



Recycling of low value components using high purity pre-treatment, direct recycling and green hydrometallurgical approaches for recycling of Lithium Ion and Sodium Ion batteries.

D2.1 Requirements for Direct Recycling

WP2 – Direct Recycling

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1. Deliverable Description

Direct recycling scheme from used battery active material will be developed, in which the target includes preservation of the active material structure. Optimization of the scheme will be based on the performance of active material produced, safety and commercial viability. This deliverable will be a result of Tasks 2.1 – 2.5.

2. Introduction

2.1 Direct Recycling Description

Direct recycling describes the process of re-using active material from a battery, whilst preserving the structure of the material, and not separating the material into the constituent elements, as is the case with hydrometallurgical processing. Direct recycling of cathodic active material requires the active material to have the cation content replenished, to replace losses which occur during cell cycling or material extraction processes. It is envisaged that materials which are described as unsuitable for direct recycling in this report will be better suited to hydrometallurgical processing, which can tolerate a wider variety and quantity of impurities.

Direct recycling is sensitive to impurities, which can be divided into two categories: electrochemically inert material (i.e: dead weight), and contaminants which can electrochemically interfere e.g: through doping into the structure.

2.2 Potential Contaminants

Potential contaminants in recycled active materials include copper and aluminium from the current collectors, binders such as

Polyvinylidene fluoride (PVDF) or carboxymethyl cellulose + styrene-butadiene rubber (CMC+SBR), conductive additives such as carbon black or carbon nanotubes, plastics from the separator, and steel and plastics from casing materials. In Na-ion Batteries, as Cu is not used as a current collector, this is less likely to be a contaminant.

Material for direct recycling must be a single component of active material. A mixture of anodic and cathodic active material is unsuitable, as is a mixture of different cathodic active materials, as may be found when different battery chemistries are processed together. Different cathode chemistries may also be found in blended cathodes, such as the 1st Generation Nissan leaf, which comprised a mixture of LMO and NCA.

2.3 Consequences of Contamination

Different contaminants will influence the direct-recycled material differently. From the literature, electrochemically detrimental contaminants such as Cu and Al impurities affect the performance of the cells decreasing their capacity when compared to that pristine NMC811 (~ 200 mAh g⁻¹). Contaminants for Na-ion batteries are expected to be similar to those of Li-ion batteries, but with a lower/ no Cu content,

For mixed cathode materials, weak organic acids such as ascorbic acid can be used to separate Mn-rich phases from Ni-rich phases. This method can also be utilised for separating Na-ion from Li-ion cathodes. (Joule 2024, 8, 2735)

3. Effects of Current Collector Contamination

Current collectors represent ~40% of the weight of the cell and are likely to be a significant potential contaminant in material used for direct recycling. Here we discuss the likely impact of such contaminants, with reference to both literature and UoB experimental work.

3.1 Effect of Cu and Al contamination in Li-ion Battery Materials

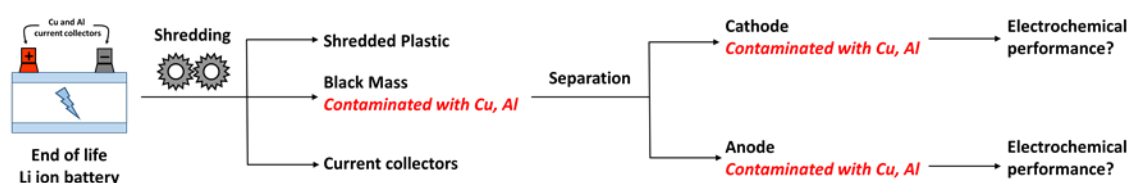


Figure 1: Origin of Cu and Al contaminants in the recycling of NMC811 based cells.

To test the consequences of contaminants, samples of NMC811 were ball milled with Cu foil (1 wt. %) and Al foil (0.5 wt. %). As a control, pristine NMC811 sample was also ball milled without any Cu or Al addition. The samples were then used to make coatings using PVDF and carbon black as binder and conductive additive respectively. The coatings were calendared and cut into disks and assembled into coin cells with Li foil as the anode.

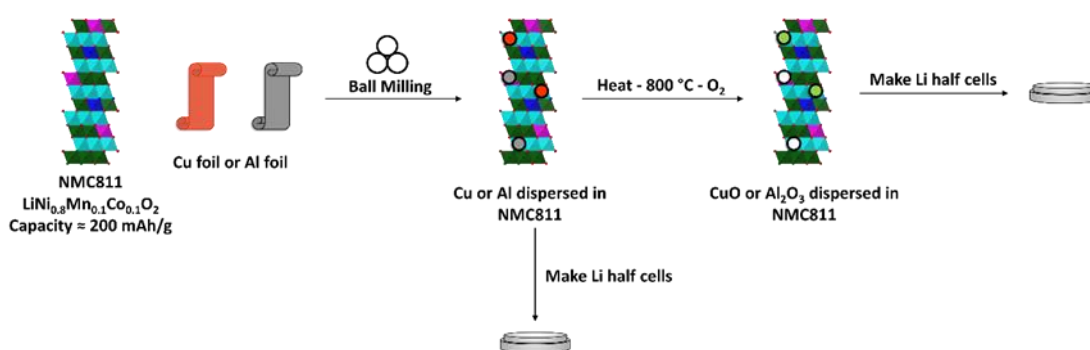


Figure 2: Flowchart for testing the effect of contaminants in NMC811.

3.2 NMC811 coin cell with 1 wt% added Cu

We observed shorting in cells made with Cu contaminated NMC811 (Figure 1a). At cathodic potentials, the $\text{Cu}^0 \rightarrow \text{Cu}^{1+} \rightarrow \text{Cu}^{2+}$ redox couple is active. Cu^{1+} and Cu^{2+} ions

can dissolve in the electrolyte and deposit on the anode causing shorting of the cells (J. Power Sources 2022, 518, 230760).

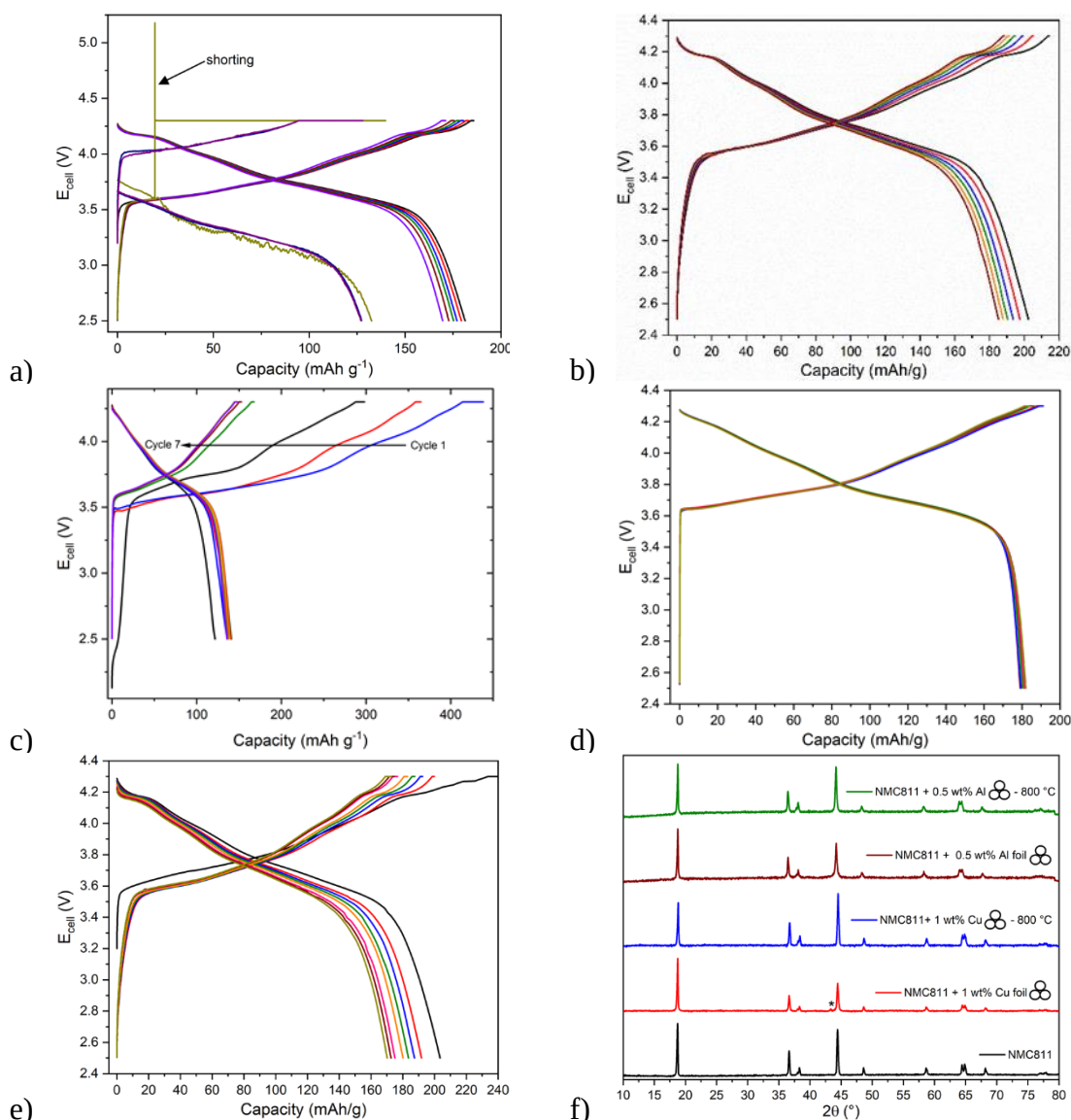


Figure 3: Electrochemical data for NMC811 with **a)** 1 weight % Cu showing shorting of the cell. **b)** NMC811 with 0.5 weight % Al showing capacity fading within the first few cycles **c)** NMC811 with 1 weight % Cu, heated to 800 °C showing poor performance. **d)** NMC811 with 0.5 weight % Al, heated to 800 °C. **e)** Pristine NMC811 ball milled without any metal additives showing capacity fading. **f)** PXRD patterns of NMC811 samples after ball milling and heating to 800 °C. Asterisk indicates the peak arising from Cu metal.

If the Cu contaminated NMC811 is heated to 800 °C to oxidise the copper and assembled into cells, it does not cause shorting. However, these cells show poor performance with low discharge capacities (Figure 1c).

Al metal contamination in NMC811 is less detrimental to cell performance than Cu. Although, no shorting or unusual charging capacities are observed, the cells show a capacity fading within the first few cycles. (Figure 1b).

Capacity fading in NMC811 can be eliminated by heating the Al containing NMC811 to 800 °C, however these cells have a lower capacity (180 mAh g⁻¹) compared to pristine NMC811 (Figure 1d).

Electrochemical testing ball milling NMC811 without any added Cu or Al metal retains the first cycle capacity of ~ 200 mAh g⁻¹ (Figure 1e). However, capacity fading is observed which is caused by the ball milling process. Similar fading can be seen in the other samples.

Existing literature on synthesised NMC955 suggests that 1 % Al content may be beneficial to electrochemical performance. (Chemical Engineering Journal, 2024, 492, 152298). However, there are no reports on the effect of impurities on milled NMC samples.

In all our samples, the structures are preserved on ball milling as evidenced by unchanged PXRD patterns. We are on the process of analysing cell parameters, which would help in proving if Cu or Al have doped into the structure.

Observations made by Wu et al. (J. Power Sources 2021, 494, 229774) and Fink et al. (J. Power Sources 2022, 518, 230760) show that Cu is more detrimental to the performance of the cells made with NMC111 and NMC622. Zhang et al, (Nano Energy 2020, 78, 105214) showed that Cu content up to 0.34 % improves the performance of NMC622 but Cu content higher than 1 % has the opposite effect. For our high nickel samples (NMC811), Cu ions caused shorting and poor performance which is consistent with the literature.

4. Routes for Direct Recycling of Li-ion Battery materials

4.1 Direct recycling of graphite

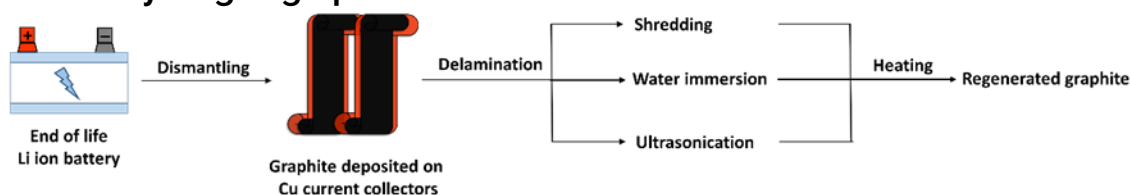


Figure 4: Flowchart for recycling of graphite. Delamination is done using various methods in the literature such mechanical shredding, water immersion (J. Mat. Chem Chemistry A 2023, 11, 9579; Sustainable Materials and Technologies 2023, 35, e00542) and ultrasonication (Green Chemistry 2021, 23, 4710).

Direct recycling of graphite involves the disassembly of the battery and separation of the anodes which consist of graphite coated on copper foil. To delaminate the graphite from the foil multiple methods have been developed. In industry, shredding is preferred due to its scalability and cost effectiveness. However, the purity of the material is strongly affected due to cross contamination. A more recent development in delamination protocols is immersing the complete anode sheets in water (J. Mat. Chem Chemistry A 2023, 11, 9579) The presence of lithium in spent graphite causes formation of hydrogen on reaction with water, which aids in the delamination process. Ultrasonication at high frequencies (20 kHz), can cause cavitation bubbles which can

effectively separate graphite from the copper foil, but can also damage the Cu foil and the graphite (Green Chemistry 2021, 23, 4710).

4.2 Direct recycling of NMC-based Cathodes

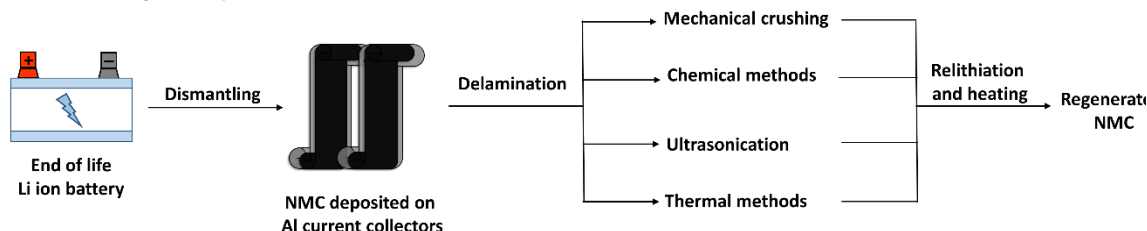


Figure 5: Flowchart for the direct recycling of NMC-based cathodes. The delamination methods include mechanical crushing (J. Sustain. Metall.,2019, 5, 402), chemical methods which include treatment with ethylene glycol (ChemSusChem 2020, 13, 5664), NaOH (J. Power. Sources 2005, 152, 278) or molten salts (ACS Sustain. Chem. Eng. 2019, 7, 8287), ultrasonication (Green Chemistry 2021, 23, 4710) and thermal methods (J. Sustain. Metall.,2019, 5, 402).

NMC811 is a valuable cathode material due to its high capacity and low cobalt content. Delamination of NMC811 coated on aluminium foil could involve the use of methods which have been applied to other NMC-based cathodes. One chemical method is where NMC532 and NMC622 cathodes were treated with ethylene glycol and heated at 160 °C (ChemSusChem 2020, 13, 5664). Other methods include treating the foils with 10 % NaOH for 5 hours at room temperature (J. Power. Sources 2005, 152, 278). In the molten salt procedure, a mixture of NaCl and AlCl₃ was heated to 160 °C with the cathode which results in delamination of the cathode material. (ACS Sustain. Chem. Eng. 2019, 7, 8287). High intensity ultrasonication involves the use of 20 kHz sound waves to cause cavitation bubbles that delaminate the NMC811 (Green Chemistry 2021, 23, 4710). Another strategy includes heating the foils to above 500 °C to decompose the PVDF binder. (J. Sustain. Metall.,2019, 5, 402).

Once the NMC811 material is separated and collected, its lithium content is analysed using PXRD, and ICP-OES measurements. For relithiation, lithium carbonate or lithium hydroxide can be added to the mixture followed by heating to high temperatures under oxygen or air. The possible conditions for this step are compiled in a review by Malik et al. (Materials Energy Today 2022, 28, 101066).

4.3 Direct recycling of LFP

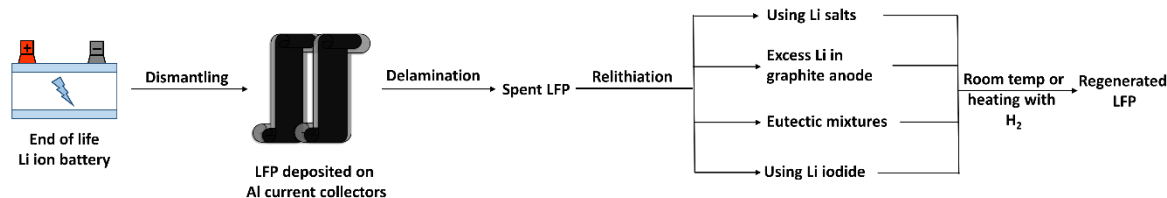


Figure 6: Flowchart for recycling of LFP. Delamination is performed with methods similar to that for NMC based cells. LFP can be relithiated by adding extra lithium and heating under inert or reducing atmospheres (Nat Commun 2023, 14, 584; Green Chem., 2021,23, 3963), using lithium loaded graphite in half cells (Chem. Commun., 2020,56, 245), and deep eutectic mixtures (RSC Sustain., 2023, 1, 2341), lithium iodide at room temperature (J. Power Sources 2023, 579, 233248).

For lithium iron phosphate (LFP) based cells, the delamination strategies are similar to those used for NMC based cells. However, relithiation methods are significantly different as the spent LFP contains FePO_4 and hence a reducing agent must be used to convert Fe^{3+} to Fe^{2+} . For LFP, heating a mixture of LiOH or Li_2DHBN with FeSO_4 at 800°C with hydrogen as the reducing agent can be used for relithiation (Nat Commun 2023, 14, 584; Green Chem., 2021, 23, 3963). Wang et al have reported a procedure that uses pre-lithiated graphite with spent LFP in coin cells which can efficiently recover LFP (Chem. Commun., 2020, 56, 245). In the eutectic mixture process, LFP is mixed with lithium acetate dissolved in ethylene glycol in combination with hydroquinone at room temperature (RSC Sustain., 2023, 1, 2341). Another room temperature strategy utilises a mixture of lithium iodide and delithiated LFP in acetonitrile. (J. Power Sources 2023, 579, 233248).

5. Routes for Direct recycling of Na-Ion Batteries

SIBs have just started to be commercialised in the last few years, and hence there are no reports on recycling SIBs. However, since the cell construction is similar to that of lithium-ion batteries, similar direct recycling methods can be considered.

5.1 Direct recycling of Cathodes

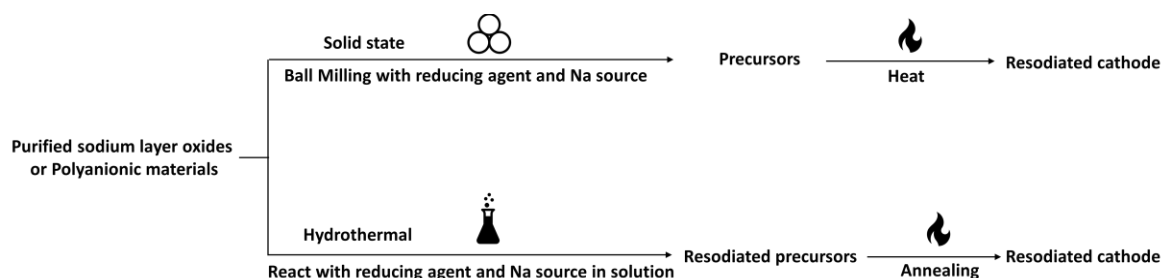


Figure 7: Flowchart for recycling of sodium layer oxides and polyanions.

Similar to LIBs, SIBs also use layered oxides (such as $\text{Na}[\text{Ni}_x\text{Fe}_y\text{Mn}_{1-x-y}] \text{O}_2$, NFM) and polyanionics (such as NaFePO_4) as cathode materials. Thus, the direct recycling methods developed for LIB cathodes, e.g. solid state synthesis and low temperature

routes can also be applied to resodiate SIB cathode materials. The potential routes are demonstrated in Figure 7.

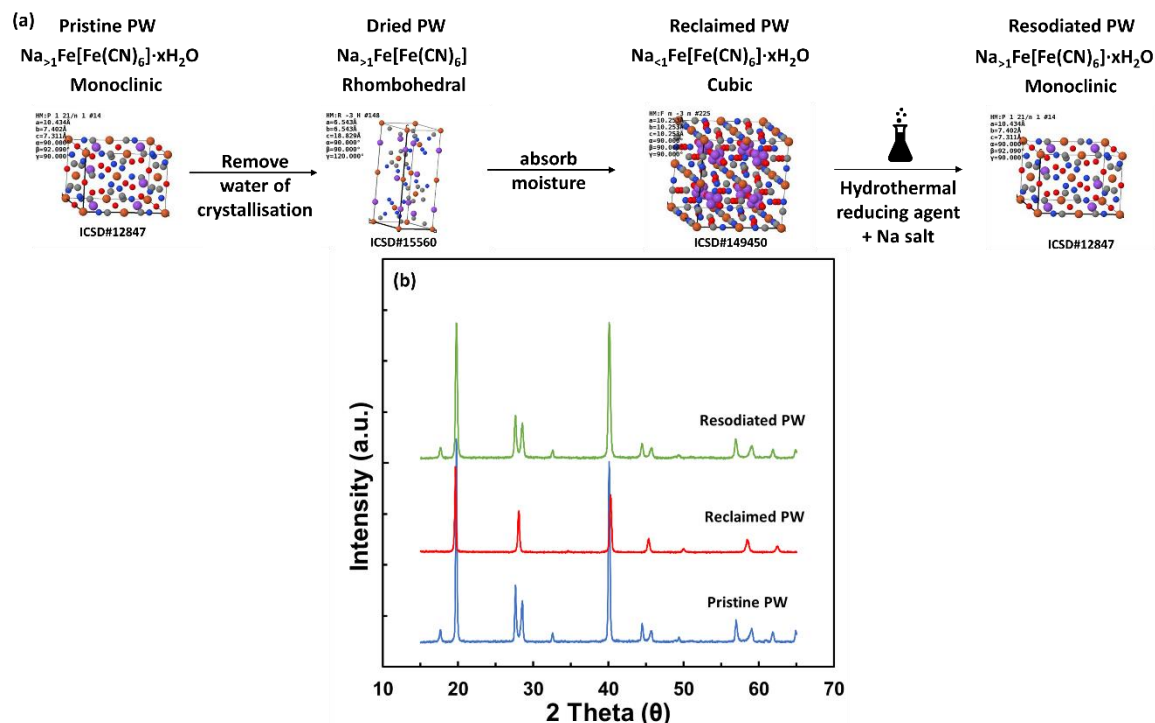


Figure 8: (a) PW structure change from pristine to fully dried, reclaimed and resodiated. The crystal structure graph refer to ICSD#12847, 15560 and 149450, corresponding to monoclinic, rhomboidal and cubic structure, respectively. (b) XRD patterns of pristine, reclaimed and resodiated PW.

Beyond layer oxides and polyanions, Prussian blue analogues (PBAs) have been developed for high performance SIB cathode materials in recent years. Figure 8 (a) demonstrates PBAs crystal structures which have open three-dimensional channels. The general formula is $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]_{1-y}\square_{(1-y)} \cdot n\text{H}_2\text{O}$, where $\square$ is the vacancy defects in the structure. When the PBA structure is rich in Na ($x > 1$), the colour of the material starts to turn white and so these are named Prussian white (PW). Furthermore, PW has high levels of water of crystallisation in the structure, which reduces the cycling performance. Hence it is necessary to fully remove the water of crystallisation and this results in changing of crystal structure from monoclinic to rhomboidal. When dried PW is exposed to atmosphere, it rapidly absorbs moisture and oxidises to PB, which leads the structure to transform to cubic. Nevertheless, PW will be decomposed over 250 °C and produce cyanide. Thus, lower temperature methods are more suitable for direct recycling of PW. UoB developed a potential hydrothermal method to resodiate reclaimed PW by mixing with a reducing agent and Na salt at low temperatures, and the XRD patterns (Figure 8b) demonstrated that reclaimed PW was successfully resodiated.

5.2 Direct recycling of Hard Carbon Anodes

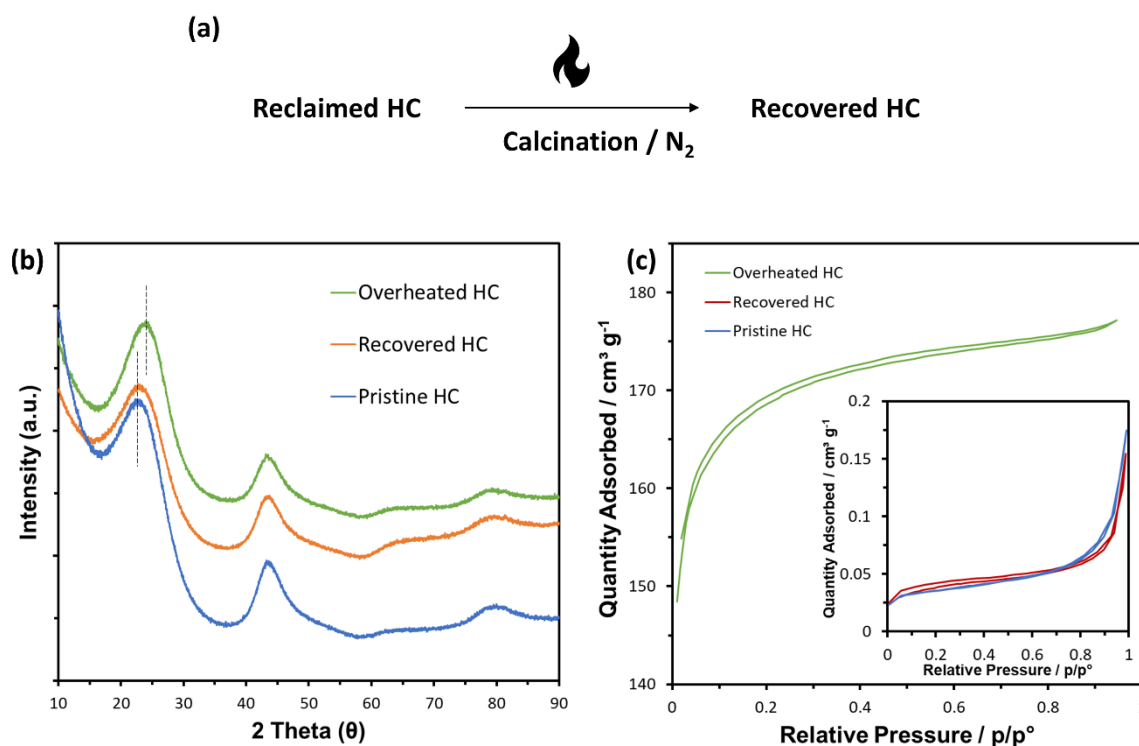


Figure 9: (a) direct recycling route for HC, (b) XRD patterns and (c) N₂ adsorption-desorption isotherm of pristine, recovered and overheated HC.

Similar to LIBs, carbon materials are common anode materials for SIBs. However, because Na⁺ is larger than Li⁺, Na⁺ needs a larger carbon layer distance to insert into the structure. Hence, hard carbon (HC), which has larger layer distance and disordered structure, has been used as an anode material for SIBs. Due to the disordered structure, HC's structure is stronger than that of graphite and shows the possibility of recovery of performance with a simple heat treatment. The reclaimed HC also binder (CMC/SBR), conductive carbon and SEI layers generated during battery cycling and so calcination under N₂ can be used to remove binder and SEI layers (Figure 9a). UoB found reclaimed HC needs an optimal calcination temperature to recover its performance. Figure 9b and c show the HC with a high calcination temperature not only results in a smaller layer distance, but also results in a larger surface area and consequently first cycle loss. This may be due to the interactions between HC surfaces and binder materials and reduce the HC cycling performance.

6. Other General Factors to consider in Direct Recycling

6.1 Particle Size and Condition

Particle sizes and shapes must be taken into consideration. From the literature, secondary particles have sizes between 10 – 20 μm, while primary particles must have sizes between 0.1 – 2 μm. (Materials Today Energy 2022, 28, 101066; Materials Research Bulletin 2012, 47, 73). Excessively fine particles will result in a large first cycle loss and must form part of larger secondary particles or should be sent for

hydrometallurgical processing. Particles which are damaged or cracked may be more susceptible to further damage during fast-charging. Such particles would require heat treatment.

6.2 Changes in the Ratio of elements

The ratio of transition metals present in cathodic active material is susceptible to change. “Cross-talk” between electrodes can cause partial dissolution of transition metals such as Mn from the cathode, and precipitation of Mn in the anode, resulting in a Mn deficiency in NMC.

6.3 Obsolete Chemistries

End of Life Batteries may include electrode materials which are obsolete, and for which there is little/ no demand in the market. These cathode chemistries should be upcycled into more relevant chemistries, or sent for hydrometallurgical recycling. (See Revitalise Deliverable 1.2)

7. Conclusions and Final Recommendations

Materials suitable for use in direct recycling must be single-component, high purity materials, with a suitable particle size range.

- Material for direct recycling should consist of only a single cathode, or single anode material. Mixed cathode materials will add costs related to hydrometallurgy.
- Avoid or reduce milling samples for longer time periods as this may reduce the particle size excessively, and cause capacity fading.
- Keep Cu content below 0.1 %, as higher copper content can cause shorting of cells and a decrease in working capacity (J. Power Sources 2022, 518, 230760; Nano Energy 2020, 78, 105214). The effect of Al contamination is not as severe as copper, but we recommend limiting Al contamination to 0.1 % as preliminary experiments show it may negatively affect performance.
- Because Na-ion materials are low cost, low-cost resodiation methods should be prioritised.
- Na-ion anodes: Interactions between the binder and the carbon surfaces need to be considered.
- For all Direct recycling approaches, safety factors need to be considered, e.g: limiting temperature and avoiding acidic conditions for PW to avert production of HCN.

Optimum materials are likely to be sourced from production scrap, e.g: failed slurries and coatings, electrode offcuts, and quality control reject cells. Production scrap can be used to initially optimise direct recycling routes which can then be applied to end-of-life materials. End of Life materials are more likely to suffer particle cracking, partial leaching and greater contamination, which will require more extensive purification processes.