Investigative study of upcycling spent synthetic $LiNi_xMn_yCo_zO_2$ (NMC) cathodes enabled by ultrasound-assisted hydrothermal treatment

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Abstract

Nickel manganese cobalt oxide (NMC; $LiNi_xMn_yCo_zO_2$) cathodes are characterized by relatively high energy density, good thermal stability, and long cycle life, making them a popular choice for use in electric vehicle (EV) lithium-ion batteries (LIBs). The composition of NMC cathodes in terms of the ratio of the three elements Ni, Co, Mn has evolved over the last few years, with the trend being increasing the nickel content at the expense of cobalt and manganese. This trend is driven by ethical sourcing issues and the high cost of cobalt but also performance improvements rendered by the Ni-rich composition. As the EV batteries retire at an accelerating rate the recycling of NMC cathodes will have to be done in consideration of the possible adverse environmental impact associated with the current commercial practice involving either pyrometallurgy (high temperature) or hydrometallurgy (chemical dissolution) routes. As researchers strive towards creating a closed-loop system for lithium-ion batteries, a new approach has emerged, direct recycling. The process is regenerative and does not separate the elements individually, rather leaves the active cathode compound intact and returns it back to its original chemical composition, crystal structure, and functionality. Direct recycling includes upcycling, which involves simultaneous cathode chemical composition alteration to reflect the higher nickel content desired in the new NMC cathodes. This research after a critical review of the different hydrometallurgical recycling technologies has experimentally investigated both direct recycling and upcycling of low and high nickel NMC cathodes, NMC 111 and NMC 622 in an effort to identify and confirm processing parameters for further development. The processing route investigated comprised chemical delithiation of pristine NMC cathode materials by controlled oxidation with $K_2S_2O_8$; hydrothermal re-lithiation in a LiOH concentrated solution assisted by ultrasound pre-treatment to promote defect-free crystal structure restoration; and short annealing. Preliminary cycling tests show the regenerated/upcycled NMC samples to be functional but further optimization work is required.

Abrégé

Les cathodes à l'oxyde de nickel-manganèse-cobalt (NMC; $LiNi_xMn_yCo_zO_2$) se caractérisent par une densité énergétique relativement élevée, une bonne stabilité thermique et une longue durée de vie, ce qui en fait un choix populaire pour les batteries lithium-ion (LIB) des véhicules électriques. La composition des cathodes NMC en termes de ratio des trois éléments Ni, Co, Mn a évolué au cours des dernières années, la tendance étant d'augmenter la teneur en nickel au détriment du cobalt et du manganèse. Cette tendance est motivée par des questions éthiques d'approvisionnement et par le coût élevé du cobalt, mais aussi par les améliorations de performance apportées par la composition riche en Ni. Comme les batteries des véhicules électriques se retirent à un rythme accéléré, le recyclage des cathodes NMC devra être effectué en tenant compte de l'impact environnemental négatif possible associé à la pratique commerciale actuelle impliquant soit la pyrométallurgie (haute température), soit l'hydrométallurgie (dissolution chimique). Alors que les chercheurs s'efforcent de créer un système en boucle fermée pour les batteries lithium-ion, une nouvelle approche a vu le jour, le recyclage direct. Il s'agit d'un processus régénératif qui ne sépare pas les éléments individuellement, mais qui laisse le composé cathodique actif intact et lui redonne sa composition chimique, sa structure cristalline et sa fonctionnalité d'origine. Le recyclage direct comprend l'upcycling, qui implique une modification simultanée de la composition chimique de la cathode afin de refléter la teneur plus élevée en nickel souhaitée dans les nouvelles cathodes NMC. Après un examen critique des différentes technologies de recyclage hydrométallurgique, cette recherche a étudié expérimentalement le recyclage direct et l'upcycling de cathodes NMC à faible et forte teneur en nickel, NMC 111 et NMC 622, dans le but d'identifier et de confirmer les paramètres de traitement en vue d'un développement ultérieur. La voie de traitement étudiée comprenait la délithiation chimique des matériaux cathodiques NMC vierges par oxydation contrôlée avec $K_2S_2O_8$; la relithiation hydrothermale dans une solution concentrée de LiOH assistée par un prétraitement aux ultrasons pour promouvoir l'homogénéisation; et un recuit court. Les essais de cyclage préliminaires montrent que les échantillons de NMC régénérés/upcyclés sont fonctionnels, mais des travaux d'optimisation supplémentaires sont nécessaires.

I dedicate this thesis to my children, Kapreese and Delanney, my husband Peter and my late father, Dave. For always believing in me and being my biggest fan. To God who faithfully gives me strength and courage to keep going. I am truly a better person because of them.

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Contributions of Authors

Conceptualization, K.D., G.P.D; investigation, K.D.; writing-original, K.D.; writing-review and editing, G.P.D.

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List of Abbreviations

UN	United Nations
IEA	International Energy Agency
EV	Electric Vehicle
LIB	Lithium-ion Battery
ICE	Internal Combustion Engine
US	United States
UK	United Kingdom
COVID-19	Corona virus disease 2019
DRC	Democratic Republic of Congo
USABC	United States Advanced Battery Consortium
SOH	State of Health
EOL	End of Life
R&D	Research and Development
PVDF	Polyvinylidene fluoride
LCO	Lithium cobalt oxide
NMC	Nickel manganese cobalt oxide
LFP	Lithium iron phosphate
LMO	Lithium manganese oxide
NRC	National Research Council of Canada
DL	Delithiated
HT	Hydrothermal treatment
SA	Short Annealing
RTMS	Reciprocal Ternary Molten Salts
FIB-SEM	Focused Ion Beam Scanning Electron Microscopy
GHG	Green House Gas Emissions

Chapter 1 Introduction

1.1 Motivation

Global efforts are being made to reduce the CO_2 emissions and meet major international agreements such as; Kyoto Protocol, Paris Agreement and UN Sustainable Development Goals [1]. The transportation sector has the highest reliance on fossil fuels and accounted for 37 % of global CO_2 emissions in 2021. A wide range of policies is introduced to promote modal shifts to the least carbon-intensive travel options. As well as operational and technical energy efficiency measures to lower the carbon intensity of all transport modes are required to meet the decarbonization targets [2]. The IEA has identified a rapid transition to electrification of road vehicles as one key factor in decreasing emissions to 6 Gt by 2030. In response to the international agreements, electric vehicles (EVs) worldwide are predicted to reach 140 million by 2030. By comparison, at the end of 2021, 16.5 million EVs were on the road [2].

Lithium-ion batteries (LIBs) are the most common type of battery used in electric vehicles. Securing resources needed to support the transition to EVs from ICEs (internal combustion engines) has seen several countries, Canada, US, EU, Japan, and South Korea, list metals such as lithium, cobalt, nickel, copper and aluminum as critical [3] [4] [5] [6] [7].

China produces approximately 63 % of the cathodes and 85 % of the anodes for battery manufacturers. The COVID-19 global pandemic forced manufacturers to decrease production as a result of lockdowns in China. An astounding 70 % of the global production of cobalt comes from mines in the Democratic Republic of Congo (DRC). Child labor, unethical practices, human rights issues are all of concern to countries relying on cobalt supplied by DRC [8]. The global leaders for producing nickel are China and Russia. With the war between Russia and Ukraine, the nickel supply has been disrupted. Countries with mineral resources have tight mining policies that make increasing extraction with the addition of new mines unrealistic. Bottlenecks in the supply chain as a result of the COVID-19 pandemic, war, and mining restrictions has contributed to supply shortages [9].

The major goals for battery manufacturers are safer batteries that, cost less, provide longer driving range, have fast charging capability and don't use imported "conflict" minerals. Battery researchers are constantly changing the chemistries to achieve these goals. However, as the demand for these batteries continues to grow, so does the need for a sustainable and efficient waste management strategy for end-of-life (EOL) LIBs. The United States

Advanced Battery Consortium (USABC) states when an EV LIB's state-of-health (SOH) reaches ~80 %, i.e., 80% of its original storage capacity, the battery is considered "spent" and has to retire [10]. Critical mineral supply risks can be reduced through the recycling of EOL LIBs. However, depending on the technologies utilized, recycling LIBs could lead to air pollution, solid waste such as metal-rich ash, and water pollution from toxic leachate. The development of commercially feasible and sustainable (ecologically, environmentally and economically) recycling processes for spent EV LIBs is imperative [11].

The typical process involved in recycling LIBs includes various steps; collection, sorting, shredding, metal extraction and refining or repurposing. LIBs are first collected from various sources such as electronic devices, EVs and stationary energy storage systems. The batteries are then sorted according to their chemistry, as different types of batteries have different chemical compositions and require different recycling processes. The most valuable component of a LIB is its cathode. The cathode chemistries of LIBs include, but are not limited to, $LiFePO_4$ (LFP), $LiCoO_2$ (LCO), $LiMnO_2$ (LMO), and $LiNi_xMn_yCo_zO_2$ (where x = y = z = 0.33, NMC 111; x = 0.5, y = 0.3, z = 0.2, NMC 532; x = 0.6, y = 0.2, z = 0.2, NMC 622; x = 0.8, y = 0.1, z = 0.1, NMC 811) [12]. The most common chemistries include lithium nickel-manganese-cobalt (NMC) [13]. The NMC battery chemistry has evolved to increase the EV range, lessen charging times and reduce the cost. The older NMC batteries contained more cobalt which was found to be very unethically sourced and expensive. Newer chemistries have increased the nickel content, which has decreased the cobalt content.

Once sorted, the batteries are disassembled into its constituent components such as current collectors (Al and Cu) and electrodes (graphite anode and NMC cathode) that are shredded into small pieces. This shredded cathode material is often referred to as black mass and contains other than NMC, the PVDF binder and conductive carbon. The black mass then moves into extractive metallurgy facility for separation and purification of the valuable metal components. Currently at the commercial level, two different recycling methods are used; pyrometallurgy and hydrometallurgy. These technologies focus on the recovery of the metals with the highest economic value, cobalt and nickel [14]. Pyrometallurgy is a process that uses high temperatures to melt and separate the metals from the other materials. It typically operates around 1000°C, which causes the organic components to burn off and the metals, Co, Fe and Ni, to melt into alloys [12]. The melted metals are then separated from the remaining materials and can be further refined into pure metals. This process is particularly useful for recycling large volumes of batteries quickly. The negative aspect of pyrometallurgy is that lithium is lost and reports to the slag. The process is also very energy intensive and poses an environmental threat in terms of air pollution. Hydrometallurgy, on the other hand, uses aqueous chemical solutions (typically various acids) in which metals such as cobalt, nickel, manganese and lithium are dissolved and separated from other components such as plastics and graphite anode. The dissolved metals are then extracted from the leaching solution and purified through various methods such as solvent extraction and precipitation followed by filtration. Once the cobalt, nickel, manganese and lithium are recovered and purified, they can be used in synthesis of new batteries or other products. This process is desirable because lithium can be recovered, it is more energy-efficient than pyrometallurgy and produces less air pollution, but it can be slower and more expensive [15].

Both pyrometallurgy and hydrometallurgy have their advantages and disadvantages, and the choice method will depend on the type and quantity of batteries being recycled. From a sustainability stand point, both processes have drawbacks such as high acid and generally chemical consumption, high energy consumption and GHG emissions. This has driven research scientists and engineers to come up with alternatives that are more environmentally responsible and energy efficient.

To address this issue, direct recycling of lithium-ion active cathode materials has emerged as a promising solution. In this processing option, the cathode compound, e.g., NMC is not decomposed by leaching or smelting but rather separated and regenerated to its original full functional state. This approach in other words is non-destructive rendering the recycled active material ready for reuse in new battery manufacturing.

Direct recycling offers several benefits, including reducing the demand for mining new raw materials, decreasing the environmental impact of battery production and reducing the amount of waste in landfills. Additionally, the process can help improve the overall sustainability of the battery life cycle and contribute towards a circular economy [15].

1.2 Scope of Thesis

Direct recycling is a complex and challenging process that requires significant research and development to optimize, making it the focus for many research groups worldwide. It is the scope of this thesis to comprehensively review the current state of LIB recycling technologies as far it concerns NMC cathodes that constitute the larger type of EV material used and embark into an experimental investigation of several aspects of direct recycling and upcycling of low-Ni (NMC111) to high-Ni (NMC-622) cathodes. In particular, (1) the present study has determined the conditions for inducing a controlled extent of chemical delithiation of different NMC cathode chemistries with a strong oxidant, potassium persulphate; (2) demonstrated the effectiveness of hydrothermal relithiation in fully restoring the α-$NaFeO_2$ layered structure of pristine NMC111 and NMC622. (3) Hydrothermal relithiation was further shown to yield enhanced reconstruction of the composition and crystalline structure when ultrasound mixing was applied. (4) Finally, based on the above understanding, the upcycling of low nickel NMC into a high nickel NMC was successfully accomplished by performing short annealing in the presence of pre-calculated co-addition of nickel sulphate and lithium carbonate. Characterization confirmed that NMC622 was produced out of NMC111.

1.3 Thesis Organization

This thesis is manuscript based and is presented in five chapters, followed by Appendices of supporting information. Chapter 1 gives a general introduction to the motivation and objectives of this thesis. Chapter 2 provides a comprehensive literature review on the present state of the art LIB recycling technologies and new R&D trends with emphasis on hydrometallurgical processes and the emerging direct recycling approach. The Chapter is based on a manuscript submitted for publication to *RSC Sustainability*. In Chapter 3, the main body of the thesis deals with the experimental investigation of direct recycling and upcycling of NMC 111 and 622 cathodes. This Chapter is based on a manuscript prepared for submission to a special issue of the Elsevier journal *Next Energy*. Chapter 4 provides a global discussion and Chapter 5 summarizes the Conclusions.

Chapter 2 Literature Review

This Chapter covers the literature review for current recycling technologies for NMC Li-ion battery cathodes. Both current industrial practice and new developments and state-of-the-art research approaches are presented. The Chapter is based on a comprehensive literature review submitted for publication in the *Royal Society of Chemistry Sustainability Journal*[1].

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[1] Krystal Davis and G. P. Demopoulos, Hydrometallurgical recycling technologies for NMC Li-ion battery cathodes: Current industrial practice and new R&D developments & trends, *RSC Sustainability*, to be submitted (April 2023)

Abstract

The supply chain for raw materials needed to fulfill the demand for lithium-ion battery (LIB) manufacturing is less than certain. Department of Energy (DOE) has estimated an 87 per cent decline in cost of manufacturing batteries between 2008 and 2021, making the affordability of electric vehicles (EV's) economically feasible. With the stress and uncertainty of securing the raw materials, predicted price increases in metals such as lithium and nickel could jeopardize the economics in EV battery production by an increase of \$3/kWh in 2022. Lithium-ion battery recycling could help alleviate the demands on critical virgin materials. This would realize a price parity goal, \$100/kWh, for internal combustion engines (ICE) and EV's. Simultaneously, recycling could reduce waste in landfill sites as 1 M tonnes of LIBs which are set to retire by 2030. Recycling could bring countries under the Paris Agreement closer to reaching net-zero greenhouse gas (GHG) emissions targets in 2050, moving the transport sector to 100 per cent electrification. This review paper will focus primarily on spent nickel-manganese-cobalt (NMC) lithium-ion batteries commercially recycled using a hydrometallurgical recycling approach as well as current research developments that have reached the pilot scale or have the potential for large scale application. The paper concludes with the observation that hydrometallurgy-assisted direct recycling offers by far the most advantageous from a sustainability perspective approach as opposed to currently pursued total dissolution methods aiming on metal recovery only.

2.1 Introduction

Lithium-ion battery production is projected to reach 440 GWh by 2025 as a result of the decarbonisation efforts of the transportation sector which contribute 27 per cent of the total GHG emissions [1, 2]. An EV lithium-ion battery is deemed “spent” when it has reached a state of health which is less than 80 per cent, typically after 10 years of use [3]. The battery can then either go for a second life in a stationary storage system or be recycled for the valuable metals. Recycling lithium-ion batteries has been recognized as a way to secure the supply chain and reduce environmental impacts if they go to landfill sites [4]. Recycling can contribute to an overall reduction in the GHG emissions that are associated with the battery industry [5]. Battery chemistries have evolved over the years, two factors have driven research and innovation; increasing density, thus battery life and range, and reducing material costs [6]. The most common battery chemistry in EV LIB cathodes are lithium, nickel, manganese and cobalt oxide (NMC) batteries. The cathode can be any mixture of LiNixMnyCozO2, NMC (where x+y+ z =1). Other chemistries such as lithium iron phosphate LiFePO4 (LFP), LiNixCoyAlzO2(NCA) (where x+y+z =1), lithium manganese oxide $LiMnO_2$ (LMO) and lithium cobalt oxide LiCoO2 (LCO), are commercially available but for this study we will look at the NMC battery only [7]. The NMC cathode has become economically more desirable, the cobalt content has decreased (NMC 111, NMC 523, NMC 622, NMC 811) improving not only overall cost but also lessening the environmental and ethical impacts. The energy density has also improved with the increase in nickel content, NMC 811, improving the range although challenges still remain with the long cycling stability of Ni-rich NMC cathodes [8].

Some of the LIB raw materials have been listed as critical in countries like Canada, USA, Europe, Japan and South Korea, making recycling equally critical from economic and environmental perspectives [9]. Sourcing and securing a sustainable supply chain for manufacturing LIBs means social issues are equally taken into account. The Democratic Republic of Congo (DRC) holds 70 per cent of the world’s cobalt resource. The country has artisanal and small-scale mines (ASM) dominated by Chinese owned companies [10] [11]. This gives the Chinese LIB manufactures security over international manufacturers for cobalt supply. For years, human rights groups have reported severe social issues in mining operations in the DRC forcing companies in improving the ASM standard for mine safety and child labor to ensure cobalt is mined responsibly [11].

The components of LIBs, their structures, and their charge-storage mechanisms may impact the design and selection of the recycling process [6]. With reference to current commercial recycling of LIB NMC cathodes, it is the hydrometallurgical processing route which offers the greatest versatility and lowest energy demand [1]. Several hydrometallurgical recycling facilities are operating around the world and recovering all critical metals i.e., Li, Co, and Ni at the highest extraction level and purity as opposed to pyrometallurgical operations that recover typically Co and Ni only at lower levels. Hydrometallurgical processes, however like in the case of pyrometallurgical processes, they aren't without fault. They use large quantities of chemicals and generate waste solutions that need to be treated and re-used within the plant in order the whole operation meets sustainability standards. In this regard, increasingly research has focused on green recycling considerations to decrease the environmental impact and operation costs associated with these methods. The most important development recently is the promising direct recycling approach, which does not decompose the entire active cathode material into the constituent elemental components which have after to be completely re-manufactured like the pyro- and hydromet routes do. Instead, the technology aims to direct regeneration of the NMC oxide itself for example by employing hydrothermal relithiation to restore its structure into full functional form [1]. Our paper builds on previous reviews as is the one by Larouche et al [12] by opting to focus on latest market trends and state-of-the-art hydrometallurgical recycling processes that have reached an advanced level of development as per recent patent literature and company reports. Many of these processes are at the pilot scale, yet to be commercialized. Some of the processes described recover only cathode metal components (Ni, Co, Li, Mn), while others are targeting a circular economy approach, recovering all components of the spent battery (graphite, Cu, Al, electrolyte, plastics etc.).

2.2 Demand of Lithium-ion Batteries

As climate change takes the forefront of many countries' roadmaps, greenhouse gas emissions reduction becomes a main priority. The Paris Agreement was born as a legally binding international treaty on climate change that includes 191 countries and the European Union. The goal to decrease the global warming temperature to 1.5 degrees Celsius brings challenges to countries to achieve climate neutrality. According to the World Bank, the transportation sector contributes 20 per cent of the GHG emissions globally. This number could grow to 60 per cent by 2050. The reduction of climate impact from the transportation sector is critical. Electric vehicles (EVs) have the potential to significantly reduce GHG emissions. Renewable energy technologies such as LIBs are important to put an end to the era of fossil fuels. This has driven a lot of research and development within battery technology. The main objectives are to increase the battery range and decrease the cost in order to strongly compete with internal combustion engine cars (ICE). The data shows that the adoption of EVs has taken off exponentially. The sales of EV cars have increased by 297 per cent, between 2016 and 2020. After a decade of growth, in 2020 the global electric car stock hit 10 million, shown in Figure 2-1. Although China had the largest fleet in 2020, 4.5 million EVs, Europe had the largest annual increase, 3.2 million EVs [13].

Figure 2-1 Global electric passenger car stock, 2010-2020 [2] ***[77]***

According to the latest EV outlook report from BloombergNEF, 60 per cent of new car sales worldwide must be electric by 2030 if a net-zero scenario is to be achieved [14].

2.3 LIBs Are a Source of Critical Materials

Raw materials that have been deemed economically important and have a high supply risk, are identified as critical raw materials. Countries have developed a list of critical raw materials that require strategic planning to achieve sustainability and resource security. With the onset of the rapid change from ICE to EV in the automotive industry, the demand on raw metals and minerals that make up a battery is surging [15].

Demand for raw materials like graphite, lithium and cobalt is predicted to increase 500 per cent by 2050, according to the World Bank [2]. Several countries have revisited their list of

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[2] *"*This is a work derived by Krystal Davis from IEA material and Krystal Davis is solely liable and responsible for this derived work. The derived work is not endorsed by the IEA in any manner.*"*

critical materials in light of the EV era. The USA, EU, Japan, South Korea and Canada have released a list of critical minerals/metals [9][19][78][79][80].

Table 2-1 List of Critical Metals/Minerals for USA, EU, Japan, South Korea and Canada [4][9][19][78][79][80]

Mineral/Metal	**Country**				
	USA	**EU**	**Japan**	**S. Korea**	**Canada**
Aluminum (Bauxite)	x				x
Antimony	x	x	x	x	x
Arsenic	x				
Barite/Barium	x	x	x		
Beryllium	x				
Bismuth	x	x			x
Cesium	x				x
Chromium	x		x	x	x
Coal			x		
Cobalt	x	x	x	x	x
Coking coal	x	x			
Copper	x		x		x
Fluorspar	x	x			x
Gallium	x	x	x	x	x
Germanium	x	x			x
Graphite	x	x	x		x
Hafnium	x	x			
Helium	x				x
Indium	x	x	x	x	x
Lithium	x	x	x	x	x
Magnesium	x	x		x	x
Manganese	x		x	x	x
Molybdenum			x	x	x
Nickel			x	x	x
Niobium	x	x	x	x	x
Phosphate rock		x			
PGM/PGE	x	x	x	x	x
Potash	x				x
Rare earth elements	x	x	x		x
Rhenium	x		x		
Rubidium	x				
Scandium	x				x
Selenium				x	
Silicon					
Strontium	x				
Tantalum	x	x	x		x
Tellurium	x			x	x
Tin	x				x
Titanium	x		x	x	x
Tungsten	x	x	x	x	x
Uranium	x		x		x
Vanadium	x	x	x	x	x
Zinc			x		x
Zirconium	x			x	

Table 2-1 shows 44 minerals/metals identified as critical, 9 of which are consistent between all countries: antimony, cobalt, gallium, indium, lithium, niobium, PGE/PGM, tungsten and vanadium. The minerals/metals lithium, nickel, cobalt, manganese, graphite, aluminum, and copper are required to manufacture LIBs, highlighted in green in Table 2-1 [9]. The EU Commission estimates that demand for cobalt and lithium will increase by a factor of 4 and 10, respectively, by 2030; and 10 and 40, respectively, by 2050 [16]. Cobalt is mainly mined as a by-product in nickel and copper mines. The supply of cobalt is of real concern because it is limited to a few countries such as DRC, Australia, Cuba, Philippines, Russia and Canada [17]. Figure 2-2 shows the Global Cobalt Reserves which is dominated by DRC, 3.6 M tons, and Australia, 1.4 M tons. Although Australia has substantial reserves, they only mine 4 per cent of the global production of cobalt. Due to the ethical and environmental concerns of mining in the DRC, the need to eliminate global dependence on this metal is crucial [10].

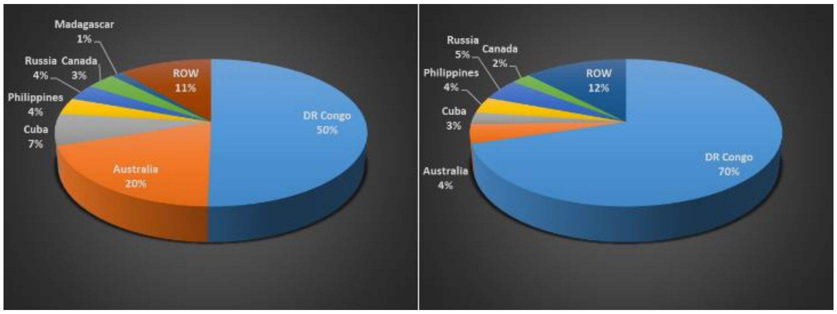


Figure 2-2 Right: Global Cobalt Reserves 2020, by country (in metric tons), Left: Global Production of Cobalt 2020, by country (% share of production) ***[18]***

The raw materials needed to fulfill the supply that is being demanded to achieve net-zero emissions is not possible through mining alone. The current mines and projects that are under construction will only be able to produce 50 per cent of the projected lithium and cobalt, and 80 per cent of the required copper by 2030 [19]. Spent lithium-ion batteries contain between 5-20 weight per cent of cobalt, 5-7 weight per cent of lithium, and 5-7 weight per cent of nickel, these concentrations are higher than what is naturally available from raw materials. Recycling is an economical solution to the raw material shortage [20].

The estimation of material intensity of NMC lithium-ion battery packs (kg/kWh) has been done by Argonne National Laboratory using their BatPaC modeling, it can be seen in Table

2-2 [21]. The weight of lithium includes both the electrolyte and cathode. The cathode contains nickel, cobalt and manganese. Aluminum weights include current collectors, cell terminals, thermal conductors and module and battery enclosures. Copper weight is derived from the cell current collectors, terminals, thermal conductors and module and battery enclosures. The anode is responsible for the graphite weight [21].

Table 2-2 NMC lithium-ion battery pack composition by weight (kg/kWh) ***[21]***

Material	**NMC 111**	**NMC 532**	**NMC 622**	**NMC 811**
Lithium	0.141	0.136	0.118	0.1
Nickel	0.351	0.508	0.531	0.6
Cobalt	0.352	0.204	0.178	0.075
Manganese	0.328	0.285	0.166	0.07
Aluminum	3.11	3.07	3.017	2.921
Copper	0.677	0.661	0.605	0.549
Graphite	0.978	0.981	0.96	0.961

The change in NMC battery chemistry has evolved from high cobalt NMC 111, to high nickel NMC 811, see Figure 2-3 a, from 2010 to predicted 2030. The chemistry advancements can be credited principally for the reduction in cost of an EV battery [23].

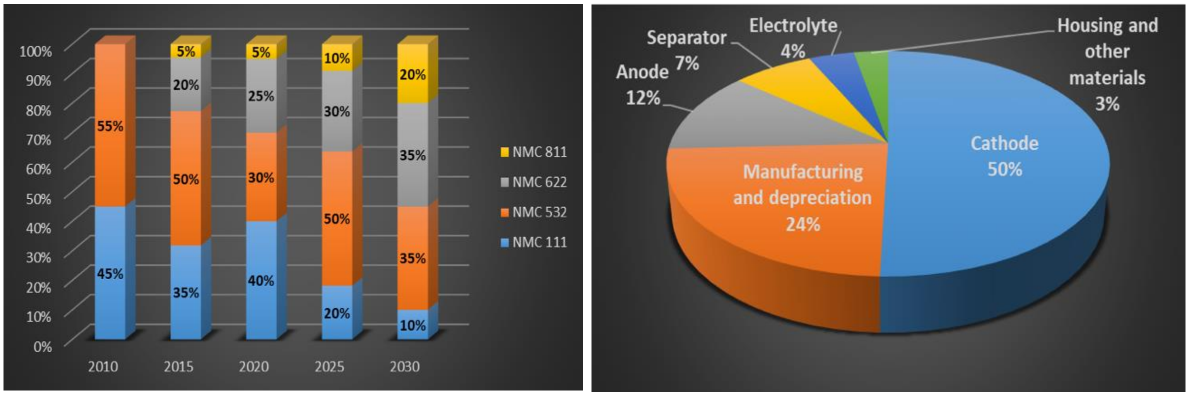


Figure 2-3 a) NMC cathode chemistry evolution ***[23]***, b) The cost of a lithium-ion battery ***[14]***

The average cost to produce a lithium-ion battery for an electric vehicle (EV) has significantly declined from $1200/kWh in 2010, to $132/kWh in 2021. S&P Global Platts has forecasted the EV battery manufacturing cost will reach price parity with ICE, at $100/kWh by 2026 [24]. BloombergNEF has broken down the overall cost of a battery cell, see in Figure 3b.

The cathode accounts for the half of the average cell cost, while the anode is 12 per cent of the cell cost.

The battery metals supply chain, particularly metals that make up the cathode, are experiencing pricing increases. Metals like lithium, nickel and cobalt have seen extreme increase in prices between 2020 and 2022, while manganese, aluminum, copper and graphite have also increased since 2020, refer to Table 2-3. Lithium pricing surged by nearly 500 percent between 2020 and 2021 [25]. Platts Analytics expect prices to stop rising in 2022 as the supply chain becomes more secure [24].

Table 2-3 Price comparison for battery materials needed for NMC LIBs in USD/tonne ([1] global average price for Li_2CO_3, [2]Price for spherical 15 µm graphite)

Material	2022	2020	Price Source
Lithium[1]	27327	7250	[16]
Nickel	32424	15090	[17]
Cobalt	81860	33000	[18]
Manganese	2400	1565	[19]
Aluminum	3048	1582	[20]
Copper	9820	6788	[21]
Graphite[2]	3800	3400	[22]

2.4 Current Industrial Hydrometallurgical Recycling Practice

2.4.1 General

The hydrometallurgical recycling process uses aqueous chemistry and follows three main steps, leaching, impurity removal/solution purification, and the production of the metal salts by precipitation/crystallization, see Figure 2-4. Leaching uses acids (or bases) at low temperatures in an oxidizing or reducing environment to dissolve valuable metals. The impurity removal and purification steps separate the valuable metals from unwanted metals via selective chemical reactions. Methods used are typically precipitation by neutralization (pH adjustment), liquid-liquid reactions (solvent extraction), and ion exchange. The production of metal salts can be done by crystallization (e.g., $NiSO_4.6H_2O$ via vacuum application) or ionic compound precipitation (e.g., Li_2CO_3 via use of Na_2CO_3 or CO_2 as reagents). Electrochemical reduction or electrolytic reduction to produce high-purity metals from which salts to be obtained afterwards via leaching and vacuum crystallization is another option [4] [33].

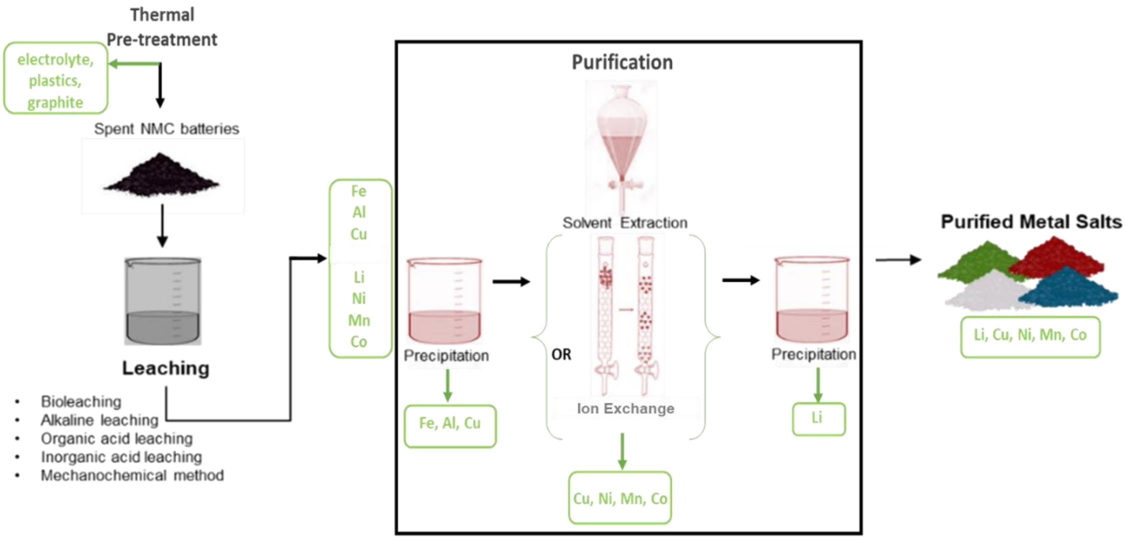


Figure 2-4 Recycling using hydrometallurgical processing, adapted with permission from ***[34].***

The main advantage of hydrometallurgical recycling over pyrometallurgy is the high recovery (greater than 99 per cent, >90% for Li) of the purity pay metals, Ni, Co, Mn, Li, low impurity content and a lower energy consumption [20]. A comparative flowsheet between hydromet and pyromet processing of LIBs is illustrated in Figure 2-5. Lithium is only recovered with hydrometallurgy, as lithium carbonate. Another benefit to the hydromet process is that it can adapt to a mixed cathode feed stock. Eliminating the need to separate the spent batteries based on chemistry [1]. The pyrometallurgical process, can only recover Co, Ni and Cu as alloys. The alloys require further refinement to produce the desired metal salts [35].

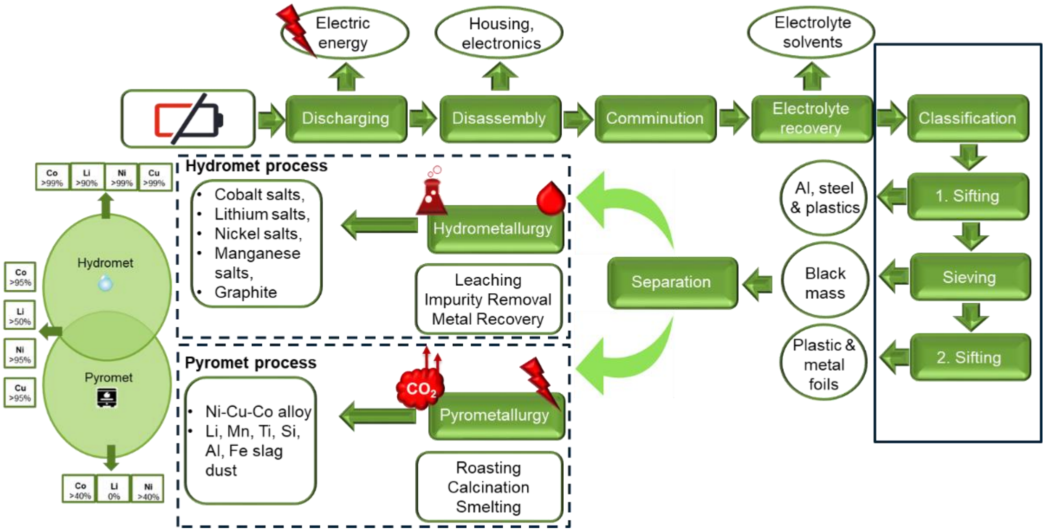


Figure 2-5 Lithium-ion battery recycling flowsheet overview comparing hydromet and pyromet processes

2.4.2 Solution Chemistry

When recycling lithium-ion batteries, the most common hydrometallurgical method uses sulfuric acid and hydrogen peroxide-the latter as metal reducing agent. The following chemical equation, Equation 2-1, describes the leaching process.

Equation 2-1

$$2LiM^{3+}O_{2(s)} + 3H_2SO_4 + H_2O_2 \rightarrow 2M^{2+}SO_{4(aq)} + Li_2SO_4 + 4H_2O + O_2$$

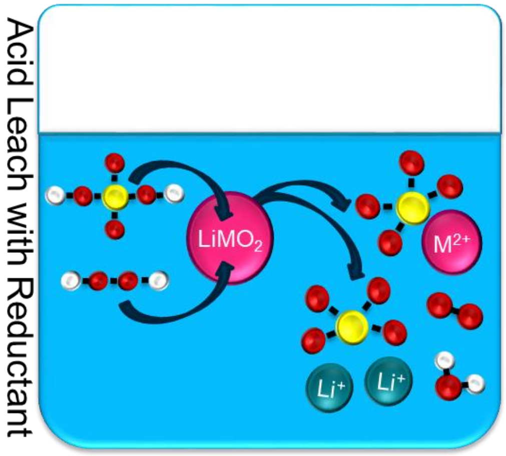


Figure 2-6 Typical Acid Leach with Reductant for NMC Recycling, where yellow = sulfur, red = oxygen, white = hydrogen, M = metal (Ni-Mn-Co), M^{2+}= metal ions (divalent).

Cathode transition metals, such as Co and Mn, have low solubility because in a discharged cathode they are in the +3/+4 valence states. The strong M-O bonds make leaching difficult. Reducing the metals to a divalent state allows for higher leaching efficiency. It is understood that the hydrogen peroxide, H_2O_2, behaves as a reducing agent which converts Co^{3+} into the soluble Co^{2+} metal ion. The addition of peroxide has improved the leaching efficiency to greater than 95 percent [36]. The by-product from the addition of H_2O_2 is water and oxygen gas. A graphic schematic of the reductive dissolution of LMO_2 by Equation 1 can be seen in Figure 2-6. This is a greener alternative than using other reducing agents such as sulfur dioxide, SO_2, which produces sulfurous acid when mixed with water.

Once the leached metals, Li^+, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, and Al^{3+}, are in solution, they are selectively separated in the impurity removal and purification stage. Typically, multiple precipitation and solvent extraction stages are used to separate and purify the metals in solution. Metals such as Cu (anode current collector), Fe and Al (cathode current collector), are considered to be impurities in this process. These metals are removed from solution by neutralization as hydroxides taking advantage of their solubility differences from the valuable metals (Ni, Co, Mn) as per diagrams (A) and (B) in Figure 2-7. The separation of Ni, Mn and Co (following the removal of Fe, Al, Cu) is difficult to achieve using pH and temperature adjustment alone as the solubilities of Ni(OH)2, $Mn(OH)_2$ and $Co(OH)_2$ are too close which would promote co-precipitation as a mixed metal hydroxide, for this reason are left in solution to be separated by non-precipitation methods Meanwhile, lithium has a high solubility and is recovered at high pH, around 11 by precipitation with sodium carbonate, Na_2CO_3 as Li_2CO_3, following the recovery of Ni, Co, Mn.

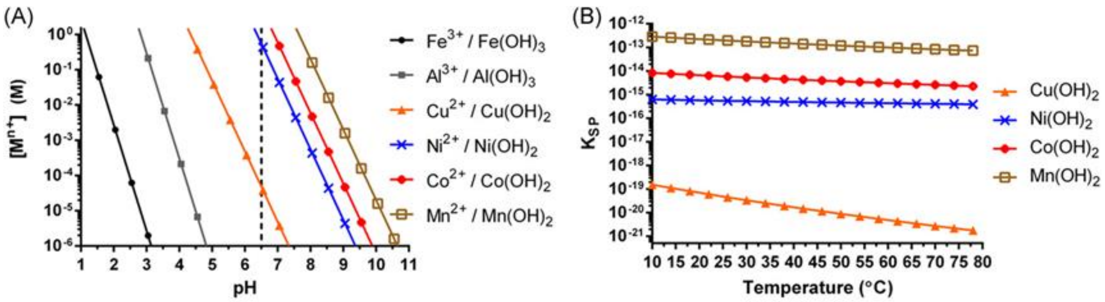


Figure 2-7 Solubility diagram for metal hydroxides at 25 °C (A), temperature effect on metal hydroxide solubility product (B), reproduced with permission from ***[36]***.

The Ni-Mn-Co -containing solution following the impurity (Fe, Al, Cu) removal stage is advanced to purification where the metals are selectively separated using methods like solvent extraction and/or ion exchange. Most hydromet processes have adopted solvent extraction to separate the three metals due to its high selectivity (upon proper extractant selection) and recovery efficiency [37]. The extraction of the transition metals M^{2+} (Ni, Mn, Co) from the leach solution is done with cationic extractants (present in the organic solvent in dimer form, $(HA)_2$), see Equation 2-2. The extraction reaction process is depicted in Figure 2-8.

Equation 2-2

$$M^{2+}{}_{aq} + 2(HA)_{2_{org}} \leftrightarrow MA_2 \cdot 2HA_{org} + 2H^{+}{}_{aq}$$

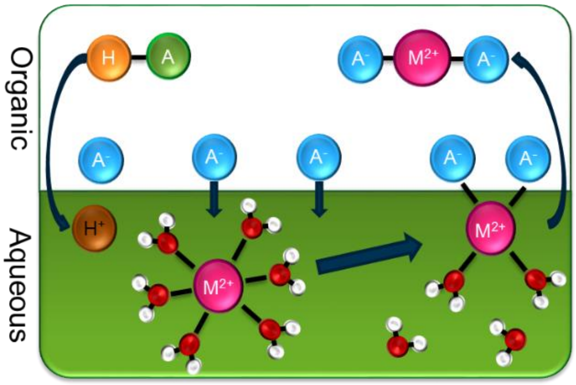
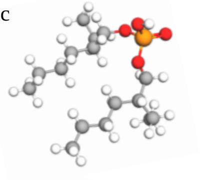
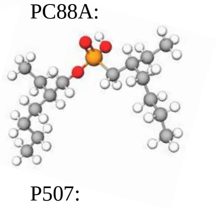
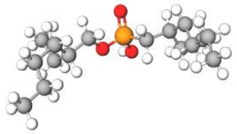
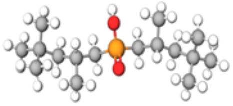
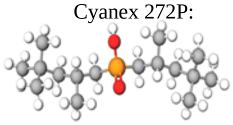


Figure 2-8 Graphical illustration of Solvent Extraction Reaction for Transferring Metal Ions from Aqueous Phase to Organic Phase, where HA= acid form extractant, A^-= acid extractant anions, M^{2+}= metal ions (divalent), red = oxygen, white = hydrogen ***[38]***.

The selection of solvent extraction reagents (extractants) depends on composition of feedstock solution and the ionic state of key elements [39]. Various extractants have been researched to separate and purify critical battery metals. The process uses time, pH, aqueous/organic (A/O) ratios, and concentration of extractant to control which metal ion will be selectively removed. Table 2-4 illustrates certain examples of different extraction conditions that have been reported. Many extractants have been used. By far as per well established practice of Co/Ni solvent extraction (consult for example the seminal book by G. M. Ritchey and A. W. Ashbrooke “Solvent Extraction: Principles & Applications to Process Metallurgy)” in commercial use for metallurgical nickel extraction plants the organophosphorus acid extractant family attracts the biggest interest.

There are three types of organophosphorus acids (see their structures in Table 2-4): organic phosphoric, exemplified by D2EHPA (di-(2-ethylhexyl) phosphoric acid); organic phosphonic such as 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, marketed as PC88A or P507; and organic phosphinic, bi(2,4,4-trimethylpentyl) phosphinic acid, marketed as Cyanex 272P or Mextral 272P. The organophosphorus acids may be graded according to their acidity (pKa) as follows: phosphoric > phosphonic > phosphinic. The more acidic the extractant the lower the pH at which can extract a metal, the faster the extraction rate, the lower the separation efficiency. For example, in Co/Ni separation, the extraction of Co follows the order D2EHPA > Phosphonic > Phosphinic, while the reverse happens in terms of Co/Ni separation efficiency Co: phosphinic > phosphonic > D2EHPA. A sample of extraction results with these reagents reported from NMC recycling studies is provided in Table 2-4.

Table 2-4 separation of Ni, Mn, and Co from Spent NMC leach Solutions using Organophosphorus Acid Extractants ***[40, 37].***

Category	**Extractant**	**Applications**	**Solution Composition (g/L)**	**Extraction Conditions**	**Extraction Efficiency**	**Ref**
Organic phosphoric acid extractant	D2EHPA: 	◦ Mn extraction and impurity ions ◦ Co-extraction Co-Ni-Mn from Li	Co: 0.175, Ni: 0.099, Mn: 5.269, Li: 1.248	T: 300 s, pH: 5, A/O: 0.5, 20 % vol D2EHPA,70-75% saponification	Mn: 97%	***[41]***
		◦ Separate Ni and Co	Co: 6.438, Ni: 0.089, Mn: 6.312, Li: 1.602	T: 300 s, pH: 3.5, A/O: 1:1, 15 % vol Mextral272P	Mn: 97.1%	***[42]***
Organic phosphonic acid extractant	PC88A: 	◦ Separate Ni	Ni: 2.54, Li: 4.82	pH: 6.5, A/O: 1, 0.15 M PC88 A	Ni: 99.9%	***[43, 44]***
	P507: 	◦ Separate Ni and Co	Co: 20, Ni: 0.5, Li: 2.5	pH: 3.5, A/O: 1.5, 25 % vol P507	Co: 95%, <5% Ni and Li co-extraction	***[43, 45]***
Organic phosphinic acid extractant	Cyanex/Mextral 272P: 	◦ Separate Co	Co: 7.18, Ni: 4.29, Mn: 0.045, Li: 1.49	T: 300 s, pH: 4.5, A/O: 1:1, 20 % vol Ni loaded Mextral272P	Co: 97.8%	***[46]***
	Cyanex 272P: 	◦ Separate Co/Li and Co/Ni	Co: 13.8, Ni: 0.015, Mn: 0.011, Li: 2.04	pH: 5.5-6, A/O: 0.5, 0.4 M Cyanex 272, 50% saponification	Co: 95-98%, ~1% Ni extraction	***[47]***
Blended extractants	D2EHPA + Versatic 10 acid		Co: 11.4, Ni: 12.2, Mn: 11.7, Li: 5.3	pH: 4.5, A/O: 1, 0.43 M D2EHPA and 0.7 M Versatic 10 acid	Mn: 98.33%, Co: 1.06% Ni: 4.11% and Li: 0.25% co-extraction	***[48]***

The above results can be understood on the basis of the respective metal extraction equilibria which provide the selectivity series. The phosphinic acid (Cyanex 272/Mextral 272), which is commonly used to separate cobalt from nickel in sulphate media exhibits the selectivity series illustrated in Figure 2-9 [49].

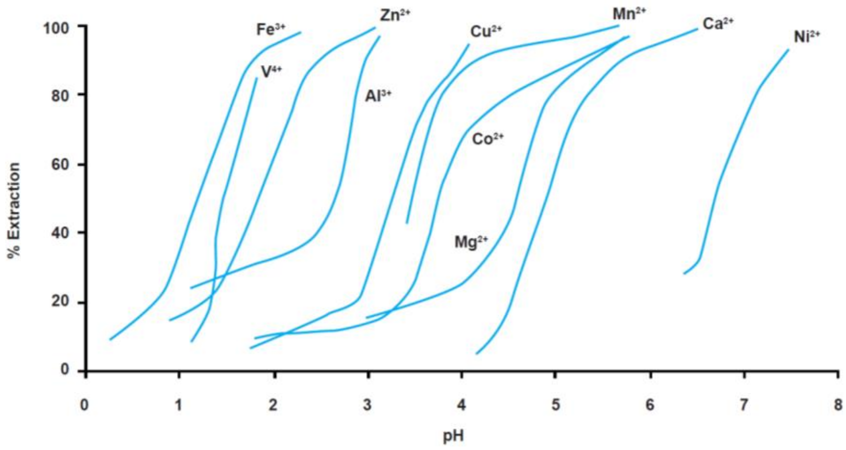


Figure 2-9 Extraction Equilibria of Metals (in %) Using Cyanex 272 vs. pH in Sulphate Solutions ***[49].***

Whereas D2EHPA is commonly used to separate Mn from Co, Ni and Li. The respective selectivity series can be seen in Figure 2-10.

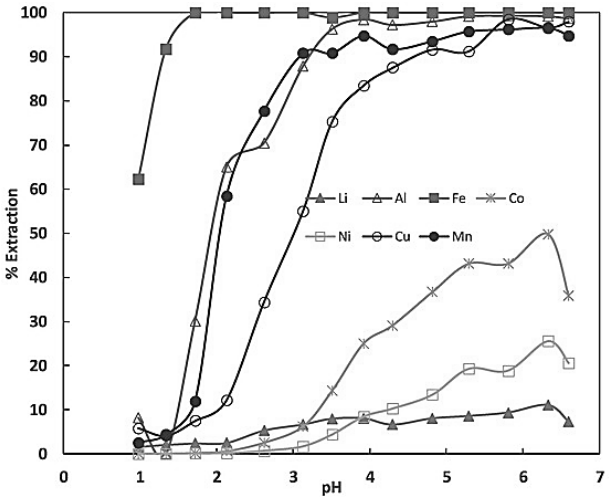


Figure 2-10 Extraction Equilibria of Metals (in %) Using D2EHPA vs. pH in Sulphate Solutions ***[50].***

Metal separations are often enhanced by using a blend of two extractants, as is the example shown in Table 2-4, where a carboxylic acid extractant (Versatic 10, neodecanoic acid) was used in mixture with D2EHPA [43].

2.4.3 Applications

Meshram et al. studied the separation and production of a high purity Co sulphate, 99.9%, from spent LIBs. Figure 2-11 shows the process flowsheet they developed for cobalt recovery using high cobalt feedstock containing Co, Li, Mn, and Ni sulphate solution. Two solvent extraction steps were used, the first separates Mn using D2EHPA, and the second uses Cyanex 272 to separate Co from Ni and Li [40].

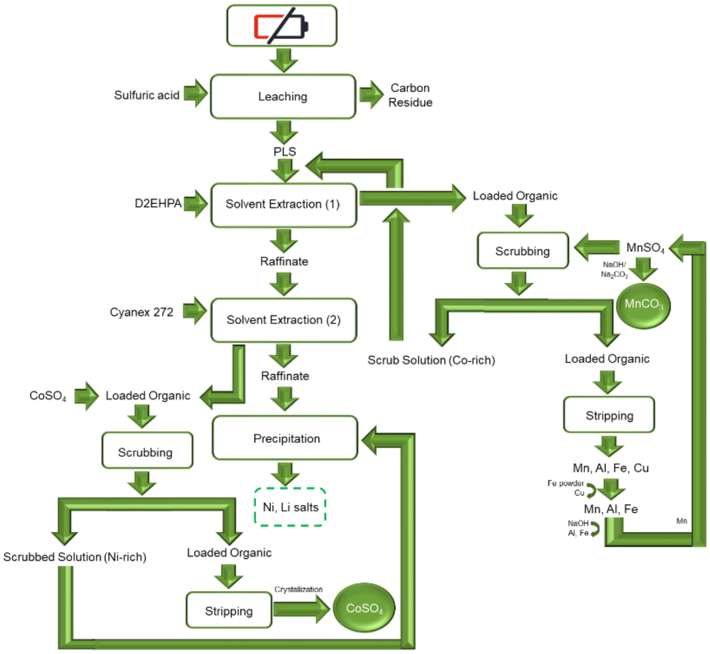


Figure 2-11 Hydrometallurgical Flowsheet for Recovery of Lithium, Nickel, Manganese, and Cobalt from LIBs using Solvent Extraction, Adapted from ***[50].***

There are several commercial hydrometallurgical LIB recycling facilities in operation today. Recovering valuable metals in spent LIBs using recycling started with the "Toxco" process in 1994, rebranded as Retriev Technologies company in 2013 [51] [52]. The Toxco process (Supplementary Figure 1[3]), located in Canada, treats the spent batteries with liquid nitrogen, -196°C, to deactivate them. Once frozen, the batteries are shredded and then report to an aqueous solution with high pH. The material is then sent through a hammer mill, the metallic components are screened and treated with a shaker table to separate aluminum from plastics. The cathode material is sent to the filter tank. The filter cake is rich in graphite and metal oxides, this is referred to as black mass. Metal oxides are then subjected to hydrometallurgical processing.

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[3] Found in Appendix Supplementary Figure 1 at the end of the thesis.

Lithium is recovered as lithium carbonate or lithium phosphate [36]. The overall process recycles 60 per cent of the battery pack materials and has an annual capacity of 4500 tonnes [53].

On a pilot scale, Retriev has patented a process that further treats and regenerates the cathode material. The black mass undergoes thermal treatment to remove the binder and a froth flotation treatment to remove the graphite anode material. The metal oxides from the cathode material are recovered in the non-floated portion and regenerated with LiOH addition (Supplementary Figure 2)[4] [54]. Expansion in the North American market has allowed for the addition of hydrometallurgical separation and purification process improvements but this has yet to be commercialized.

Umicore (Belgium) has the largest capacity, 7000 tonnes/year, amongst the commercial recycling plants using a hydrometallurgical method. The process recovers nickel and cobalt using a combination of pyrometallurgy and hydrometallurgy. Lithium and aluminum are lost as slag in the shaft furnace, shown in Supplementary Figure 3[5]. There appears they are employing two different leaching steps with different chemistry but no details are available.

High temperature is used to treat waste gases, avoiding toxic emissions. Overall, the process recovers ~70 per cent of the metals (but not Li), 10 per cent graphite and 15 per cent of the plastics. The current grade of the recovered metals is not suitable for new battery application [53]. There have been improvements announced at the pilot scale [54].

Brunp Recycling/CATL (China) process has an annual capacity to treat 30 000 t/yr. of spent LIBs [54]. The recycling process includes discharging, thermal pre-treatment, mechanical treatment and hydrometallurgy (acid leaching, solvent extraction, crystallization). The process has a 99+ per cent metal recovery of nickel, cobalt and manganese but very few details have been disclosed. It is further unclear if the copper, aluminum and graphite is recovered in their process (Supplementary Figure 4[6]).

GEM Ltd, also known as Green Eco-Manufacturer Hi-Tech Co., Ltd, is located in China. The recycling company has an annual production of 5,000 tonnes per year. The process begins with pre-treatment which sorts the battery components using comminution (Supplementary

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[4] Found in Appendix in Supplementary Figure 2 at the end of the thesis.

[5] Found in Appendix in Supplementary Figure 3 at the end of the thesis.

[6] Found in Appendix in Supplementary Figure 4 at the end of the thesis.

Figure 5[7]). Metals such as, copper, aluminum, iron, cobalt and nickel, are separated using a hydrometallurgical method and then re-synthesized into salts [7]. The electrolyte is not recovered in this process.

In another application, Accurec (Germany) operates a lithium-ion battery recycling plant that includes thermal, mechanical, pyrometallurgy and hydrometallurgy[8]. The recycling plant treats 3000 tonnes of lithium-ion batteries annually. Accurec has recently announced that they have new technology being implemented that will allow for the recovery also of lithium and graphite [7].

Nickelhütte Aue GmbH (NHA) has been recycling Li-ion batteries in Germany since 2011 [7]. Thermal pre-treatment, pyrometallurgy processing, and hydrometallurgy methods make up the recycling process. The flow diagram, in Supplementary Figure S7[9] depicts NHA's process [55]. The pyromet treatment smelts the spent batteries in a batch furnace to obtain Ni-Co-Mn matte product. A rotary kiln is used to thermally pre-treat the batteries. Limited information is available regarding the specifics of the hydrometallurgy treatment. The overall process capacity is 7,000 tonnes per year [7].

The Duesenfeld lithium-ion battery recycling process, LithoRec[10], completely discharges the battery packs before physical separation. The process isolates the electrode coatings and removes fluoride before leaching. The metals are then separated from graphite. Then lithium, cobalt, nickel and manganese are separated using various extraction methods. The metals are then purified and recovered as battery-grade salts, ready for new cathode manufacturing[11]. The mechanical recycling rate is 72 per cent, the recovery of electrolyte and graphite bring the overall recycling efficiency to 91 per cent. The separator film and high boiler portion of the electrolyte make up the unrecycled 9 per cent. The process implemented in Germany has an annual capacity of 3,000 tonnes [7].

SungEel HiTech, located in Korea, primarily focuses on LIBs recycling. They have a plant capacity that treats 8,000 tonnes of spent LIBs annually. The process involves mechanical separation followed by a hydrometallurgical processing[12]. The company announced in 2020, it

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[7] Found in Appendix in Supplementary Figure 5 at the end of the thesis.

[8] Found in Appendix in Supplementary Figure 6 at the end of the thesis.

[9] Found in Appendix in Supplementary Figure 7 at the end of the thesis.

[10] Found in Appendix in Supplementary Figure 10 at the end of the thesis.

[11] Found in Appendix in Supplementary Figure 8 at the end of the thesis.

[12] Found in Appendix in Supplementary Figure 9 at the end of the thesis.

will be expanding operations to a new site that will triple the current capacity to 24,000 tonnes per year [7, 56].

Dowa Holdings Co. Ltd (Japan) currently treats 1,000 tonnes of spent LIBs a year. The process includes disassembly, thermal pre-treatment (rotary kiln), pyromet and hydromet processing[13]. Details regarding the process technology, efficiency and recovery rates are not available [7].

2.5 Current State-of-The Art Approaches in Hydromet-Based Recycling

2.5.1 Life Cycle Analysis

The life cycle analysis of commercial pyro- and hydro- metallurgy recycling methods was compared to the direct recycling method by Argonne National Laboratories using the EverBatt model, shown in Figure 2-12 [57]. The hydrometallurgy method consumed the highest energy, a result of high chemical/material usage [1]. Greenhouse gas emissions between pyro- and hydromet were around 2 kg/kg cell. The economics were better for hydrometallurgy when compared to pyrometallurgy route because of the higher and more efficient recoveries of high value cathode materials. The advantages for investing research into direct recycling are illustrated in all three sectors of the analysis, energy consumption, GHG emissions and revenue potential.

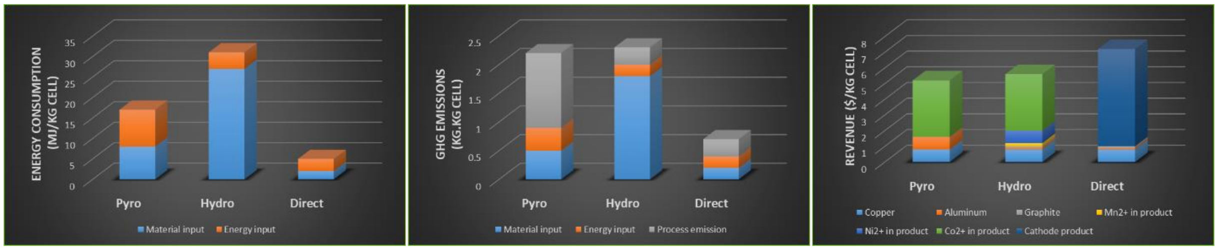

Figure 2-12 Life cycle analysis for pyrometallurgy, hydrometallurgy and direct recycling (pyro, hydro, direct) (a) energy consumption, (b) GHG emissions and (c) revenue from outputs, adapted with permission from ***[1].***

2.5.2 Direct Recycling Concept

Direct recycling has emerged as a more efficient means to recycle NMC cathodes. The traditional recycling processes (hydrometallurgical and pyrometallurgical) decompose the

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[13] Found in Appendix in Supplementary Figure 9 at the end of the thesis.

cathode into high purity elemental products. The separated elements then need to be remanufactured into new cathodes, which is energy-intensive and has a high chemical consumption. Direct recycling maintains the cathode's chemical compound structure through selective regeneration treatment and separation of non-active components enabling its reuse in new battery assembly[14] [57]. Sloop et al. first patented this concept in 2016, [58, 59]. As per ReCell center's modeling work direct recycling has the lowest impacts for all cost and environmental categories [57]. This modeling was done for NMC 111 chemistry, which now is evolving to higher Ni and lower Co content, e.g., NMC 532, 622 and 811, in order to reduce dependency on cobalt and thereby decrease the overall cost and environmental footprint, with the added benefit increased capacity/energy density [60]. Typically, direct recycling (Figure 2-13) consists of three processing steps: (1) selective chemical delithiation (if NMC cathode in discharged state), (2) hydrothermal re-lithiation, and (3) thermal processing/annealing [61].

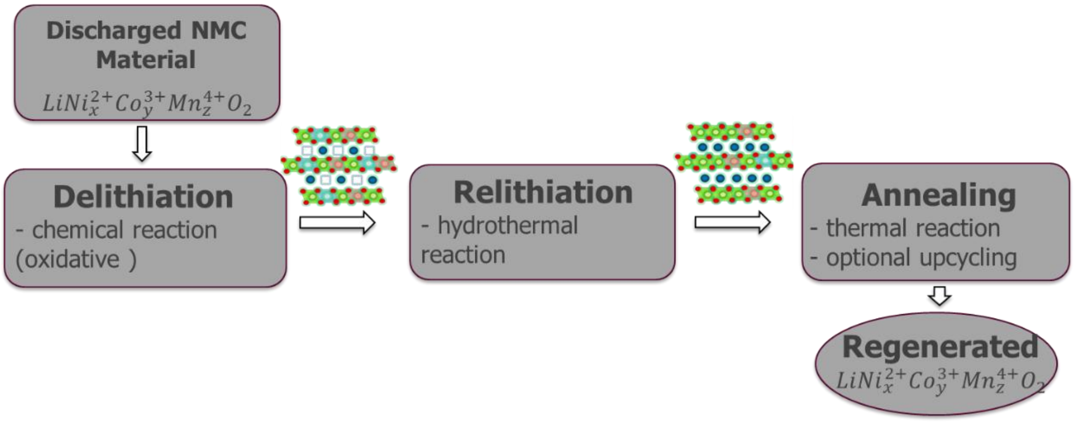

Figure 2-13 Typical Direct Recycling Process of LIBs Containing NMC Cathode

Hydrothermal treatment to induce re-lithiation [1] of the delithiated NMC cathode is done in an autoclave with lithium hydroxide solution, to bring the Li back to ideal stoichiometry, 1.0. [62] as per the following reaction (Equation 2-3).

Equation 2-3

$$Li_{1-x}Ni_xCo_yMn_zO_2 + xLiOH \rightarrow LiNi_xCo_yMn_zO_2 + \frac{x}{2}H_2O + \frac{x}{4}O_2$$

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[14] It should be noted that prior to direct recycling the cathode material is separated from the current collector and other cathode components (carbon and binder) by delamination involving mechanical and physicochemical separation steps. Refer to Appendix Additional Information on Direct Recycling for more information.

Once the target Li concentration has been achieved, a final short annealing treatment is required to restore the layered crystal structure. To compensate for lithium loss during the high temperature annealing, generally 5 mol% excess lithium as carbonate salt is added [1].
This method is non-destructive to the active NMC particles and regenerates their functionality in terms of lithium capacity and conductivity [63].

An interesting variation of the direct recycling approach is the upcycling method which in addition to regenerating NMC it seeks to change its composition from low-Ni to Ni-rich stoichiometries, e.g., from NMC 111 to NMC 622. Upcycling (Ni-enrichment) typically is done during the thermal/annealing stage with the addition and mixing of extra Ni salt to hydrothermally relithiated NMC material [62]. In the following section the latest hydromet process developments aiming are first reviewed and the section ends with description of the first large scale applications of the new direct recycling technology.

2.5.3 Latest Hydromet Developments

France is home to Recupyl, now TES-AMM recycling company. The spent batteries are crushed under an inert gas blanket. The material is then separated by size (to separate black mass in a fine powder from shredded battery components like collector foils, separator and casings), by magnetic separation (removes steel casings) and density separation (separates electrode foils from plastics). Finally, the separated material is subjected to dual leaching treatment to yield partially-delithiated metal oxide cathode and Li_3PO_4 as by-product (See Figure 2-14). Any remaining lithium can be precipitated as Li_2PO_4 using H_3PO_4. The process can also recover cobalt as a hydroxide using NaClO, or elemental cobalt via electrolysis [54]. The annual capacity of the Recupyl process is 110 tonnes.

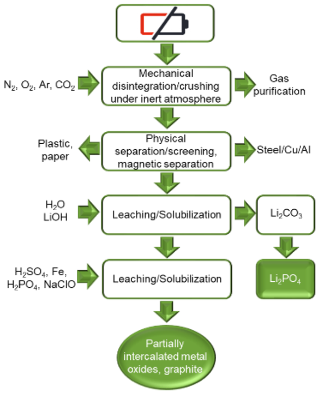

Figure 2-14 Recupyl LIB recycling process ***[54].***

Volkswagen (VW) adopted the LithoRec process from Duesenfeld [43] and is now recycling LIBs on a pilot scale. This is the automaker's attempt to secure the raw materials needed and solve the supply chain shortage in house. The recycling of spent batteries will save VW from expensive procurement and disposal of raw materials. They target to recycle over 90 per cent of spent batteries at the Salzgitterplant plant in Germany [64].

Aalto University (Finland) has developed a laboratory-scale process that targets 99 per cent overall recovery using an improved combination of pyro- and hydrometallurgical steps (See Figure 2-15). The process involves mechanical separation of spent LIBs followed by screening of cathode material from metal foils [8]. The cathode material is subjected to acid leaching with sulfuric acid because of the economic advantages. There is though provision for extra alkali leaching, using sodium hydroxide, in case recovery of rare earth elements -as alkali double sulphates- is justified. The manganese is oxidatively precipitated with potassium permanganate. The iron impurity is removed with sodium hydroxide addition to pH 5.5. The cobalt, nickel and lithium continue into solvent extraction. The recycle of sodium hydroxide is used to precipitate REEs [39].

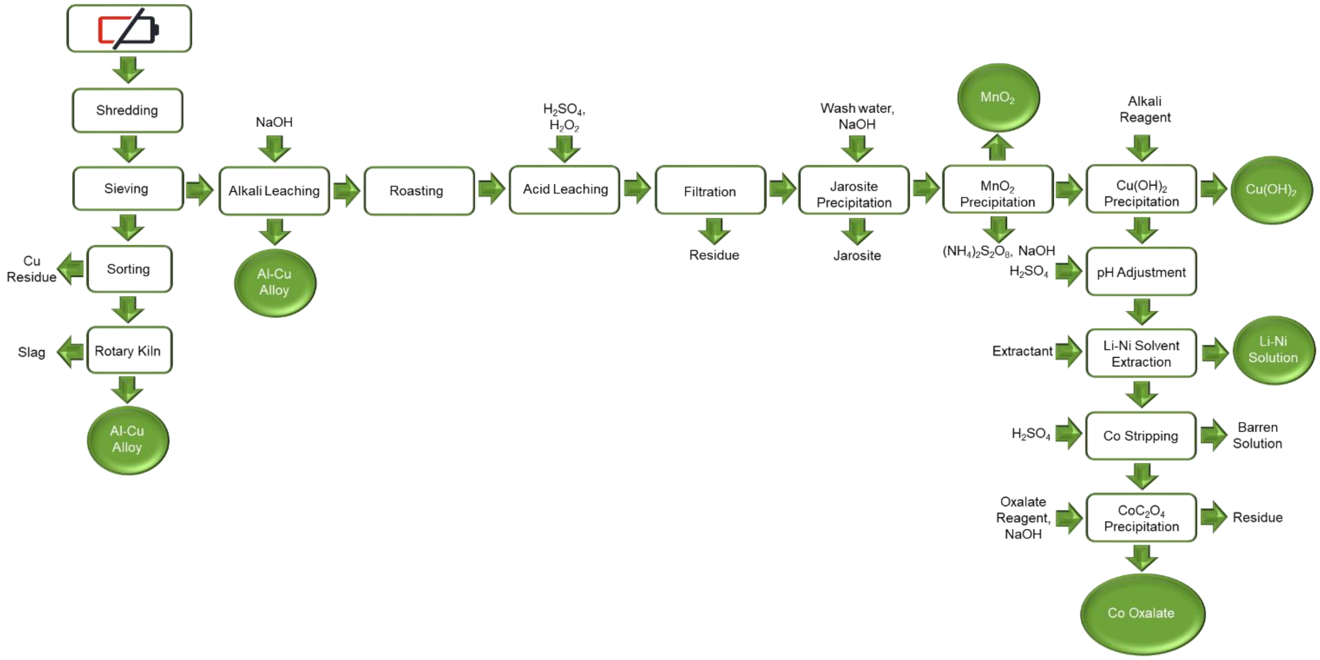

Figure 2-15 Aalto University LIBs recycling process ***[7].***

American Technology Company, located in the USA, uses automated dis-assembly of batteries (high separation of low-value by-products, targeted removal of contaminants) and selective hydrometallurgical processing to obtain battery grade purity cathode products (Figure 2-16) [65]. The commercial recycling facility is under construction. The facility will treat 20 000 tonnes of spent LIBs annually.

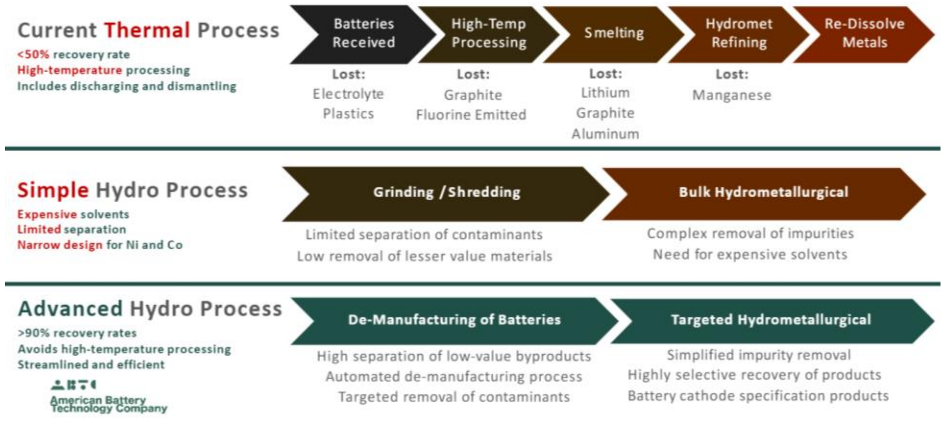

Figure 2-16 American Battery Technology streamlined recycling process ***[65].***

Lithion Recycling received $125 M in funding to build the first recycling plant in Quebec, Canada. Construction of the plant was expected to begin in late 2022/early 2023, following the successful demonstration plant. The hydrometallurgical process operations are outlined in, where in Figure 2-17 (A) the leaching circuit is presented while in Figure 2-17 (B) the metal separation steps [66]. Batteries are physically separated and shredded to separate the black mass from the foils before it is sent to hydrometallurgy processing area. Leaching is done in H_2SO_4 followed by removal of Fe and Al impurities by neutralization and copper by sulfide precipitation before Li/Ni/Co/Mn are separated via a combination of precipitation and solvent extraction steps. The lithium metals are then crystallized in sodium sulphate, producing lithium and sodium sulphate crystals. The lithium is finally recovered by addition of sodium carbonate to produce lithium carbonate. The company claims the hydrometallurgical route, has a recovery rate of 95 per cent battery metals, which are purified for re-entry into the battery production chain [67].

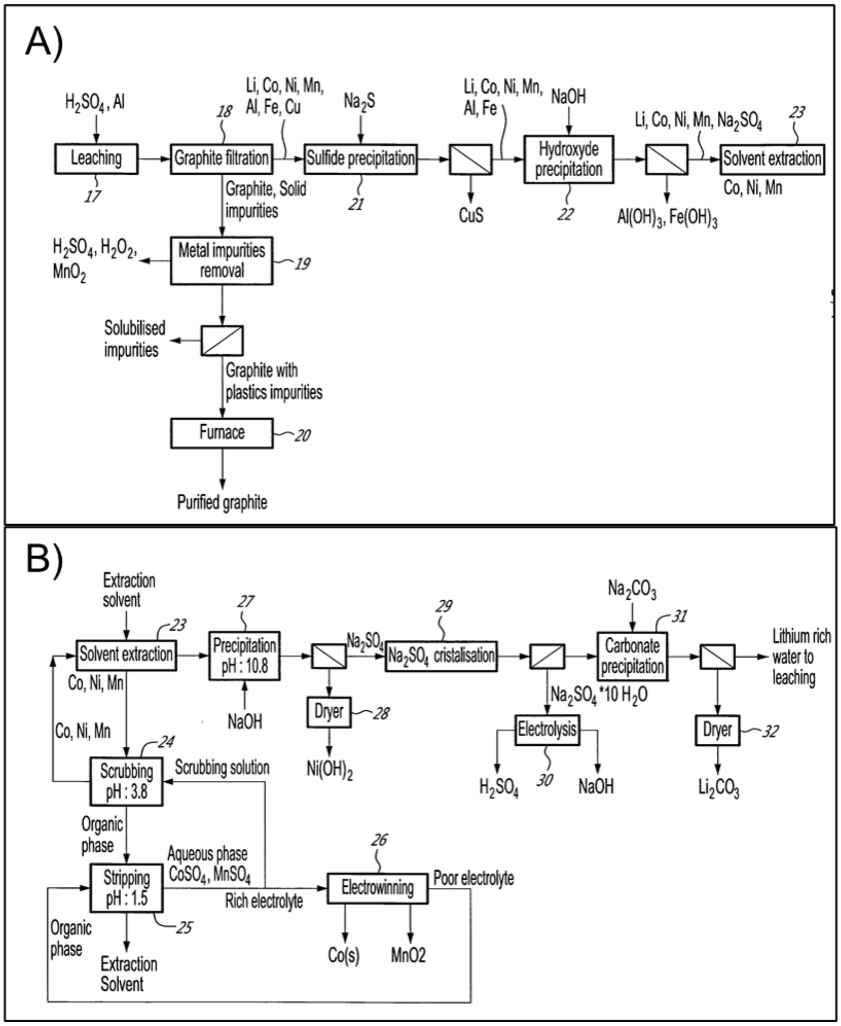

Figure 2-17 Lithion Recycling Patented Hydromet process (A) leaching circuit and (B) Metal separation for recovery of all value metals and graphite from spent NMC ***[66]***.

Li Cycle is another LIB recycling company located in Canada developing a spoke and hub operation for the North American market. The facility treats all types of LIBs and brings them from a charged state to inert product. A combination of mechanical separation and hydrometallurgical resource recovery techniques are used. The mechanical separation and size reduction produces a black mass free of foil components. Then the black mass is forwarded to a hydrometallurgical circuit for recovery of both cathode and anode materials. The graphite and copper sulfide are recovered in the first two stages of the patented process. Then manganese is recovered through solvent extraction and a secondary mixing stage as a carbonate. Cobalt and nickel are both recovered through solvent extraction and crystallization as a sulphate. Sodium sulphate is then recovered through crystallization process. Finally, lithium is treated and crystallized as a carbonate (Figure 2-18). Li-Cycle plans to have seven spokes and one hub in North America and Europe by later in 2023. The Li Cycle process will have greater than ninety-five per cent recovery rate [68].

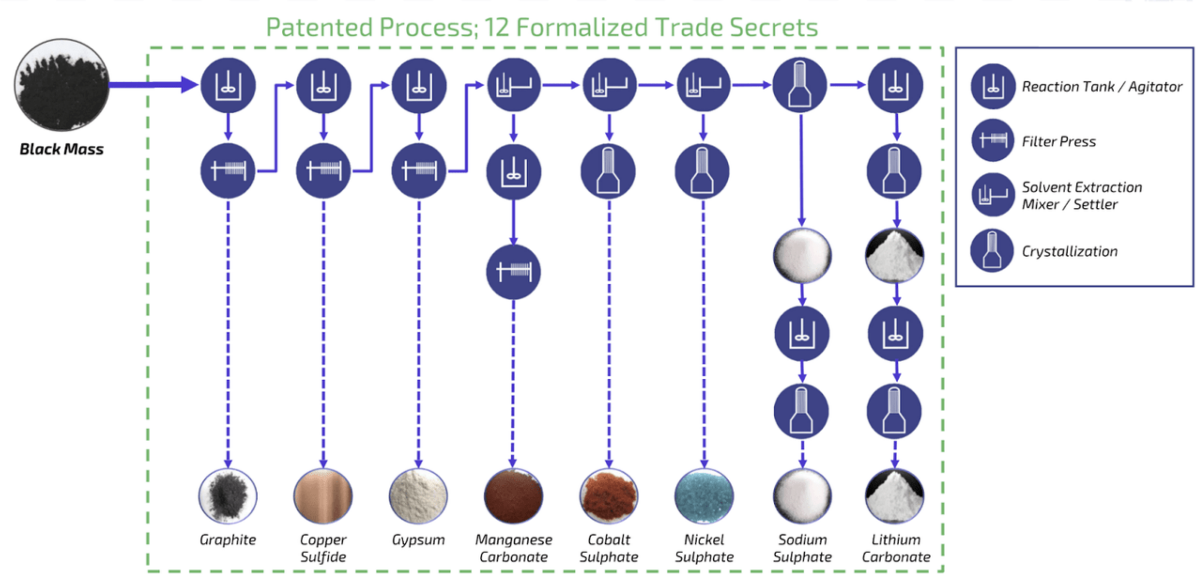

Figure 2-18 Li-Cycle Hydromet Process for Recycling lithium-ion batteries ***[68]***.

2.5.4 First Direct Recycling Application

American Manganese is a recycling company that is using a direct recycling/upcycling approach. The patented process, RecycLiCo^{TM}, has achieved up to 99 per cent recovery of lithium, cobalt, nickel and manganese. Lithium is recovered by electrodialysis. A three-compartment cell regenerates lithium hydroxide and sulfuric acid from lithium sulphate solution. The Li+ moves to the cathode compartment and the SO_4^{2-} moves to the anode compartment, as shown in Figure 2-19 [69]. The demonstration plant is currently being built and will process 500 kg of spent cathode per day. This will be the first hydrometallurgical cathode recycling and upcycling plant in North America [70].

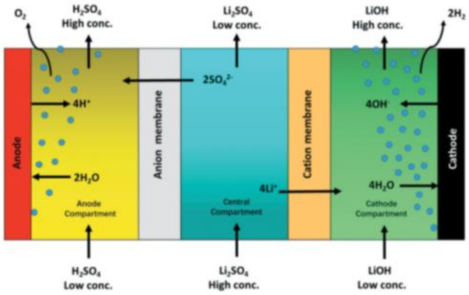

Figure 2-19 American Manganese RecycLiCo^{TM} process, a three-compartment membrane electrodialysis cell for generating LiOH and H_2SO_4 ***[70]***.

Battery Resourcers, now Ascend Elements, is expected to open a 154 000 square foot facility to process 30 000 tonnes of spent LIBs per year in Georgia, USA. Using a hydrometallurgical and direct recycling approach, the process, Figure 2-20, has shown superior performance of recycled cathode materials [71]. The patented Hydro-Cathode^{TM} process claims that upcycled battery materials have 50 per cent longer cycle life and 88 per cent higher power capacity than pristine cathode materials [72].

Figure 2-20 Ascend Elements (Battery Resourcers) LIB recycling process ***[72].***

OnTo Technology LLC has applied their patented process, Cathode-Healing^{TM} Direct Recycling to recalled batteries in at least one case study. The key features of this process include, extraction of electrolyte using supercritical CO_2, shredding, electrode harvest, flotation, Cathode-Healing^{TM}, and rebuilding cells using recycled cathode and anode materials [73]. The cathode healing method, classified as a direct recycling process, uses two-steps, hydrothermal and heat treatment. The hydrothermal treatment can be described as a relithiation process. The lithium is regenerated by using lithium solution (possible hydroxide) to add Li^+ back into the structure, as well as repair the microstructure defects using heat [63].

2.6 Discussion: Challenges and Trends

Currently the recovery of value metals, primarily derived from the cathode, has been the focus of commercial recycling companies using pyro- and hydro- metallurgical techniques [20]. With recent supply chain security issues, more companies are looking to improve the current commercial recycling methods in terms of enhanced recovery efficiencies and sustainability. The hydrometallurgical process route achieves the highest recovery of metals such as: nickel, cobalt, and lithium, with low impurity compared to the pyrometallurgical method. Both processing routes involve high temperature and or high use of chemicals, creating environmental issues and operating costs [74]. Companies such as Retriev Technologies, Umicore, Brunp/CATL, GEM Ltd, Accurec, Duesenfeld and SungEel HiTech all use a hydrometallurgical route to recycle spent LIBs. A combination of pyro/hydrometallurgy is used by Nickelhütte Aue GmbH and Dowa Holdings [7]. Table 2-5 summarizes the current commercial lithium-ion battery recyclers that use hydrometallurgy. Duesenfeld is the only company that recovers the electrolyte while Retriev and Duesenfeld both show the recovery of graphite in their processes [54, 7].

Table 2-5 Summary of Commercial Hydrometallurgical Lithium-Ion Battery Recycling Operations

Company	**Location**	**Capacity (tonnes/year)**	**Method Used to Expose Active Materials**	**Method Used to Recover Recyclable Metals**	**Primary Recovered Materials**	**Secondary Recovered Materials**	**Lost Materials**	**References**
Retriev Technologies	Canada	4500	Wet mechanical treatment	Flotation, alkaline precipitation	Li_2CO_3, MeO	Steel, Cu, Co, Al, graphite	Plastics	***[54]***
Umicore	Belgium	7000	Dismantling/Physical separation	Acid leaching, solvent extraction	Co, Ni, Cu, Fe, $CoCl_2$	Slags: Al, Si, Ca, Fe, Li, Mn, REE	Electrolyte, plastics, graphite	***[54]***
Brunp/ CATL	China	100000	Discharging, thermal pre-treatment, mechanical treatment	Hydromet: H_2SO_4/H_2O_2, Na_2S, or NaHS reductive acid leaching, SX	Ni-Mn-Co hydroxides, Co-Ni sulphates, Co chloride	unknown	unknown	***[7]***
GEM Ltd	China	30000	Sorting, comminution	Hydrometallurgy, high temperature treatment	Co, Ni, Cu, Al, Fe	unknown	Electrolyte, binder,	***[7]***
Accurec	Germany	4000	Sort, dismantle, milling, separation, agglomeration	Vacuum thermal treatment, reductive leaching H_2SO_4	Li_2CO_3, Co-Alloy	Metallic alloy	Electrolyte, polymers, graphite	***[54]***
Nickelhutte Aue GmbH	Germany	3000	Thermal pre-treatment	Pyro- and hydro-metallurgical treatment	Ni, Cu, Co	Slags	unknown	***[7]***
Duesenfeld	Germany	2000	Discharge, inert physical separation: two-stage crushing, air classification	Drying, calcination, leaching	Li_2CO_3, metal oxides	Al-Cu, plastics, electrolyte	graphite	***[7, 54]***
SungEel HiTech	Korea	8000	Mechanical pre-treatment in water	Hydrometallurgical process	Co, Mn, Ni, Li_2CO_3	Cu, Al	unknown	***[7]***
Dowa Holdings	Japan	1000	Dismantle, thermal pre-treatment	Pyro- and hydro-metallurgical treatment	Co, Ni, Cu	unknown	unknown	***[7]***

Although the cathode metal constituents are recovered, providing economic viability in each process listed in, the cathode only accounts for 50 per cent of the battery mass. Valuable components are lost such as graphite, which makes up 12 per cent (0.978 kg/kWh) of the total for a NMC 111 battery, and aluminum and copper, which account for 3.11 kg/kWh and 0.677 kg/kWh respectively [22]. Although the hydrometallurgical and pyrometallurgical processes are widely used commercially, there is much need for next-generation recycling technologies that embrace the circular economy model thus rendering the fast-growing industry sustainable.

Some of the challenges of the hydromet process route that require R&D attention is adaptation towards direct recycling rather than total dissolution followed by metal recovery as practiced today. Further, the reduction of chemical reagent usage by adopting green chemistry alternatives, one such example is the use of CO_2 as lixiviant as demonstrated recently by Larouche et al. in the case of LFP direct recycling [75]. Other challenges are manganese oxidative state control, fluorine (electrolyte) handling, recovery of valuable lithium as battery-grade LiOH or Li_2CO_3 and graphite in a marketable form [1].

A closed-loop recycling process of lithium-ion batteries could save up to 50 per cent of mined raw materials [76]. The environmental impacts can be lowered with a 70 per cent reduction in CO_2 emissions and up to 70 per cent energy consumption savings according to the EverBatt model, developed by Argonne National Laboratory [57].

Emerging recycling technology, direct recycling/upcycling, will need more research to determine the realization of commercialization and compete with current hydro- pyro-metallurgy processes. Direct recycling technology still doesn’t address one of the major challenges with LIB recycling, the need to sort based on battery chemistry. There is no evidence that this process can handle a “mixed cathode” feed stock [57]. The current state-of-the-art hydromet recycling technologies are summarized in Table 2-6. Companies using direct recycling are American Manganese, Ascend Elements (Battery Resourcers) and OnTo Technology LLC.

Table 2-6 Summary of State-of-the-art advanced stage lithium-ion battery recycling processes

Company	Location	Capacity (tonnes/year)	Stage	Method Used to Expose Active Materials	Method Used to Recover Recyclable Materials	Primary Recovered Materials	Secondary Recovered Materials	Lost Materials	Reference
Recupyl	France	110	Active	Dry mechanical treatment under inert atmosphere	H_2SO_4/H_2O_2 reductive acid leach, selective precipitation	Li, metal oxides, graphite	Steel: Cu/Al, plastic	unknown	[31, 32]
Volkswagen	Germany	unknown	Pilot scale	Physical separation, shredding, drying, sieving	Hydrometallurgy	Co, Ni, Mn, Li	Steel, separator, Al, Cu	Electrolyte, plastics	[19]
Aalto University	Finland	unknown	Concept laboratory process	Shredding, sieving	Al smelter, leaching	CoC_2O_4, Al-Cu Alloy	Jarosite, MnO_2, $Cu(OH)_2$, Li-Ni solution	Graphite, binder, plastic, Cu, water	[54]
America Battery Technology	USA	20000	Under construction	Automated dismantling process	Hydrometallurgy: impurity removal	unknown	unknown	unknown	[22]
Lithion	Canada	5000	Under construction	Physical separation, shredding, drying, sieving	Hydrometallurgy, distillation	Ni, Co, Mn, Li	unknown	unknown	[23, 24]
Li-Cycle	Canada	5000	Planned	Mechanical separation, size reduction	Hydrometallurgy	Ni, Co, Mn, Li	Steel: Cu/Al, graphite	Electrolyte, plastics	[25]
American Manganese	Canada	180	Planned	Shred, separate	Direct Recycling/ Hydro upcycling	NMC hydroxide, Li_2CO_3	unknown	unknown	[26, 27]
Ascend Elements (Battery Resourcers)	USA	30000	Planned	Discharge, shred, mag sep, sieve, dense media, ambient	Hydromet/ Direct Recycling: NaOH, H_2O_2, H_2SO_4 and Na_2CO_3	Li_2CO_3, cathode powder	Ferrous metals	Electrolyte	[54]
OnTo Technology LLC	USA	unknown	unknown	Supercritical CO2, physical disassembly	Hydromet/ Direct recycling: heat treatment, LiOH leaching	cathode powder, Li_2CO_3	Electrolyte, graphite, Fe, Al, Cu, plastics	unknown	[20, 30, 33]

2.7 Conclusion and Perspective

In summary, the need to secure a reliable supply chain that is sustainable for lithium-ion battery manufacturing is imperative. The current EV market demand creates an exponential increase in materials needed to manufacture LIBs. Mining raw materials will not be sufficient to meet this demand. Hydrometallury has been the most widely adopted recycling method, it is an effective route to recycle expensive cathode materials but comes at a cost, high energy consumption and greenhouse gas emissions. Improvement to the process is also required to recycle additional products such as lithium and graphite, bringing a closed loop. The new direct recycling approach and its upcycling variant shows a promising green recycling potential. The process is simpler and more effective in regenerating the cathode materials and restoring its electrochemical performance, without total decomposition/dissolution and re-fabrication. Hydrometallurgical innovations hold a lot of promise in rendering direct recycling and upcycling a commercial reality but further R&D efforts need to be intensified. The challenge all current recycling processes face is the feed stock needs to be indiscriminate to the different LIB cathode compositions. Upfront sorting and separation are less than ideal. By far NMC cathodes however due to volume and common element make-up (Li, Ni, Mn, Co) even if of variable composition (111, 532, 622, 811) should be a priority in developing direct hydromet-assisted recycling technologies rather than the current practice of total dissolution and metal recovery only.

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Chapter 3 Scope of Research

The literature review of the NMC cathode recycling technologies presented in Chapter 2, identified direct recycling to be the most favorable from a sustainability perspective [15] [23]. In this context it was decided to focus the present experimental investigation on the key steps involved in direct recycling including upcycling of NMC cathodes.

As previously discussed in Chapter 1, the most abundant prolific cathode chemistry is NMC hence its selection as this study's focus. The composition of NMC cathodes varies, ranging in nickel content from the first low-Ni type, NMC 111, introduced in 2011, to the more recent Ni-rich one, NMC 622 [24]. As a result, several variations of EV NMC cathode compositions will be available for recycling. Hence it was important for this research to cover a low nickel and a high nickel NMC cathode. With the gradual shift from low-Ni to high-Ni composition, it becomes apparent that when an EV battery reaches its end-of-life, its chemistry will be outdated and it will be advantageous to regenerate it into newer Ni-rich chemistry. The conversion of the old chemistry of a recycled NMC cathode into the new chemistry, constitutes what it is called upcycling and this possibility makes direct recycling very favorable.

For the purposes of this research, the following aspects are investigated following previously described in literature procedures with the aim of establishing the baseline for further process developments and optimizations:

1. Experimental verification of direct recycling of a low and high nickel NMC cathodes through modified chemical delithiation, hydrothermal treatment and annealing.
2. Subject to upcycling the low-Ni NMC cathode by using nickel sulphate salt (not tested before) as extra nickel source during annealing and comparing obtained composition to pristine high-Ni NMC.
3. Examine the effect ultrasound mixing has on hydrothermal treatment in inducing enhanced crystallinity of the directly recycled NMC cathode material.

Chapter 4 Experimental Study

The content of this chapter is based on a manuscript[15] to be submitted for publication in a special issue of the journal *Next Energy* with theme *Direct Recycling of Li-ion Batteries, What's Next?*

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[15] Krystal Davis and G. P. Demopoulos, Investigative study of upcycling spent synthetic NMC cathodes enabled by ultrasound-assisted hydrothermal treatment, to be submitted, May 2023

Abstract

It is imperative that a sustainable approach to the proper processing of lithium-ion batteries (LIBs) as they reach their end-of-life (EOL) is realized as 11 million metric tonnes are expected to reach EOL by 2030. Conventional recycling processes currently in practice, such as pyrometallurgy and hydrometallurgy, are not fully sustainable options due to their high energy/chemical consumption, greenhouse gas (GHG) emissions and economic dependability on the profit of cobalt and nickel. These traditional processes break down the active cathode material (e.g., $LiNi_xMn_yCo_zO_2$, NMC) and recover only the value metals for use in new re-synthesis manufacturing. By contrast direct recycling that has emerged recently aims in regenerating EOL LIB cathodes without any break down of the active compound's crystal structure. This process is heralded as a front runner in battling climate change and economics. As battery NMC cathode chemistries evolve to higher energy/nickel-rich formulations, the direct recycling approach needs to be adapted to include upcycling. Upcycling is when a compositional change in the chemical structure occurs, such as low-Ni NMC 111 is upgraded to high-Ni NMC 622. In this work, the baseline is established for direct recycling of low and high nickel NMC cathodes by analyzing the three key steps of chemical delithiation, hydrothermal relithiation, and annealing. Application of ultrasound mixing prior to hydrothermal relithiation is shown to enhance the crystallinity of regenerated NMC structure as it increases the reaction area by cavitation affect. Lastly upcycling of NMC 111 to NMC 622 using pre-calculated co-addition of excess $NiSO_4$ and Li_2CO_3 during annealing, following the hydrothermal relithiation step, is successfully demonstrated.

4.1 Introduction

With the onset of the rapid change from internal combustion engine (ICE) to electric vehicle (EV) in the automotive industry, the demand on raw materials that make up a battery is surging and is predicted to increase as much as 500 % by 2050. Elements such as, Li, Ni and Co all have severe supply issues in the near future. These shortfalls even take into account the new mines that are probable and highly probable to start [1].

With the stress and uncertainty of securing the raw materials, predicted price increases in lithium and nickel could jeopardize the economics in EV battery production by an increase of $14/kWh in 2023. Recycling could help alleviate the demands on critical virgin materials. This would help bring price parity, $100/kWh, between ICE and EV's sooner than the predicted 2026 [2]. Simultaneously, recycling could reduce waste as 11 M tonnes of LIBs are set to retire for example by 2030. This will help countries to reach the set goal of 20 % electrification of transport sector by 2030 [3].

There are currently large-scale commercial recycling facilities for lithium-ion batteries which employ either a hydrometallurgical process, pyrometallurgical process or a combination of the two to recover valuable metals like Co, Ni, and in some cases Li [4] [5]. Presently, the hydromet processes are overall more economical than pyrometallurgical ones due to the high recovery and purity of pay metals including lithium, but they are associated with high energy/chemical consumption, and GHG emissions [6]. Although the economics are better than both pyrometallurgy and the combination hydro/pyro processes, the climate impacts are still of concern. There is a new recycling processing route that has become a frontrunner in both battling climate change and economics, direct recycling. Without any dissolution in a chemical solvent, direct recycling aims in preserving the cathode material's functional structure. Due to its advantages over alternative recycling procedures in terms of energy consumption, cost, and environmental impact (refer to Figure 4-1 [12].

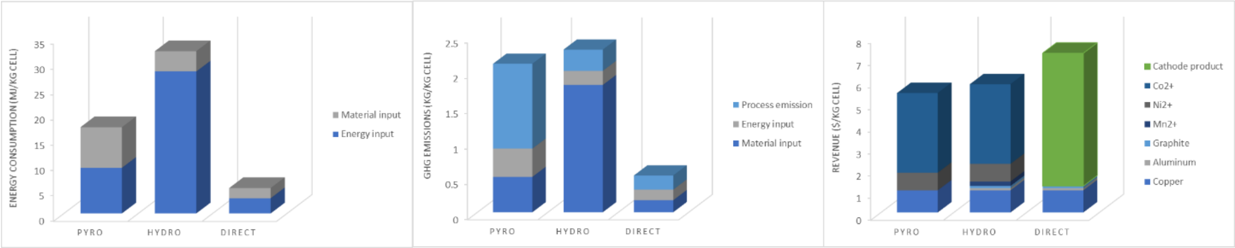

Figure 4-1. Life cycle analysis of pyrometallurgy, hydrometallurgy and direct recycling processes; a) energy consumption b) GHG emissions c) potential revenue, adapted with permission from ***[12].***

Cathodes are the positive electrodes representing the most expensive component of a Li-ion battery. Typically, a cathode accounts for approximately 51 % of the cost of a lithium-ion battery, making it desirable to recycle [7]. A schematic of the lithium-ion battery is illustrated in Figure 4-2.

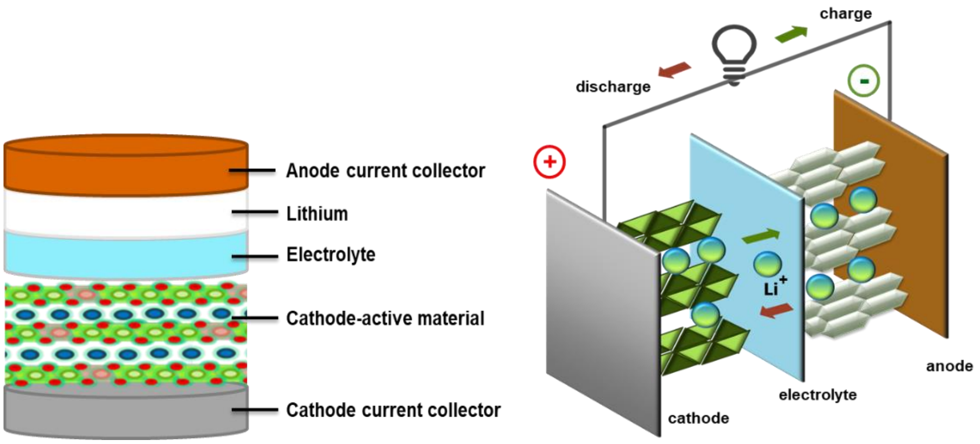

Figure 4-2. Lithium-ion battery schematic diagram (left), schematic of lithium-ion battery cell charging/discharging mechanism (right).

The most common cathode active material (CAM) is NMC made of lithium, nickel, cobalt and manganese: $LiNi_xMn_yCo_zO_2$. With the fluctuations in the market value of these metals, the cost of the cathode has increased dramatically. According to Benchmark Mineral Intelligence cathode price assessment, LIBs containing high nickel cathode chemistry, such as NMC 811, could be $78/kWh. This is a nearly double the cost in January 2021. This accounts for approximately 51 % of the cost of a lithium-ion battery, making it desirable to recycle A cathode becomes degraded or deactivated over time. Cycling occurs every time a battery is charged and discharged (Figure 4-2). The cathode goes through a series of electrochemical reactions that can cause physical and chemical changes to the material. Over time, these repeated cycles can cause degradation when the lithium ions become trapped within the cathode material and do not move freely. There are a few reasons this can occur. When charging, the electronic structure of an NMC cathode undergo reversible transformation during lithium de-intercalation (Figure 4-2). Continuous cycling causes cation mixing to occur. The Ni^{3+} and Mn^{3+} migrate to the vacant octahedral Li sites. Once this occurs, there is an irreversible loss of lithium and the onset of rock-salt phase occurs [8]. The capacity of the battery is reduced and therefore a loss in performance is realized. High temperature can also accelerate the degradation of cathode material by increasing the rate of electrochemical reactions. The battery's electrolyte or cathodic material can contain impurities which interfere with electrochemical reactions. Contaminants, such as copper, within the battery cause deposits on the surface of the cathode which cause lower discharge capacity [9]. Structural changes can happen also during cycling due to arising of localized internal heat generation or strain, which will result in deactivating the cathode material. High internal temperature occurs when there is a high current state, fast charging or discharging. Aging occurs even if the battery is not in use due to storage climate, but is accelerated during high temperatures [11]. Exposure to environmental factors, moisture, light or oxygen, can also contribute to aging.

Direct recycling is a two-stage process with includes delamination/separation[16] and regeneration of the cathode active material (CAM). The regeneration stage aims to restore the reversible capacity by inserting lithium back into the CAM structure that has been lost or put *hors combat* during cycling. Different relithiation methods have been proposed from solid state synthesis [12], to special methods like Cathode Healing^{TM}, and eutectic-salts [34].

Hydrothermal regeneration involving treatment of the spent/delithiated cathode material in a Li^+ ion solution at elevated temperature, typically, 100-220°C, was first demonstrated in the case of $LiCoO_2$ cathode [35]. This approach was later shown to be also effective in the case of NMC cathodes with simultaneous restoration of their layered structure [21][36]. Lithium hydroxide is the most common source of lithium ions in hydrothermal synthesis but some

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[16] It should be noted that prior to direct recycling the cathode material is separated from the current collector and other cathode components (carbon and binder) by delamination involving mechanical and physicochemical separation steps. Refer to Appendix Part B for more information

research has been done on a combination of LiOH and KOH mixtures or LiOH and Li_2SO_4 [34][8].

Building on these promising developments further direct recycling research that can lead to optimized pathways towards scalable processing on one hand and upcycling of retiring low-Ni NMC cathodes to new generation Ni-rich NMC cathodes becomes a critical priority. High nickel, low cobalt cathodes (e.g., NMC 622, NMC 811) are predicted to be the next-generation of cathodes for LIBs. Spent cathodes available for recycling are far behind the rapidly evolving Ni-rich NMC materials because they are available years later (8-10 years on average). In response to this, upcycling that can effect a compositional change in the chemical structure, NMC 111 to 622 for example was advocated recently by researchers at US national laboratories [15][6].

To date very limited work has been reported on upcycling of NMC cathodes. As commented by Gaines et al. [6], upcycling is expected to be challenging as the increase in Ni content can easily lead to cation mixing or defects and impurity phases crippling the Li-ion intercalation kinetics. They mentioned the obtainment of promising results with the addition of $Ni(OH)_2$ but without providing details [6]. Meanwhile Wang et al. [15] have sought to insert Ni into the NMC host structure using “reciprocal ternary molten salts” achieving to convert NMC 111 to NMC 622 that has twice the mass of 111. High temperature and oxygen-rich environment during annealing are essential to achieve the oxidation of Ni^{2+} to Ni^{3+} and create similar to pristine layered structure [15].

This chapter will report the successful application of hydrothermal relithiation to upcycling of NMC cathodes using as example the conversion of 111 to 622. Firstly, the regeneration of both NMC 111 and NMC 622 using hydrothermal treatment is verified in concert with the application of ultrasound mixing to promote defect-free crystal restoration [12]. The reported results justify further research towards optimization and upscaling the hydrothermal upcycling process with real spent NMC battery materials as a truly sustainable recycling technology.

4.2 Experimental Section

4.2.1 NMC Material Delithiation

In this work synthetic “spent” NMC cathodes were prepared by chemical delithiation of commercial NMC cathodes. Pristine NMC materials, NMC 111 and NMC 622, were obtained from Toda America Inc. The oxidant, potassium persulphate (99+% A.C.S reagent grade), was purchased from Sigma-Aldrich. The chemical delithiation of the pristine $Li(Ni_xMn_yCo_z)O_2$ material was performed using a standard 2 L mechanically stirred glass reactor. In a typical test, 10 g NMC material (in powder form) was added in 1 L 0.5M $K_2S_2O_8$ solution which was heated to 50°C for 180 min. Various solution concentrations, temperatures and pHs were studied to arrive to the targeted % delithiation extent. Once completed the test, the contents were filtered, washed three times with deionized water and dried in the oven at 80°C overnight. These samples were denoted as “DL-#”.

4.2.2 Material Regeneration

Hydrothermal relithiation. For this study, the hydrothermal treatment was done by mixing 1 g of pre-delithiated NMC material with 125 mL of 4 M LiOH in a Parr 250 mLTeflon-lined autoclave bomb. Lithium hydroxide (98% A.C.S. reagent grade) was purchased from Sigma-Aldrich. The autoclave was closed under air and heated to 220°C for a duration of 4 hours. In a separate series the effect of ultrasound mixing on hydrothermal relithiation was investigated using the VCX 750 Sonics Ultrasound generator that generated ultrasonic wave with a frequency of 20 kHz. Ultrasound mixing was applied (for 10 min) by inserting the 0.5” probe inside the 250 mL Teflon liner which contained 125 mL of the DL-NMC/LiOH suspension prior to loading it into the autoclave. The relithiated material was filtered, washed three times with deionized water to remove residual LiOH, and dried in an oven at 80°C overnight. The samples after hydrothermal relithiation were identified as “HT-#”.

Short annealing regeneration. Following the relithiation treatment, 5 mol. % excess lithium carbonate (>99% A.C.S. reagent grade obtained from Sigma-Adrich) was mixed with the dried material to compensate for Li losses. It was then heated in a tube furnace to 850°C for 4 hours. The Carbolite Ltd. tube furnace, model TZF 12/100/900, was programmed with a ramping rate of 5°C/min. The final product was washed three times in hot (90°C) DI water to remove excess Li_2CO_3, filtered and dried overnight at 80°C.The samples were labeled as “SA-#”.

4.2.3 Material Characterization

Chemical analysis of solutions and solids. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 3000 DV) was used to determine the chemical compositions (Li, Ni, Co, Mn) of all samples. The solids were digested prior to ICP analysis in aqua regia on a hot plate for 90 min. All solutions were diluted in a 2 % v/v HNO_3 solution prior to analysis.

X-ray diffraction spectrometry. The crystal structure of the material was characterized using a Bruker D2 Phaser X-ray powder diffraction (XRD), equipped with a Cu K_α radiation from 2θ= 10 to 80°in a step of 0.02°/min.

Scanning electron microscopy. The morphology was examined by using a Hitachi SU-5000 scanning electron microscope (SEM) equipped with an Oxford X-Max 80mm EDX detector. The images were taken at 20 kV accelerating voltage.

4.3 Results and Discussion

A flowchart of the process followed to regenerate and upcycle NMC 111 and NMC 622 is shown schematically in Figure 4-3. The pristine NMC material was chemically delithiated (DL) prior to the two-step regeneration process, hydrothermal relithiation (HT) and short annealing (SA). The results for each step in the process are outlined below. The data reveals that regeneration of both NMC 111 and 622 as well as upcycling NMC 111 into NMC 622 yields a material that is consistent with virgin materials.

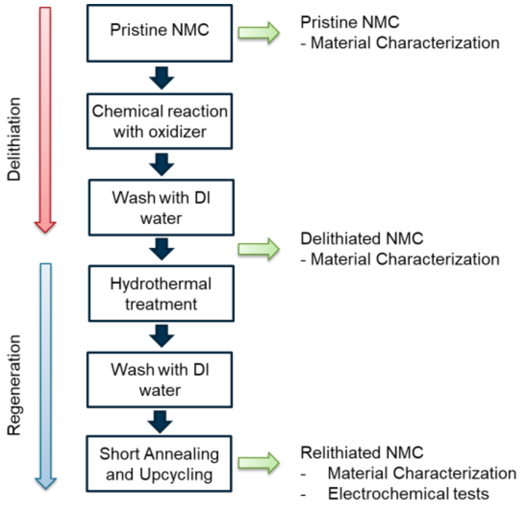

Figure 4-3. Direct recycling with upcycling process overview flowsheet

4.3.1 NMC Material Delithiation

Prior to studying hydrothermal relithiation as a basis of direct recycling and upcycling process, pristine NMC-111 and NMC 622 were chemically delithiated (DL-NMC111, DL-NMC622) in order to serve as synthetic “degraded/spent” cathodes. This was preferred over using spent material from EOL batteries as it allowed at this early research stage for a better understanding of the process chemistry by eliminating interference from impurities. Upon establishing the baseline in the current study future work will be extended into real spent NMC cathodes.

To induce delithiation the pristine NMC cathode must be subjected to chemical oxidation. In its pristine state, $LiNi_xMn_yCo_zO_2$ has Ni in Ni^{2+} state, Mn in Mn^{4+}, and Co in Co^{3+} state. Nickel provides most of the capacity via reversible Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox reactions. Cobalt prevents the undesired cation mixing between Ni^{2+} and Li^+ and provides additional capacity from Co^{3+}/Co^{4+} redox couple. Manganese remains electrochemically inert in Mn^{4+} and stabilizes the crystal structure especially when the cell is charged to a highly delithiated state [37]. This implies an appropriate oxidizing reagent must be selected that has a high standard reduction potential exceeding those of Ni and Co couples. As per data listed in Table 4-1 potassium persulphate as $K_2S_2O_8/K_2SO_4$ redox couple has a standard reduction potential of 1.96V exceeding those of Ni^{2+}/Ni^{4+} and Co^{3+}/Co^{4+} which are 1.593V and 1.416V respectively. The higher potential in potassium persulphate means it is thermodynamically powerful enough to fully delithiate the NMC material [19].

Table 4-1 Standard reduction potential (V) for NMC reaction with potassium persulphate ***[18].***

Reaction	Standard Reduction Potential (V)
Ni^{2+}/Ni^{4+}	1.593
Co^{3+}/Co^{4+}	1.416
$K_2S_2O_8/K_2SO_4$	1.960

The full delithiation of NMC 111 with $K_2S_2O_8$ is chemically described with the reaction in Equation 4-1 below.

Equation 4-1

$$2\left(Li^{+}Ni_{0.33}{}^{2+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2{}^{2-}\right) + K_2{}^{+}S_2{}^{7+}O_8{}^{2-} \rightarrow Li^{+}Ni_{0.33}{}^{4+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{4+}O_2{}^{2-} + Li_2{}^{+}S^{6+}O_4{}^{2-} + K_2{}^{+}S^{6+}O_4{}^{2-}$$

Potassium persulphate is an environmentally responsible oxidant based on its low cost, stability, nontoxic nature, weakly polluting nature, and ease of handling [19].

However, other than thermodynamics the kinetics must be favourable as well. Preliminary results at ambient temperature were not successful but after varying several parameters, it was determined that the amount of lithium removed can be controlled by adjusting the molar ratio between NMC and the oxidant, as well as the temperature, and pH. The relevant conditions and results are shown in Table 4-2.

Table 4-2. Conditions in NMC 111 chemical delithiation tests and amount of lithium removed in wt. %, all tests completed in 180 min, *DL-12 was done with NMC 622 material

Test ID	**pH**	**Temp** **◦C**	**NMC** **10g/L**	**$K_2S_2O_8$** **M**	**Li removed wt. %**
DL-3	5.2	ambient	10	0.5	<5
DL-5	5.7	ambient	10	0.2	19
DL-6	4.5	50	10	0.2	31
DL-7	4.3	75	5	0.5	99
DL-8	5.1	90	5	0.5	98
DL-9	**7.0**	**50**	**10**	**0.5**	**35**
DL-12*	**7.0**	**50**	**10**	**0.5**	**40**

On average, a battery reaches its EOL after 10 years, the cell capacity drops below 80% of the original [22]. Several delithiation tests were performed to optimize and target 20-40 % lithium removal. Figure 4-4 shows the evolution of lithium extraction with temperature. Increasing the temperature to 75°C yielded 99 % lithium removal. The pH adjustment to 7 eliminated co-extraction of other elements. It was decided that the optimal conditions, pH 7 at 50°C, which yielded a 35 % lithium extraction (DL-9) would be used for NMC 111. The same conditions were used on NMC 622 material in DL-12, yielding 40 % lithium removal.

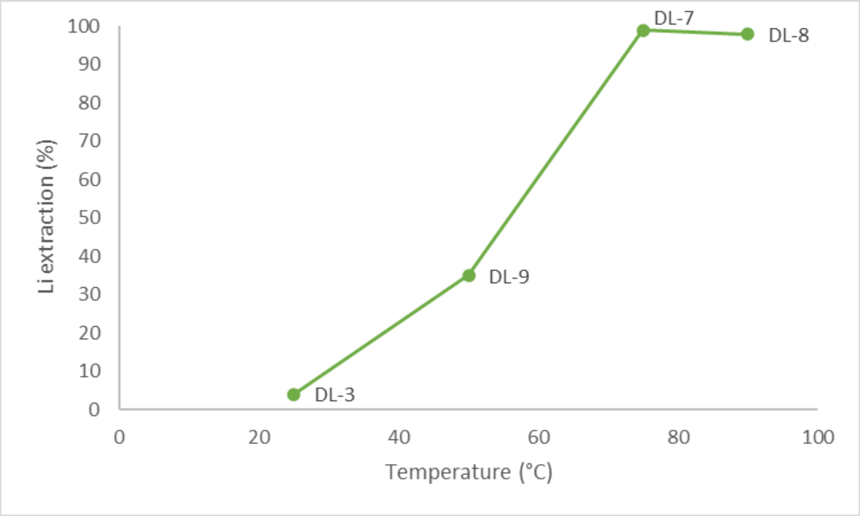

Figure 4-4 Extraction of Li from NMC 111 as a function of temperature (°C), all tests were run for 180 minutes using 0.5 M $K_2S_2O_8$.

Table 4-3 summarizes the experimentally determined stoichiometries of the pristine and delithiated materials. The composition was calculated by determining the metal molar ratios after ICP analysis of digested samples. The results[17] show lithium is removed in the 35-40 % range while transition metals maintain a typical NMC 111 and 622 composition. Since only approximately 1/3 of Li was extracted, it is postulated that this came out of the preferential oxidation of nickel only from Ni^{2+} to Ni^{3+} (due to its favourable reduction potential, 1.02 V vs. 1.59 V [19]) as per proposed half reactions in Equation 4-2 and Equation 4-3 for NMC 111 and NMC 622 respectively.

Equation 4-2

$$LiNi_{0.33}{}^{2+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2 \rightarrow Li_{0.67}\,Ni_{0.33}{}^{3+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2 + 0.33Li^{+} + 0.33^{e-}$$

Equation 4-3

$$LiNi_{0.60}{}^{2+}Mn_{0.20}{}^{4+}Co_{0.20}{}^{3+}O_2 \rightarrow Li_{0.67}\,Ni_{0.27}{}^{2+}\,Ni_{0.33}{}^{3+}\,Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2 + 0.33Li^{+} + 0.33^{e-}$$

Table 4-3 Chemical composition of pristine, delithiated NMC 111 and NMC 622 cathode materials

Sample	NMC 111	NMC622
Pristine	$Li_{1.163}Ni_{0.393}Co_{0.390}Mn_{0.392}O_2$	$Li_{1.174}Ni_{0.765}Co_{0.237}Mn_{0.250}O_2$
Delithiated	$Li_{0.766}Ni_{0.391}Co_{0.390}Mn_{0.388}O_2$	$Li_{0.768}Ni_{0.681}Co_{0.211}Mn_{0.219}O_2$

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[17] Duplicate tests performed yielded satisfactory reproducible results as discussed in Chapter 5, Figure 5-2.

The XRD patterns for pristine NMC 111 and NMC 622 as well as the delithiated material, DL-9 and DL-12 are shown in Figure 4-5. Shi et al. reported lithium deficiency indicators in XRD patterns which are consistent with the results presented in Figure 4-5 [23]. The (108)/(110) doublet peaks increase with cycling because of the decrease in *a* lattice parameter, the (003) peak shifted to lower angles as a result of the electrostatic repulsion across the van der Waals gap between $Ni_xMn_yCo_zO_2$ layers along *c* the directions, and the merging of the (006)/(102) doublet peaks indicate spinel phase [23] that is found in partially degraded NMC cathodes. The XRD results confirm the pristine structure of $\alpha - \mathrm{NaFeO_2}$.

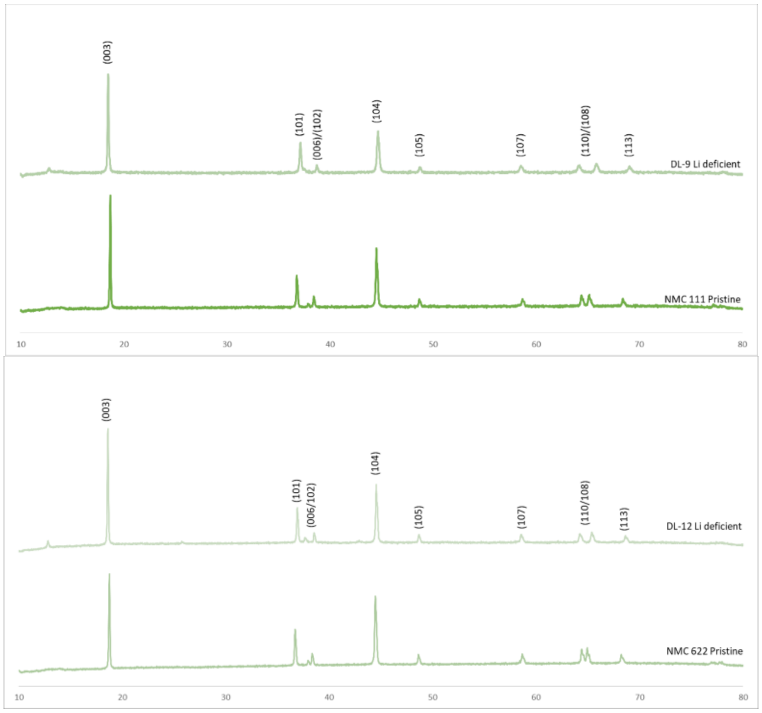

Figure 4-5 XRD patterns for NMC 111 pristine and DL-9 35 % delthiated material (top), NMC 622 pristine and DL-12 40% delithiated material (bottom). All peaks represent crystal planes of the layered NMC structure (x-axis 2θ(°), y-axis intensity (a.u.)).

NMC particle surface and bulk morphologies were examined with the aid of SEM images as shown in Figure 4-6. Delithiated NMC 111 and NMC 622 at the 500 nm magnification were compared. Layered gaps can be observed for the NMC 111 particles, (Figure 4-6d). The same layered gaps are not noticed in the NMC 622 sample, (Figure 4-6h). The particles were observed to be polycrystalline; most are around 12 µm and there are some smaller particles around 2 µm.

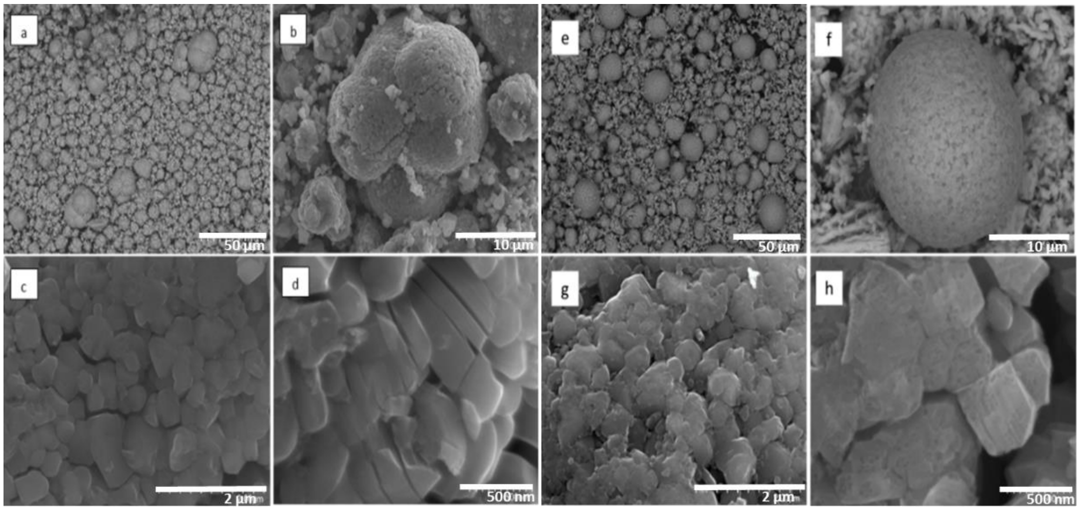

Figure 4-6 SEM images of NMC 111 delithiated material a) 50.0 µm b) 10.0 µm c) 2.00 µm d) 500 nm, and NMC 622 delithiated material e) 50.0 µm f) 10.0 µm g) 2.00 µm h) 500 nm.

4.3.2 Material Regeneration, Hydrothermal Treatment

In order to restore the delithiated NMC materials into their original structure and composition, a two-step treatment, hydrothermal relithiation (at 220°C) and short annealing at 850°C) was applied following the earlier study by P. Xu et al. [12]. Hydrothermal treatment involved suspension of delithiated NMC in a 4 M lithium hydroxide solution (as determined by Shi et al. [23]).

Li^+ ions re-inset back into the NMC structure, while simultaneously Ni^{3+} is reduced *in situ* to Ni^{2+}. The relithiation process for the case of NMC 111 is represented by the reaction illustrated in Equation 4-4 [4].

Equation 4-4

$$[0.33Li^+(aq) + 0.33OH^-(aq)] + Li_{0.67}Ni_{0.33}{}^{3+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2 \xrightarrow{220°C\ 2h} LiNi_{0.33}{}^{2+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_2 + \frac{0.33}{2}H_2O + \frac{x}{4}O_2$$

ICP-OES analysis[18] was carried out to confirm the elemental composition of Li:Ni:Co:Mn and are presented in Table 4-4. The findings show that the anticipated stoichiometric ratio of the relithiated material is consistent with the expected molar ratios of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$.

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[18] Duplicate tests with good reproducibility are reported in Chapter 5, Figure 5-2.

Table 4-4 Chemical composition for pristine, delithiated and hydrothermally relithiated NMC 111 and NMC 622 materials

Sample	NMC 111	NMC622
Pristine	$Li_{1.163}Ni_{0.393}Co_{0.390}Mn_{0.392}O_2$	$Li_{1.174}Ni_{0.765}Co_{0.237}Mn_{0.250}O_2$
Delithiated	$Li_{0.766}Ni_{0.391}Co_{0.390}Mn_{0.388}O_2$	$Li_{0.768}Ni_{0.681}Co_{0.211}Mn_{0.219}O_2$
Hydrothermal	$Li_{1.150}Ni_{0.381}Co_{0.390}Mn_{0.384}O_2$	$Li_{1.102}Ni_{0.679}Co_{0.220}Mn_{0.227}O_2$

The structure and morphology of both NMC 111 and NMC 622 materials after relithiation were also investigated by XRD and SEM. The XRD patterns shown in Figure 4-7 can be indexed to the layered hexagonal α-$NaFeO_2$ structure, related to the space group of R-3m, belonging to the layered oxide structure. The patterns do not show evidence of impurity peaks. Decreased spacing between (108/(110) doublet peaks, indicate re-insertion of lithium. The separated (006)/(102) doublets merged back together, provide evidence of the restored crystal structure.

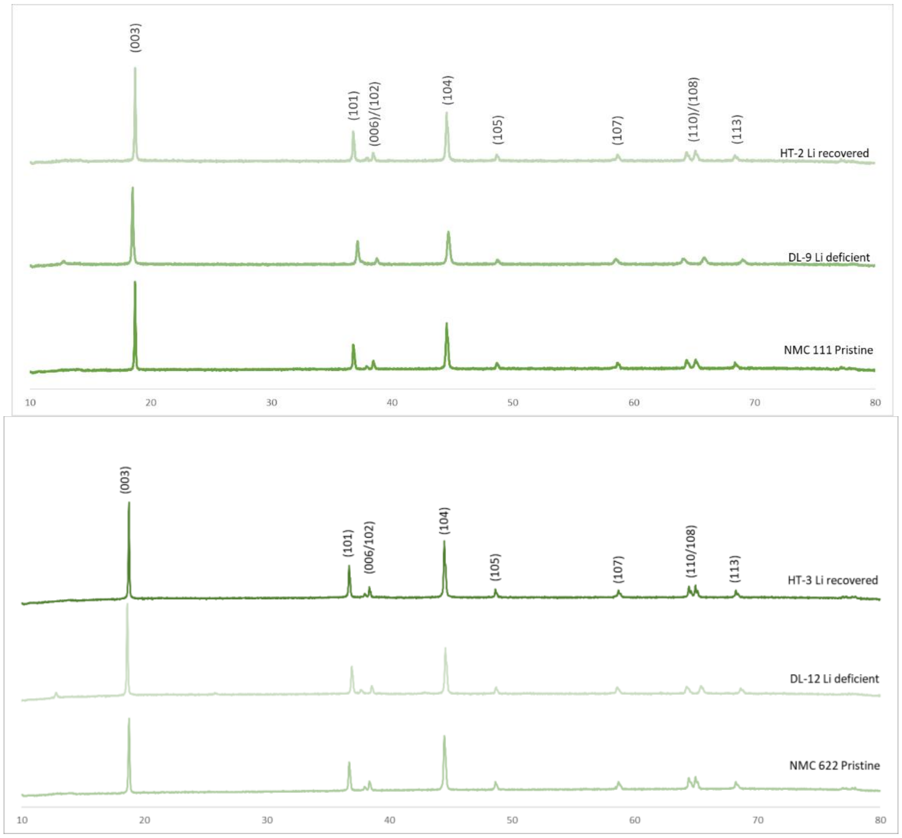

Figure 4-7 XRD patterns for pristine NMC 111, delithiated NMC 111, DL-9, and relithiated NMC 111, HT-2 (top), and pristine NMC 622, delithiated NMC 622 DL-12, and relithiated NMC 622, HT-3 (bottom) (x-axis 2θ(°), y-axis intensity (a.u.)).

The SEM results of both NMC 111 and NMC 622 are displayed in Figure 4-8. At the 10 µm scale, the secondary particles have maintained the spherical shape and are around 12 µm in diameter. The NMC 111 material shows the lithium voids in the primary particles at the 500 nm scale are filled (Figure 4-8 c and d). The NMC 622 particles show good smoothening ("healing") of the surfaces (Figure 4-8 g and h).

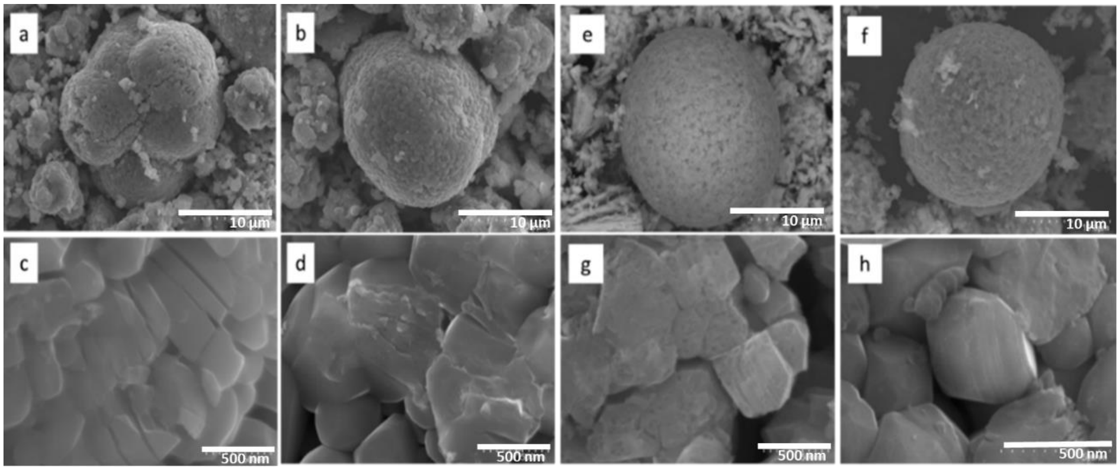

Figure 4-8 SEM images for a) and c) delithiated NMC 111 material b) and d) relithiated NMC 111 material e) and g) NMC 622 delithiated material) and h) NMC 622 relithiated material.

4.3.3 Short Annealing Treatment

A final short annealing step is needed to reconstruct the desired microstructure and crystallinity, while maintaining the stoichiometric lithium concentration (~1.0). Annealing was done at the conditions reported by P. Xu et al. [12] involving heating at 850°C in an O_2-flowing atmosphere with an extra 5 mol. % added Li_2CO_3. The extra lithium is added to compensate for any Li loss [12] as otherwise significant Ni/Li cation mixing defects will develop [22]. Meanwhile the O_2 atmosphere is critical in the case of Ni-rich NMC cathode material, such as NMC 622, which typically is made of 1:2 molar ratio of Ni^{2+}:Ni^{3+} [39], to ensure its Ni^{3+} sites are not reduced back to Ni^{2+}.

XRD was used to characterize the evolution of the structure through hydrothermal treatment and short annealing. No new peaks are noticed in any of the samples presented in Figure 4-9 which indicates the layered structure of pristine NMC 111 and 622 was maintained. After short annealing the (003) peak presented a position similar to the pristine peak. This indicates that there are no lithium deficiencies [12].

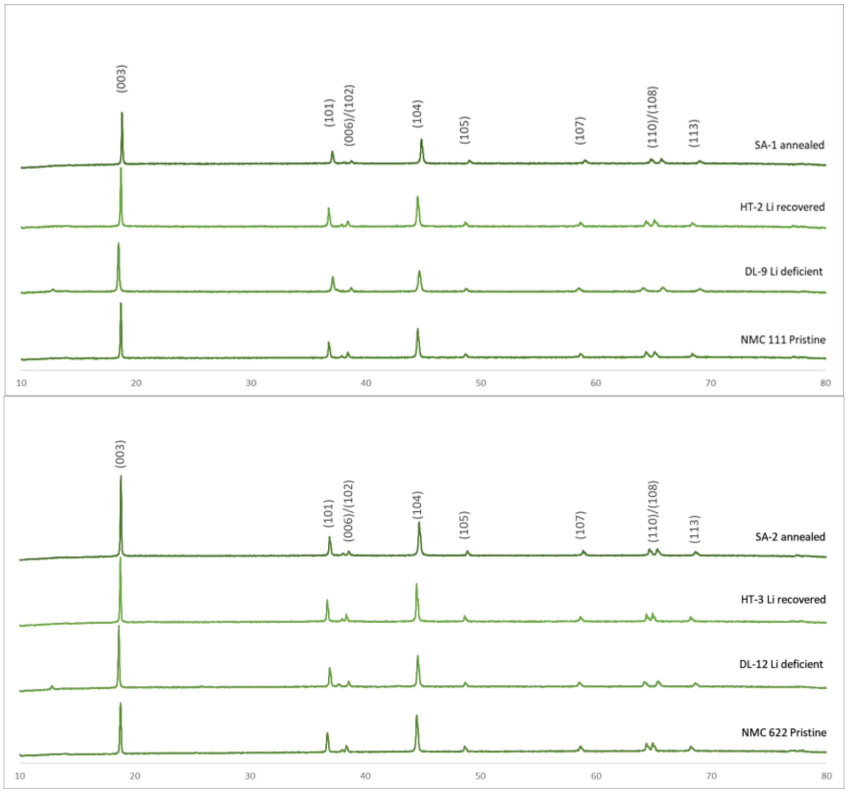

Figure 4-9 XRD Patterns for pristine NMC 111, delithiated NMC 111, DL-9, relithiated NMC 111, hydrothermally treated NMC 111 (HT-2), and annealed NMC 111 (SA-1) (top), and pristine NMC 622, delithiated NMC 622 DL-12, and relithiated NMC 622, hydrothermally treated NMC 622 (HT-3), and annealed NMC 622 (SA-2) (bottom) (x-axis 2θ(°), y-axis intensity (a.u.)).

The regenerated chemical compositions were confirmed with ICP-OES analysis to be $LiNi_{0.316}Co_{0.316}Mn_{0.311}O_2$ and $LiNi_{0.624}Co_{0.201}Mn_{0.204}O_2$. This agrees with the composition of pristine NMC 111 and 622, suggesting the successful regeneration of the materials. Crystal morphological changes of the two NMC cathode materials during the different stages of regeneration are shown in Figure 4-10.. As it can be deduced from the images, the linear gaps opened by delithiation are evidently filled up upon relithiation and ultimately the surface of both annealed materials (NMC 111, Figure 4-10 d, and NMC 622, Figure 4-10 h), have assumed a smoother look closer to their pristine versions.

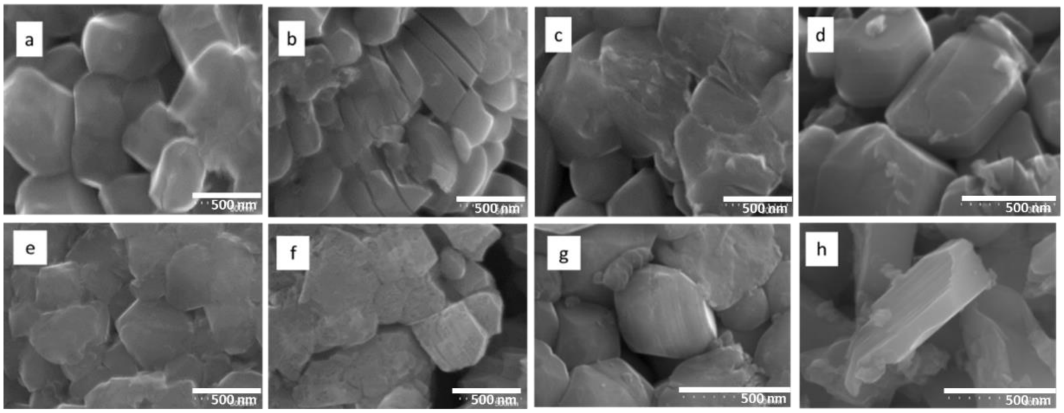

Figure 4-10 SEM images at 500 nm for a) pristine NMC 111 materials, b) delithiated NMC 111 material, c) relithiated NMC 111 material, d) annealed NMC 111 material, e) NMC 622 pristine material, f) NMC 622 delithiated material, g) NMC 622 relithiated material, and h) NMC 622 annealed material.

4.3.4 Upcycling Treatment

Having validated the direct recycling route via hydrothermal relithiation of the two commercial end members of NMC cathode family, NMC 111 and NMC 622, attention shifted to upcycling of NMC 111 to NMC 622. As mentioned earlier, very little work has been published on this subject. The work of T. Wang and co-workers [15] is the exception but in their study, relithiation and annealing was done in a Li-containing molten salt system differing from hydrothermal relithiation that has been estimated to be the most cost effective [6]. In the present work the adjustment of the nickel content of NMC (from x=0.33 to x=0.6 in the NMC molecular formula $LiNi_xMn_yCo_zO_2$) is done in the annealing stage after the hydrothermal stage. The relithiated NMC111 material from the hydrothermal treatment was mixed with pre-calculated amounts of Ni and Li chemicals to stoichiometrically increase the nickel content from 0.33 to 0.6 while maintaining the lithium ratio at 1: $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$. Upcycling is much more challenging than direct regeneration as it is prone to severe Ni/Li cation mixing that if not controlled, would not provide a fully functional cathode. Hence the co-addition of pre-calculated extra Ni along a proportional quantity of excess Li becomes necessary. Additionally, annealing should be carried out in an oxygen-rich atmosphere as the nickel must be oxidized to Ni^{3+} from Ni^{2+} to form the Ni-rich layered structure. In this study, commercial $NiSO_4{\bullet}6H_2O$ salt was used as the nickel source as opposed to $Ni(OH)_2$ that has been reported in other studies [6][15]. As for excess Li, Li_2CO_3 was used ensuring to include the extra 0.5 mol% added during annealing to compensate for Li loss. Annealing was done under 1 atm O_2 gas for 4 hours at 850°C.

Analysis of the upcycled NMC 622 material yielded a composition close to the theoretical one as it can be verified with the data shown in Table 4-5. Conversion of NMC 111 to NMC 622 will almost double the mass of NMC 111 from the extra Ni, Li and O [15].

Equation 4-5 is proposed to account for the reactive conversion of NMC 111 to NMC 622 with the co-addition of $NiSO_4$ and Li_2CO_3 (not exact numbers).

Equation 4-5

$$LiNi_{0.33}{}^{3+}Mn_{0.33}{}^{4+}Co_{0.33}{}^{3+}O_{2(s)} + 0.25\ Li_2CO_{3(s)} + 0.55\ NiSO_{4(s)} + 0.40\ O_{2(g)} \xrightarrow{850°C\ 4h} 1.50\ LiNi_{0.6}Mn_{0.2}Co_{0.2}O_{2(s)} + 0.25\ CO_{2(g)} + 0.55\ SO_{3(g)}$$

Table 4-5 Chemical composition for pristine, delithiated and hydrothermally relithiated NMC 111 and its upcycled NMC 622 product

Sample	NMC 111 upcycled to 622
Pristine	$Li_{1.163}Ni_{0.393}Co_{0.390}Mn_{0.392}O_2$
Delithiated	$Li_{0.766}Ni_{0.391}Co_{0.390}Mn_{0.388}O_2$
Hydrothermal	$Li_{1.150}Ni_{0.381}Co_{0.390}Mn_{0.384}O_2$
Upcycled	$Li_{1.068}Ni_{0.598}Co_{0.261}Mn_{0.253}O_2$

The XRD patterns for the upcycled material are displayed in Figure 4-11. The peaks from SA-5, the upcycled NMC 622 material, are aligned with the pristine NMC 622 peaks. SEM images are consistent with the XRD results. Figure 4-11 indicates similar morphological characteristics between the upcycled and pristine NMC 622 materials.

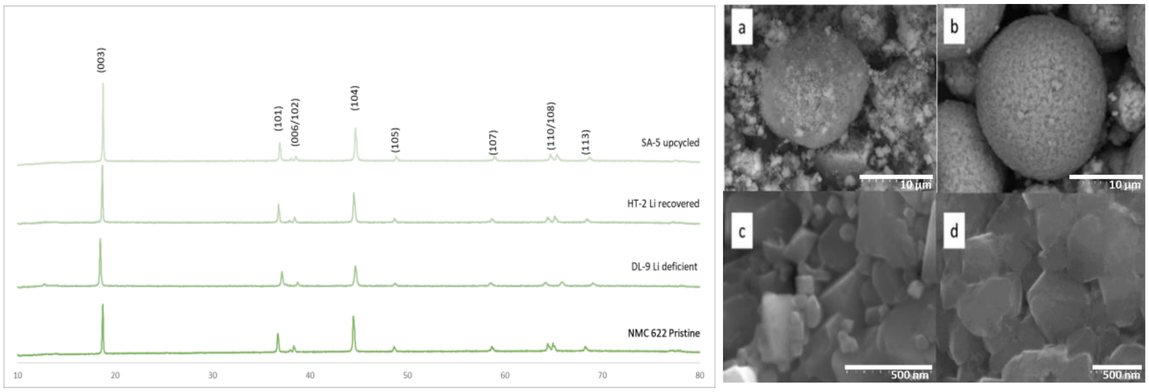

Figure 4-11 XRD patterns for pristine NMC 622, delithiated NMC 111 (DL-9), hydrothermally treated NMC 111 (HT-2), and upcycled NMC 622 (SA-5) (left) (x-axis 2θ(°), y-axis intensity (a.u.)); and the SEM images for a) and c) upcycled NMC 622 material, b) and d) pristine NMC 622 material, 10 µm (right).

4.3.5 Investigation of Ultrasound Pre-Treatment

Herein the effects of ultrasound pre-treatment on the hydrothermal stage of direct recycling of NMC 111 and 622 are described. This investigation was motivated from the fact that hydrothermal relithiation in the previous studies as well in this one did not involve stirring, an important factor in hydrothermal synthesis systems [38]. Lai et al. [16], who studied the use of ultrasound-triggered cation chelation in the synthesis of NMC precursor materials by co-precipitation, showed that ultrasound waves promoted an even distribution of Ni, Mn and Co in the material and increased the stability of the structure with low cation mixing. Thus, it was of interest to evaluate the role of ultrasound mixing can have on the crystal restoration process. Ultrasound was applied to the delithiated NMC/4M LiOH slurry prior to the hydrothermal treatment. Once hydrothermal treatment completed, the solids after filtration, washing and drying were characterized and advanced to the short annealing stage following the same procedure as previous annealing tests, SA-1 and SA-2. Chemical analysis determined the ultrasound assisted hydrothermal-annealing option to yield annealed NMC materials comparable to the pristine counterparts, $Li_{0.939}Ni_{0.384}Co_{0.405}Mn_{0.378}O_2$ and $Li_{1.105}Ni_{0.617}Co_{0.198}Mn_{0.203}O_2$, see Table 4-6. The determined bulk compositions, within experimental error, compare to those of products obtained without ultrasound pre-treatment: $LiNi_{0.316}Co_{0.316}Mn_{0.311}O_2$ and $LiNi_{0.624}Co_{0.201}Mn_{0.204}O_2$ but the extent of homogeneity remains to be determined.

Table 4-6 Chemical composition for pristine, delithiated, ultrasound assisted- hydrothermal and annealing of NMC 111 and NMC 622

Sample	NMC 111	NMC622
Pristine	$Li_{1.163}Ni_{0.393}Co_{0.390}Mn_{0.392}O_2$	$Li_{1.174}Ni_{0.765}Co_{0.237}Mn_{0.250}O_2$
Delithiated	$Li_{0.766}Ni_{0.391}Co_{0.390}Mn_{0.388}O_2$	$Li_{0.768}Ni_{0.681}Co_{0.211}Mn_{0.219}O_2$
Hydrothermal	$Li_{1.117}Ni_{0.366}Co_{0.384}Mn_{0.361}O_2$	$Li_{1.070}Ni_{0.655}Co_{0.210}Mn_{0.216}O_2$
Annealed	$Li_{0.939}Ni_{0.384}Co_{0.405}Mn_{0.378}O_2$	$Li_{1.105}Ni_{0.617}Co_{0.198}Mn_{0.203}O_2$

The materials were characterized by XRD and the peaks compared to the annealed samples without ultrasound pre-treatment. Both NMC 111 and NMC 622 XRD patterns exhibit the α-$NaFeO_2$ layered structure.

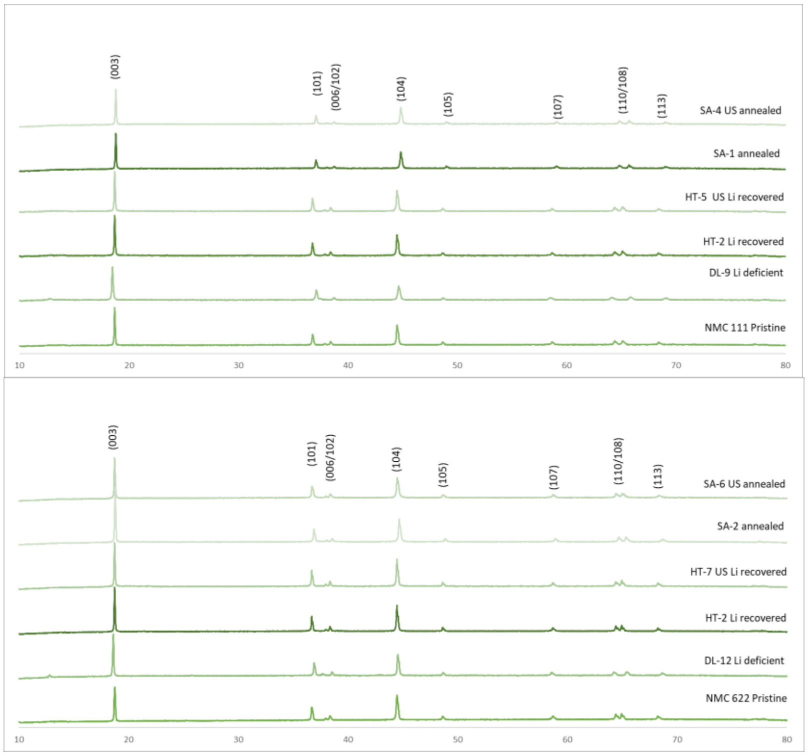

Figure 4-12 XRD patterns for pristine NMC 111, delithiated NMC 111, DL-9, relithiated NMC 111, hydrothermally treated NMC 111 (HT-2), hydrothermally treated with ultrasound (HT-5), annealed NMC 111 (SA-1), and annealed NMC 111 after ultrasound (top); and pristine NMC 622, delithiated NMC 622 DL-12, and relithiated NMC 622, hydrothermally treated NMC 622 (HT-3), hydrothermally treated with ultrasound (HT-7), annealed NMC 622 (SA-2), and annealed NMC 622 after ultrasound (bottom) (x-axis 2θ(°), y-axis intensity (a.u.)).

The surface morphology of the ultrasound pre-treated material was investigated, as shown in Figure 4-13. The higher magnification images of NMC 111 material reveal a vast difference in the smoothness/cleanliness of the surface of the material that was treated with ultrasound prior to hydrothermal stage. The surface clearly contains fewer imperfections. Meanwhile, when observing the particle morphology (10 µm scale), the ultrasound pre-treated hydrothermal sample appears to have much fewer fines (b vs. a) as well as the annealed sample (d vs. c),suggesting ultrasound has a beneficial effect in promoting crystal ripening.

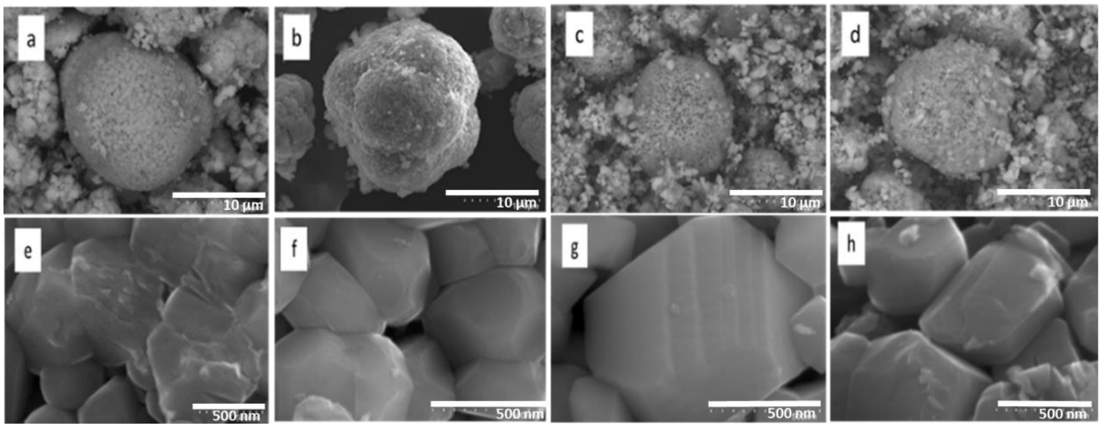

Figure 4-13 SEM images for NMC 111 material after a) and e) hydrothermal treatment, b) and f) ultrasound pre-treated hydrothermal treatment, c) and g) annealed, and d) and h) annealed following ultrasound pre- treatment,

The effect of ultrasound pre-treatment on the surface morphology of the NMC 622 material can be evaluated with the aid of the SEM images shown in Figure 4-14. The spherical morphology was maintained throughout the processing stages, as shown in Figure 4-14 a-d under 10 µm magnification but the ultrasound treated materials didn’t reveal this time a clear beneficial effect hence further investigation is required.

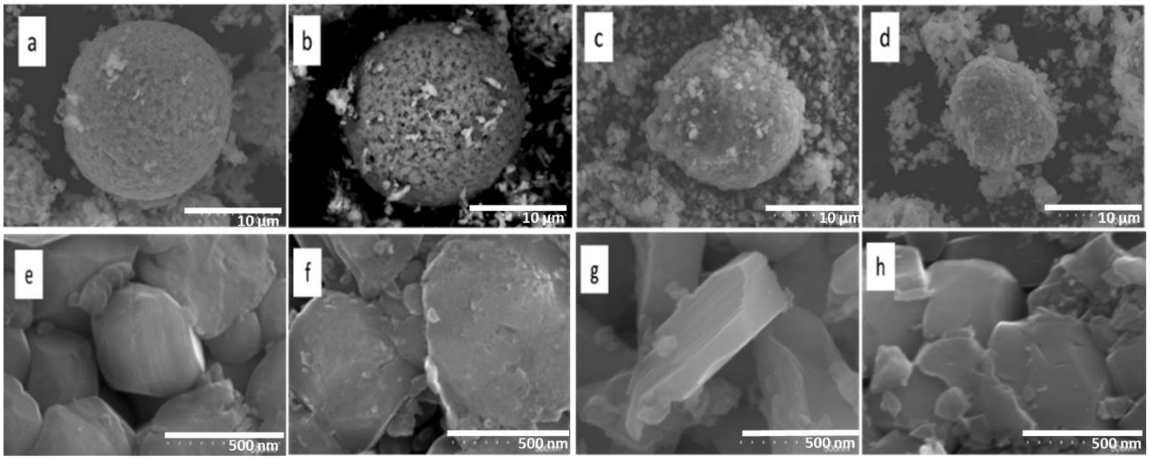

Figure 4-14 SEM images for NMC 622 material after a) and e) hydrothermal treatment, b) and f) ultrasound pre-treated hydrothermal treatment, c) and g) annealed, and d) and h) annealed following ultrasound pre- treatment.

4.4 Conclusion

In this study, the baseline was established for the regeneration by direct recycling of partially delithiated NMC 111 and 622 cathodes (serving as models of actual degraded materials) using hydrothermal treatment and short annealing. Partial delithiation was affected with the controlled use of potassium persulphate, which as powerful and green oxidant allows for tunable degree of oxidation of $Ni^{2+}/Ni^{3+}/Ni^{4+}$ and Co^{3+}/Co^{4+}. The optimal conditions for chemical ~35% delithiation of pristine NMC 111 and 622 material were determined to be at pH 7 and 50°C using 10 g/L NMC and 0.5 M $K_2S_2O_8$. The conditions for hydrothermal treatment to restore the Li content into the host structure, which were previously studied, 220°C for 4 hours in 4M LiOH solution, were confirmed to be effective. The application of ultrasound pre-treatment before hydrothermal stage showed some surface morphology difference that may lead to further improvements of the direct recycling route but further investigation is suggested. Likewise, short annealing conditions, 850°C for 4 hours in O_2 atmosphere, were also confirmed in this study. Most importantly, the present study demonstrated the successful conversion of NMC 111 to NMC 622 that can open cost-effective upcycling processing based on hydrothermal relithiation and annealing. For upcycling, unlike the use of $Ni(OH)_2$ used previously, herein it was shown that co-addition of appropriately pre-calculated amounts of nickel sulphate and lithium carbonate during annealing at 850°C is an effective and simpler method than the method using molten salts. No impurity was introduced because the synthesis of pristine NMC materials is also done in sulphate media. The upcycled material yielded a typical α-$NaFeO_2$ layered structure with surface morphology and composition of lithium and transition metals that was very similar to pristine NMC material. Future work will be to investigate the electrochemical performance of the upcycled materials on one hand and on the other the testing of the process on a spent NMC cathode. Further studies on the application of ultrasound to gain a better understanding of its affects would be interesting to conduct as well.

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Chapter 5 Discussion

5.1 Research Context and Contributions

The motivation for this topic of research derived from a thorough literature review on the established and state-of-the-art recycling approaches available for lithium-ion batteries, found in Chapter 2. It was concluded that direct recycling is emerging as the most sustainable technology option based on life cycle analysis (LCA) provided by several sources [25], [23]. The LCA study by Jiang et al. [50] shows a reduction in carbon emissions, human impact and mitigating resource depletion. Argonne National Laboratory has developed a closed-loop battery recycling cost and environmental impacts model called EverBatt [23]. EverBatt covers pyrometallurgical, hydrometallurgical and direct cathode recycling. The battery cathode chemistries included in the model are: $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC 111), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622), $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811), and $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$. This model has clearly shown direct recycling to be very competitive over hydrometallurgical processing because fewer chemicals are used and impacts from recovered materials are avoided.

In this context, the objectives of the present research, stated in Chapter 3, were to look at direct regeneration and upcycling of different NMC chemistries, low and high nickel. Obtaining cathode material that had reached a state-of-health less than 80 % was difficult and after consulting literature to determine what their samples were, it was decided to use chemically delithiated pristine NMC materials to serve as “spent” cathodes. Other direct recycling researchers have also used delithiated pristine cathodes to establish the process before introducing the more complex real spent materials [26].

The approaches used for direct regeneration and upcycling proved effective. The experimental study, discussed in Chapter 4, determined optimized conditions to control delithiation using a powerful but green oxidant, $K_2S_2O_8$ that consitutes a contribution to other groups who wish to use a similar system. No agitation was used in the hydrothermal treatment, but ultrasound pre-treatment was tested instead and results show good reproducibility. The use of ultrasound in regenerating NMC cathodes is another contribution to research. But by far the most important contribution is the experimental elaboration of upcycling of NMC 111 to NMC 622 by performing annealing with co-addition of pre-calculated nickel sulphate and lithium carbonate salts after hydrothermal relithiation.

5.2 Experimental Issues

All equipment and execution of experiments were procured and built at the NRC laboratory, while the design and analysis of tests was done under the direction of my supervisor Professor Demopoulos at McGill. The delithiation set up, the hydrothermal treatment set up, and the short annealing set up are shown in Figure 5-1. The methods used for the testing are outlined in the experimental section of the manuscript forming the basis of Chapter 4.

Figure 5-1 Delithiation set up (left) Hydrothermal reactor and Teflon liner insert (middle) and short annealing tube furnace (right).

The test work plans included repeat testing to establish confidence in the procedure and equipment used. Figure 5-2 shows the chemical compositions of two DL tests and two HT tests run with identical conditions. It was important to confirm the procedure was repeatable so that subsequent tests could be performed to produce more material for the annealing stage.

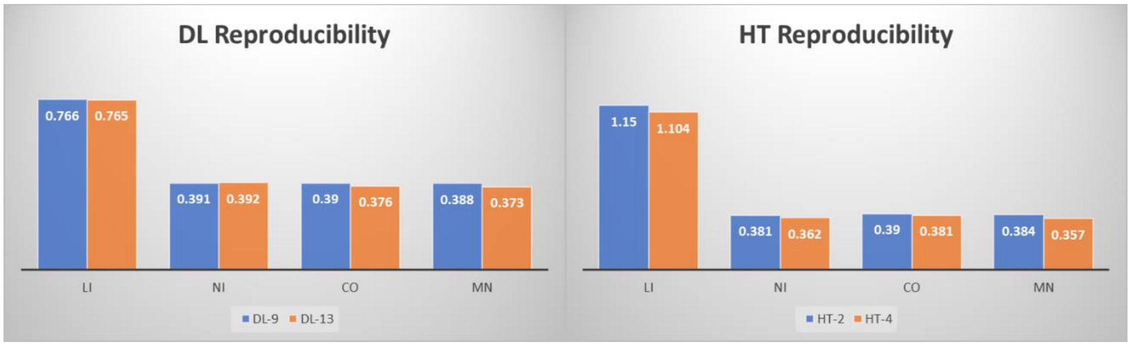

Figure 5-2 Repeat tests in delithiation (DL) and hydrothermal treatment (HT) processes.

Samples (SA-1 and SA-2) exiting the short annealing stage were found to contain a higher lithium content than the feed material (hydrothermal treated). The lithium content was 11.93 wt. % and 11.60 wt. % respectively in the SA samples and 8.0 and 7.3 wt. % in the hydrothermal samples. Lithium in NMC 111 material is reported between 7.0-8.0 wt. %, a typical value is 7.67 wt. % [27]. In the short annealing stage, lithium is added as lithium carbonate, the excess lithium was attributed to incomplete removal in the washing stage, an issue that needed to be properly addressed. There is lack of information in published works as the applied washing techniques [28]. Shi et al. did not mention washing after annealing in their process, but they had used $LiNO_3$ instead of Li_2CO_3 for their lithium source that is guessed is easier to remove [29]. Wang et al. reported washing in water to remove RTMS (reciprocal ternary molten salts). Their system used LiCl as the lithium source, they did not introduce Li_2CO_3 [26]. The solubility of lithium carbonate in water is very low, 1.31g/100mL at 20°C [30]. One research group discussed the removal of Li_2CO_3 from metallic oxides, NiO, CoO, MnO, was done using a water leaching technique. The ratio of DI water to NMC material was 30:1. The water leach was performed for 5 hours [31].

The material from SA-1 and SA-2 were washed with 200 mL of hot (60°C) DI three times and analyzed again. The samples' lithium content went down to 7.48 wt. % and 7.65 wt. % respectively (Table 5-1). All subsequent short annealing tests followed this hot washing method and the lithium content ranged from 6.5-7.7 wt. %.

Table 5-1 Chemical analysis of NMC material after short annealing stage before and after hot wash procedure

Sample	Li (wt. %)	Ni (wt. %)	Co (wt. %)	Mn (wt. %)
SA-1	11.93	18.53	18.64	17.10
SA-1 rewashed	7.48	18.25	18.36	16.82
SA-2	11.60	36.70	11.90	11.20
SA-2 rewashed	7.65	35.95	12.10	11.14

5.3 Limitations of Study and Follow up Steps

An important characterization method to directly determine if the insertion of lithium and nickel into the upcycled NMC structure was successful is to use FIB-SEM (Focused Ion Beam Scanning Electron Microscopy). For evaluating the homogeneity and uniform distribution of lithium and nickel of upcycled NMC material, the FIB could be used to slice through a specified thickness of the particle and reveal the plane for SEM imaging. This could be done in several layers, and images stacked using software, providing detailed information on the sample's morphology and microstructure. This technique allows for in-situ sample preparation of cross-sections with minimal sample damage or contamination. [32]. Future work will benefit by performing such analysis. Similarly, XPS analysis will be beneficial in asserting the oxidation states of Ni and Co as the NMC materials go through delithiation/relithation and upcycling-a task that could not be completed on time prior to submission of the thesis.

Regenerated NMC cathodes were used to prepare coin cells for battery cycling tests so to ascertain the degree to which re-functionalization of the recycled/upcycled NMC materials was achieved. Due to time limitations only a few preliminary cycling tests could be performed but more are planned in the next couple of months. The coin cell fabrication process is shown in Figure 5-3.

Figure 5-3 Coin cell battery assembly a) casting cathode onto aluminum foil b) assembly inside glove box c) coin cell fabrication schematic d) coin cell containing upcycled NMC 622 cathode material.

After four cycles, the coin cells displayed a relatively low capacity in the order of 55 mAh/g that is only about 1/3 of the theoretical capacity. The charge and discharge cycles were very consistent (see Table 5-2) with good Coulombic Efficiency of >96% after the first (formation) cycle. The poor capacity registered is attributed to improper casting technique (very viscous slurry). For example, the 8 mg/cm^2 loading points to a thick electrode (loadings 2-3 mg/cm^2 are more typical [85]) with poor electrolyte wetting/infiltration hence not all material participating in Li-ion exchange. Several more tests are planned that will include testing the pristine cathode as a reference so to overcome these early measurement difficulties.

Table 5-2 Summary of preliminary cycling data of the upcycled NMC cathode material

Cycle Index	**Voltage (V)**	**Charge (mAh/g)**	**Discharge (mAh/g)**	**CE%**
1	3.57	69.60	54.05	77.65
2	3.57	55.56	53.34	96.00
3	3.57	54.66	53.18	97.28
4	3.57	54.38	53.17	97.76

Chapter 6 Conclusion

An intensive literature review on the current hydrometallurgical recycling approaches available for LIBs was completed. Technology gaps and areas to focus were identified in the review. The state-of-the-art direct recycling of LIBs still requires further research and development. The overall objective of this Master's thesis research was to (i) investigate the direct recycling process for NMC cathodes, (ii) upcycle a low nickel NMC material into a high nickel NMC material, and (iii) study the application of ultrasound technology on the regeneration process.

The following conclusions can be drawn from this research:

1) Regeneration of synthetic "spent" NMC 111 and NMC 622 is possible through direct recycling process which includes hydrothermal treatment in LiOH solution to relithiate the "spent" NMC material, and short annealing to repair the microstructure and crystallinity. The regenerated cathode materials were of close likeness to its pristine counterpart in chemical composition, morphology and structure.

2) Upcycling of NMC 111 into NMC 622 can be achieved using the same direct recycling approach with the co-addition of nickel, as nickel sulphate and proportional amount of lithium carbonate, to stoichiometrically change the cathode composition. Upcycled NMC 622 material was a good match in composition, morphology and structure to pristine counterpart.

3) Ultrasound mixing applied prior the hydrothermal stage may improve in the re-insertion of the lithium back into the structure, decreasing crystal imperfections. There were notable differences in the NMC 111 SEM images, showing significant crystal surface smoothening in the relithiation process. However, the results were inconclusive in the case of NMC 622.

From an environmental standpoint, direct recycling is a better alternative to current commercial recycling approach of spent lithium-ion batteries containing NMC cathode material that targets only the value metals like Ni, Co and occasionally Li. Further investigation into the affects of ultrasound application on the hydrothermal stage is required. Parameters such as, lowering the concentration of LiOH, temperature and time should all be studied. Any reductions would lower the GHG emissions and cost making this process more desirable.

More research is needed to optimize conditions with parallel electrochemical performance measurements before the process is applied to real spent cathodes. New challenges may arise when the impurities from spent material are introduced. The FIB-SEM will be an important characterization method and allow for better understanding of the morphology on the nanometer scale, confirming with certainty that the regenerated particles' composition is uniform and homogeneous throughout the cathode.

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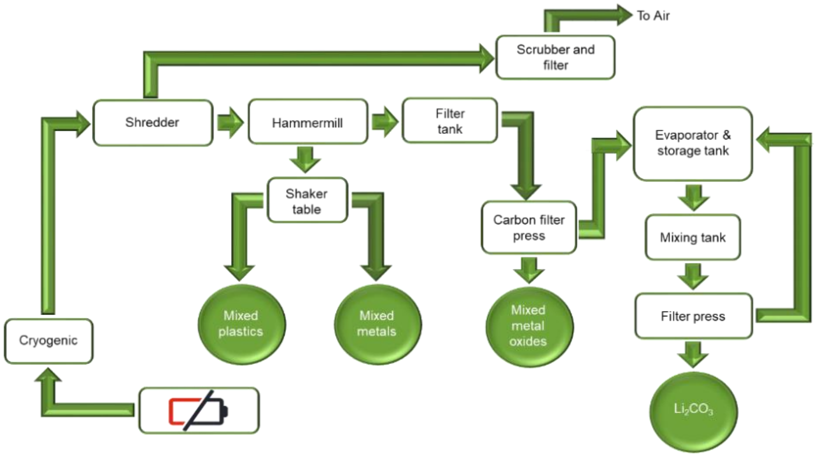
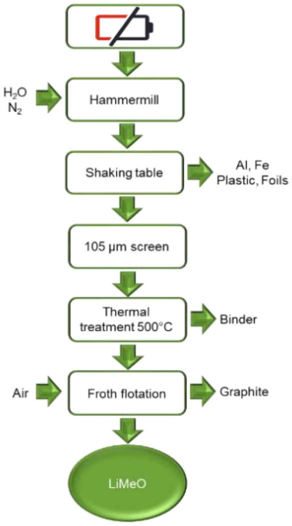
Appendix

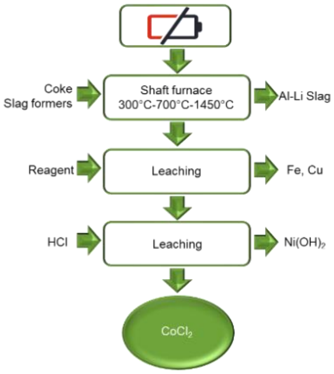
Part A: Supplementary Figures for Chapter 2



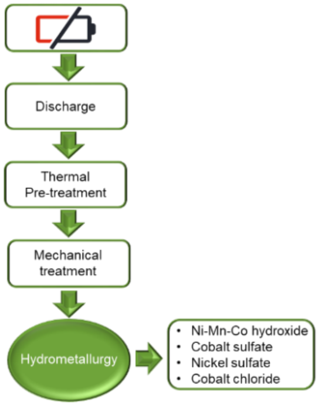
Supplementary Figure 1 Toxco recycling process (adapted from ***[2]***)



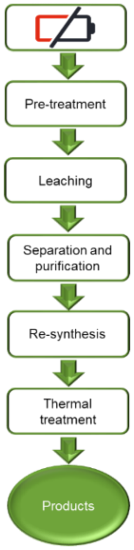
Supplementary Figure 2 Retriev LIB recycling process for cathode-grade material regeneration (adapted from ***[3]***)



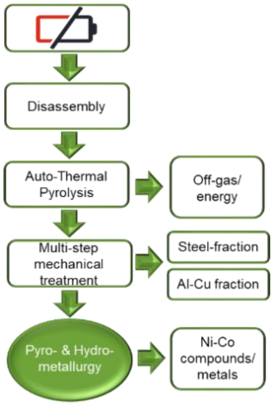
Supplementary Figure 3 Umicore LIB recycling process (adapted from ***[3]***)



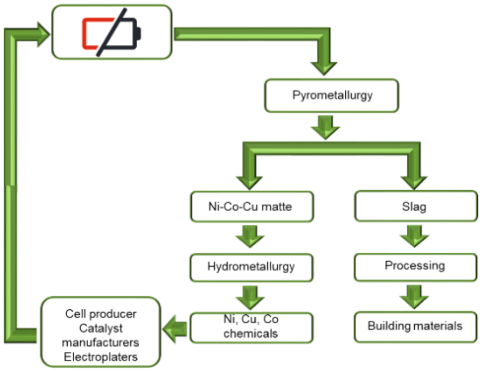
Supplementary Figure 4 Brunp LIB recycling process (adapted from ***[1]***).



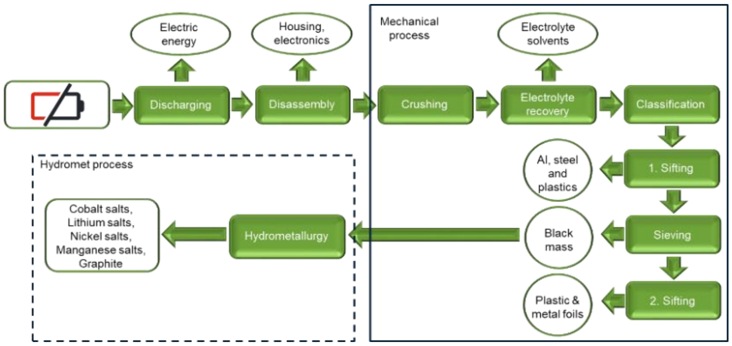
Supplementary Figure 5 GEM Ltd. recycling process ***[7].***



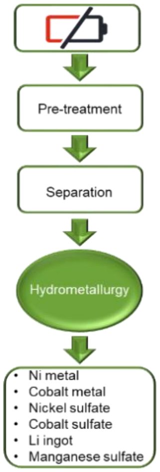
Supplementary Figure 6 Accurec Recycling GmbH LIB recycling process ***[1].***



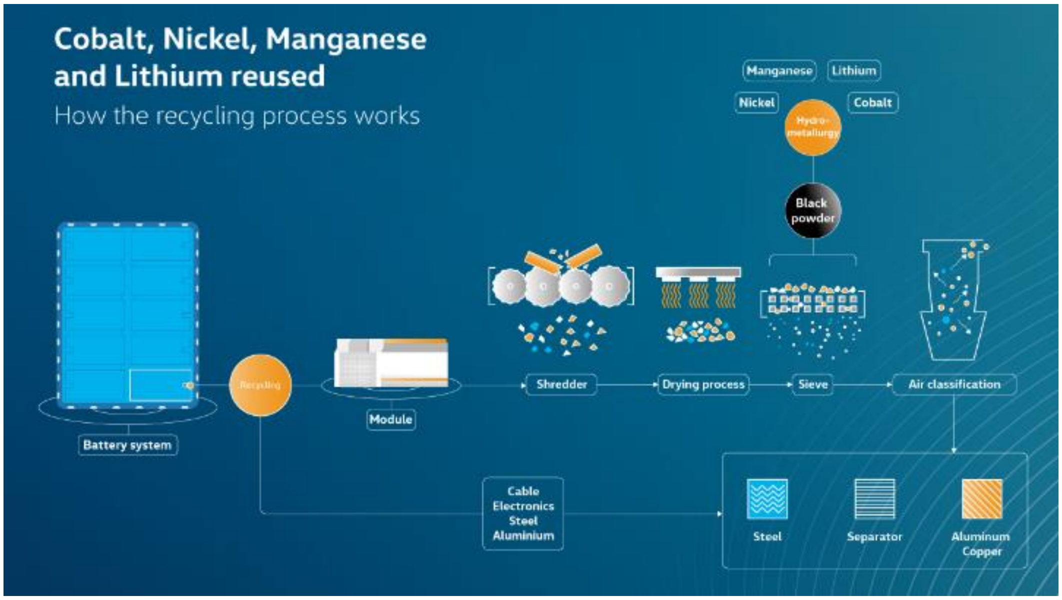
Supplementary Figure 7 Nickelhütte LIB recycling process ***[4].***



Supplementary Figure 8 Duesenfeld LIB recycling process ***[6].***



Supplementary Figure 9 SungEel HiTech LIB recycling process ***[1]***



Supplementary Figure 10 Volkswagen adopted the LithoRec process for recycling LIBs ***[5].***

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Part B: Additional Information on Direct Recycling

Delamination via Mechanical and Physiochemical Separation

Direct recycling of spent lithium-ion batteries typically includes a relithiation process to regenerate the cathode material. It should be noted that there is a prior step that includes delamination of the cathode material. Delamination essentially involves the detachment of the active cathode material (e.g., NMC compound) from the aluminum current collector via severance of the polymer binder (typically PVDF). Delamination is generally done using either mechanical or physicochemical separation with the most common being froth flotation, cryogenic grinding and solvent based separation.

Froth flotation utilizes the materials hydrophobic and hydrophilic characteristics to separate PVDF binders from the cathode material. The hydrophobic material (PVDF and carbon) is segregated in the froth phase, while the hydrophilic material sinks. The downside to this method is the potential damage to the cathode material from the intensive air flow and bubble cavitation in water [1].

Cryogenic grinding technology uses vibration in a horizontal direction with grinding media. The media collides with the cathode material in a tank. Liquid nitrogen is used to keep the tank at a targeted temperature. Undesirably, this form of grinding may cause damages to the surface of the cathode material as such its application to direct recycling may not be feasible [2].

The most popular separation technique is solvent based separation. The process relies on organic solvents in dissolving the binder, typically PVDF, hence facilitating the detachment of the cathode active material from the aluminum foils. The method is using less energy and maintains the structure and surface properties of the cathode material. However, deactivating the binder using organic solvents can introduce toxic downfalls [1].

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