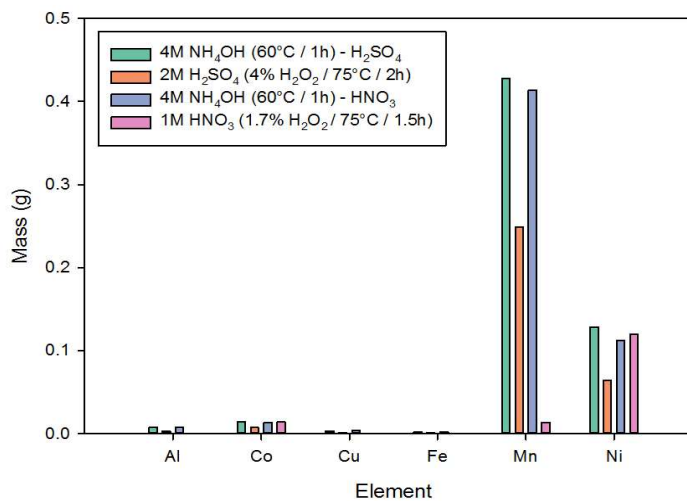
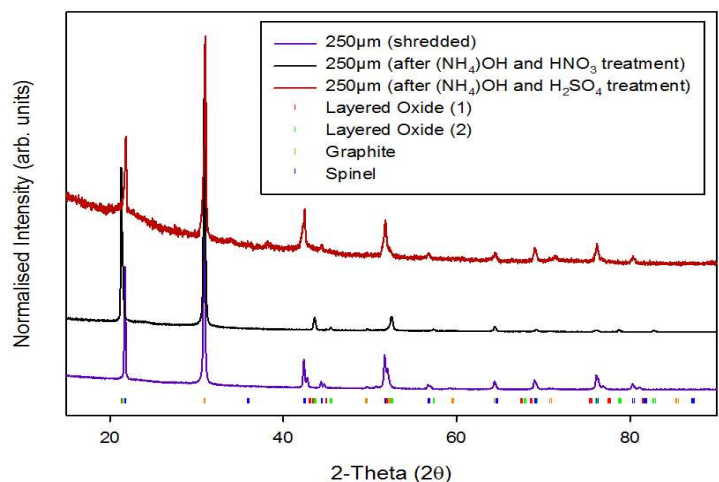


Verdict? Poor separation. Only the smallest fraction can be considered for regeneration.



# Materials processing

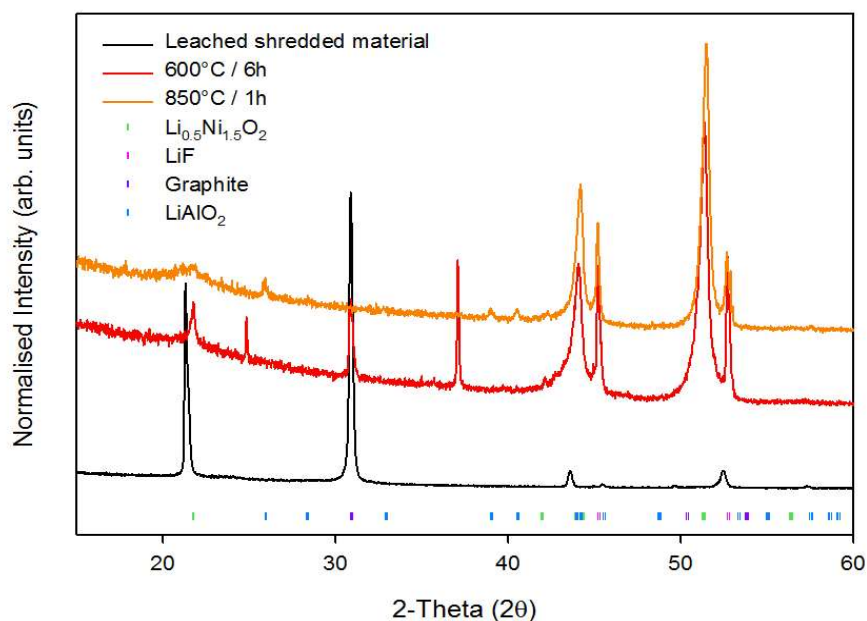
- Identified possible purification routes from the literature.
- First step – treat shredded fraction with 4M (NH<sub>4</sub>)OH (60°C/1h) to remove Cu and Al impurities.<sup>1</sup>
- Second step – Select leaching acid to leach key metals from shredded material.
  - 2M H<sub>2</sub>SO<sub>4</sub> / 4% (v/v) H<sub>2</sub>O<sub>2</sub> / 2h / 60°C<sup>1</sup>
  - 1M HNO<sub>3</sub> / 1.7% (v/v) H<sub>2</sub>O<sub>2</sub> / 1h / 75°C / S:L = 50<sup>2</sup>



Shows the importance of knowing which phases are present in shredded material before attempting purification – Nitric acid appears to remove the spinel phase while sulfuric removes the layered phase.

- A.A. Nayl, R.A. Elkhatab, S.M. Badawy, M.A. El-Khateeb, Acid leaching of mixed spent Li-ion batteries, A. J. Chem. 10 (2017) S3632–S3639.
- C.K. Lee, K.I. Rhee, Preparation of LiCoO<sub>2</sub> from spent lithium-ion batteries, J. Power Sources. 109 (2002) 17–21.

# Regeneration challenges



- After leaching, attempted to burn off the graphite and polymer.
- Added a lithium source to regenerate the layered phase at the same time.
- Instead of regeneration,  $\text{LiF}$  formation occurs.

# Summary of current progress

## • Accomplishments

- Developed low temperature routes to regenerate NMC from typical solutions produced from leaching experiments
- Initial purification studies of shredded material
- Diamond Beamtime awarded to characterise the condition of materials within EV batteries.
- Battery from Nissan leaf (Mileage of ~40,000) removed and sent to Eco-bat for shredding.

Thank you for  
listening  
Any questions?

## • Current/Future work

- Conducting the same leaching/heat treatments on the manually dismantled coated electrodes
- Evaluating methodologies used to detach electrode materials from current collectors – does the route used have any impacts on short loop recycling?
- Outreach activities being developed in conjunction with chembam (<https://chembam.com>).



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