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Hydrometallurgical recycling technologies for NMC Li-ion battery cathodes: current industrial practice and new R&D trends†

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The supply chain for raw materials needed to fulfill the demand for lithium-ion battery (LIB) manufacturing is less than certain. 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. Lithium-ion battery recycling could help alleviate the demands on critical virgin materials. This would realize a price parity goal, \$100 per kW h, for internal combustion engines (ICE) and EVs. Simultaneously, recycling could reduce waste in landfill sites as 1 M tonnes of LIBs are set to retire by 2030. In this context the recycling of LIBs becomes imperative, but this industrial activity must be done in full compliance with sustainability principles. For example, current industrial recycling technologies tend to generate a lot of waste products as only some value metals are recovered while simultaneously tend to be energy intensive with heavy chemical usage and risks of water and soil contamination. In this review we focus on spent nickel-manganese-cobalt (NMC) lithium-ion batteries that currently dominate the EV market examining primarily their recycling by hydrometallurgical processing as this route seems to be the most advocated. Our review compares the different hydrometallurgical process flowsheets seeking to highlight areas for chemical and technological improvement as they are proposed in recent patented R&D developments. The review concludes with the strong endorsement of hydrometallurgy-based direct recycling approach as the most sustainable route.

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Sustainability spotlight

Ni-Mn-Co oxides (NMC) are currently the preferred cathode materials in Li-ion batteries (LIB) powering the electric vehicle (EV) revolution. The composition chemistry of these cathodes constantly evolves while at the same time the volume of spent batteries exponentially increases demanding new advanced sustainable recycling technologies. Currently the industrial NMC recycling practice targets mainly the recovery of the valuable metals by pyrometallurgical and hydrometallurgical processes, or a combination of both. However, these have several limitations, including high energy and/or chemical consumption, incomplete recovery of metals, and GHG emissions. To overcome these limitations, there are new R&D developments in hydrometallurgical recycling technologies. One area of development is the use of novel solvents to improve metal recovery rates. Another exciting development is a paradigm-shift towards direct recycling of the active cathode material (CAM) enabled by innovative hydrometallurgical treatment that avoids breaking it down into its constituent elements. Direct recycling may be combined with upcycling, thereby further promoting circularity and less dependency on raw material extraction. Our review relates to the following UN SDGs: affordable and clean energy (SDG 7), industry & innovation (SDG 9), responsible consumption and production (SDG 12), and climate action (SDG 13).

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 percent of the total GHG emissions.¹ A lithium-ion battery is deemed “spent” when it has

reached a state of health which is less than 80 percent, typically after 10 years of use.² 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.³ Recycling can contribute to an overall reduction in the GHG emissions that are associated with the battery industry.⁴

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.⁵ 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 $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, NMC (where x , y and $z = 1$). Other chemistries such as lithium iron phosphate

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(LFP), $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, NCA (where x , y and $z = 1$), lithium manganese oxide (LMO) and lithium cobalt oxide (NCO), are commercially available but for this study we will look at the NMC battery only.⁶ 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 density has also improved with the increase in nickel content, NMC 811, improving the range.⁷

Some of the LIB raw material have been listed as critical in countries like Canada, USA, Europe, Japan and South Korea, making recycling equally critical from economic and environmental perspectives.⁸ Sourcing and securing a sustainable supply chain for manufacturing LIBs means social issues are meaningful. The Democratic Republic of the Congo (DRC) holds 60 percent of the world's cobalt resource. The country has artisanal and small-scale mines (ASM) dominated by Chinese owned companies. This gives the Chinese LIB manufacturers security over international manufacturers for cobalt supply. For years, human's rights groups have reported severe issues in mining operations in the DRC including, child labour, fatal accidents, and high corruption. Companies in need of cobalt supply are invested in improving the ASM standard for mine safety and child labor to ensure cobalt is mined responsibly.⁹

In order to enable LIB recycling, pathways for other types of batteries (NiMH, alkaline, and lead-acid) are modified to support the circular economy system. The components of LIBs, their structures, and their charge-storage mechanisms are used to design the recycling process.⁵ The current commercial approach to recycling NMC cathodes which offers the greatest extraction and lowest energy impacts, is the hydrometallurgical processing route.¹⁰ Several recycling facilities are operating globally and recovering critical metals like Li, Co, and Ni on a commercial scale using this approach. Although pyro- and hydro-metallurgical LIB recycling processes are

commercialized, they aren't without fault. They involve high temperature smelting, pyrometallurgy, and the use of large quantities of chemicals, hydrometallurgy. Lately, research has focused on developing a greener recycling approach to decrease the environmental impact and operation costs associated with the current industrial methods. The promising direct recycling approach does not decompose the cathode active material into the elemental products which need to be completely re-manufactured like the pyro- and hydro-met routes do. Instead, the direct recycling approach applies "soft" means to induce relithiation of the cathode compound, *e.g.*, NMC leaving the structure intact and re-functionalized.¹⁰ Hydrometallurgy is expected to play a key role towards this end as pointed out in the perspective section of the present paper. In this review a systematic compilation of the most important state-of-the-art hydrometallurgical recycling processes applicable to the dominant EV NMC cathode material family is presented by sourcing technical information from the recent patent literature and industrial news complementing the underlying chemistry discussion. Many of the presented processes are at the pilot scale, yet to be commercialized. Some of the processes described recover only cathode materials (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.*).

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

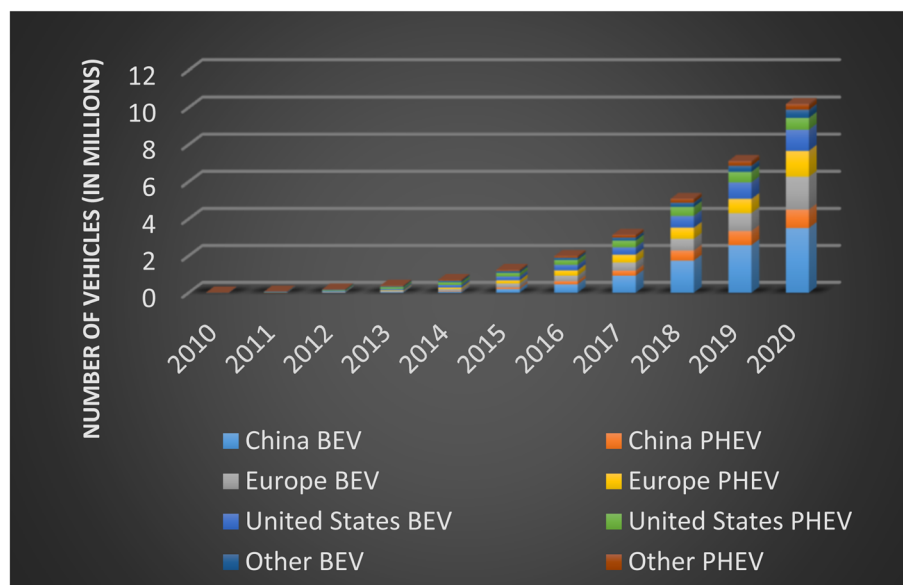


Fig. 1 Global electric passenger car stock, 2010–2020 (data sourced from ref. 12).



World Bank, the transportation sector contributes 20 percent of the GHG emissions globally. This number could grow to 60 percent 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 sources 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 percent, between 2016 and 2020. After a decade of growth, in 2020 the global electric car stock hit 10 million, shown in Fig. 1. Although China had the largest fleet in 2020, 4.5 million EVs, Europe had the largest annual increase, 3.2 million EVs.¹¹

According to the latest EV outlook report from Bloomberg-NEF, 60 percent of new car sales worldwide must be electric by 2030 if a net-zero scenario is to be achieved.¹²

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.¹³

Demand for raw materials like graphite, lithium and cobalt is predicted to increase 500 percent by 2050, according to the World Bank.¹ Several countries have revisited their list of critical materials in light of the EV era. The USA, EU, Japan, South Korea and Canada have released a list of critical minerals/metals.⁸

Table 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 metals lithium, nickel, cobalt, manganese, aluminum, and copper along with graphite that are required to manufacture LIBs are highlighted in green in Table 1.⁸ 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 2050.¹⁴ 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.¹⁵ Fig. 2 shows the Global Cobalt Reserves which are dominated by DRC, 3.6 M tons, and Australia, 1.4 M tons. Although Australia has substantial reserves, they only mine 4 percent 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.⁹

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 percent of

Table 1 List of critical metals/minerals for USA, EU, Japan, South Korea and Canada (data sourced from ref. 8)

Mineral/Metal	Country				
	USA	EU	Japan	South 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	

the projected lithium and cobalt, and 80 percent of the required copper by 2030.¹⁶ Spent lithium-ion batteries contain between 5–20 weight percent of cobalt, 5–7 weight percent of lithium, and



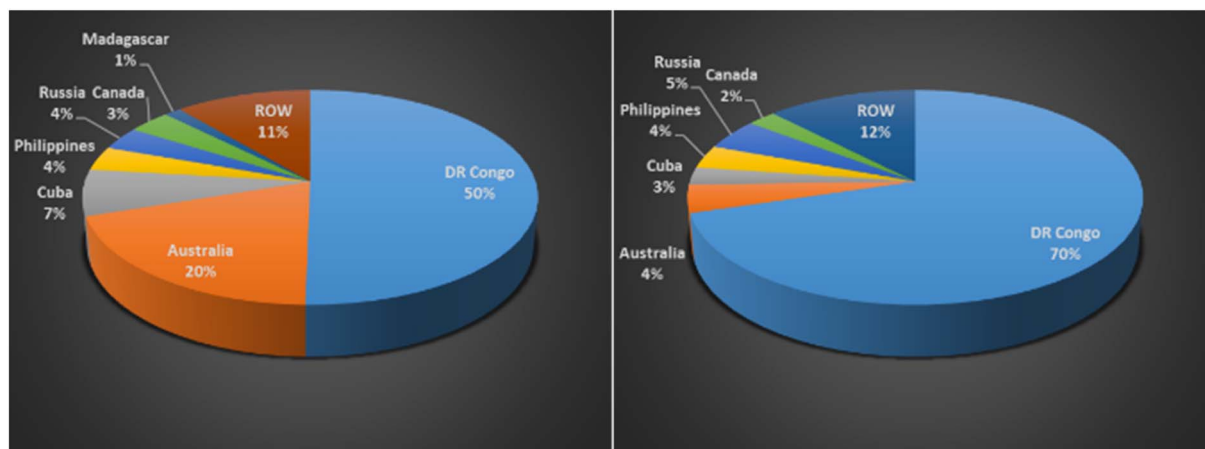


Fig. 2 (Left) global cobalt reserves 2020, by country (in metric tons), (Right) global production of cobalt 2020, by country (% share of production) (data sourced from ref. 15).

Table 2 NMC lithium-ion battery pack composition by weight ($\text{kg kW}^{-1} \text{h}^{-1}$) (data sourced from ref. 18)

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	0.75
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

5–7 weight percent of nickel, these concentrations are higher than what is naturally available from raw materials. Recycling is an economical solution to the raw material shortage.¹⁷

The estimation of material intensity of NMC lithium-ion battery packs ($\text{kg kW}^{-1} \text{h}^{-1}$) has been analyzed by Argonne

National Laboratory using their BatPaC modeling software with the main metrics presented in Table 2.¹⁸ 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.¹⁸

The change in NMC battery chemistry has evolved from high cobalt NMC 111 to high nickel NMC 811, from 2010 to predicted 2030, see Fig. 3. Cathode chemistry advancements can be credited for the reduction in cost of an EV battery.¹⁹

The average cost to produce a lithium-ion battery for an electric vehicle (EV) has significantly declined from \$1200 per kWh in 2010, to \$132 per kWh in 2021. S&P Global Platts has forecasted the EV battery manufacturing cost will reach price

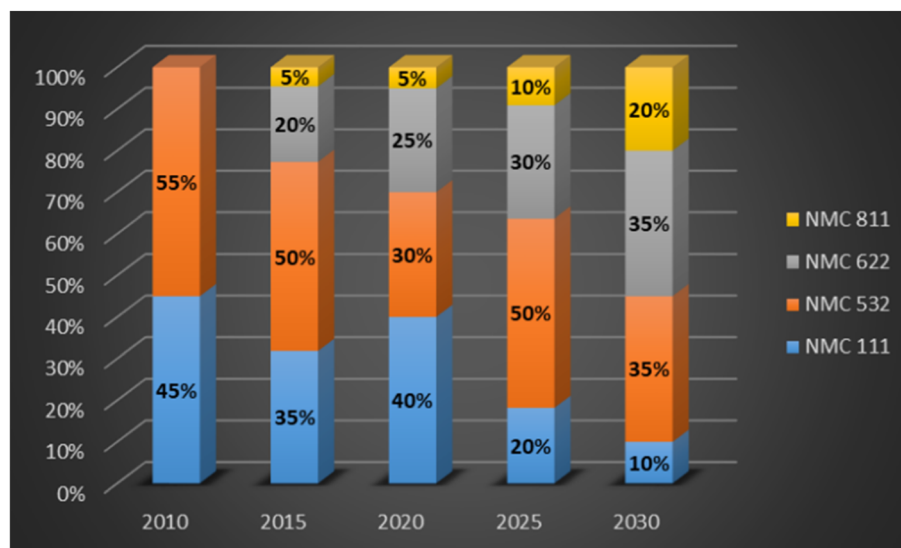


Fig. 3 NMC cathode chemistry evolution (data sourced from ref. 19).



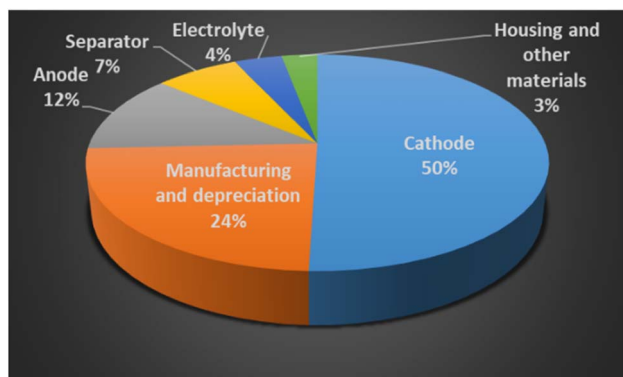


Fig. 4 The cost of a lithium-ion battery (reproduced from ref. 12 with permission from RCS, copyright 2021).

Table 3 Price comparison for battery materials needed for NMC LIBs in USD per tonne

Material	2022	2020	Price source
Lithium ^a	27 327	7250	22
Nickel	32 424	15 090	23
Cobalt	81 860	33 000	24
Manganese	2400	1565	25
Aluminum	3048	1582	26
Copper	9820	6788	27
Graphite ^b	3800	3400	28

^a Global average price for Li₂CO₃. ^b Price for spherical 15 μm graphite.

parity with ICE, at \$100 per kW h by 2026.²⁰ BloombergNEF has broken down the overall cost of a battery cell, see in Fig. 4. The cathode accounts for the half of the average cell cost, while the anode is 12 percent 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 3. Lithium pricing exploded by 496.7 percent between 2020 and 2021.²¹ Platts Analytics was expecting prices to stop rising in 2022 as the supply chain becomes more secure.²⁰

Current industrial hydrometallurgical recycling processes

General process chemistry

Hydrometallurgical recycling processing uses aqueous chemistry and follows typically three main steps, leaching of spent cathode material, impurity removal/purification of leach solution, and recovery of the metal salts, see Fig. 5. Leaching uses acids (or bases) at low temperatures in an oxidizing or reducing environment to dissolve valuable metals. The impurity removal and purification separate the valuable metals from unwanted metals/impurities *via* selective chemical reactions. Methods used are typically hydrolytic precipitation (pH adjustment),

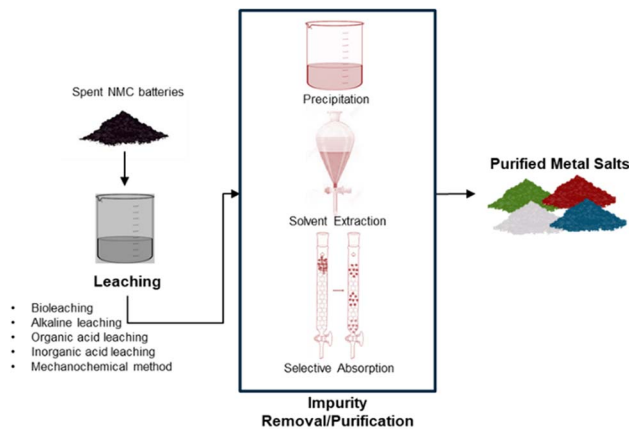
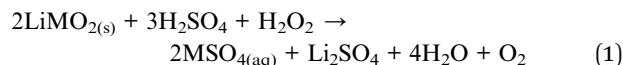


Fig. 5 Recycling using hydrometallurgical processing.

liquid-liquid reactions (solvent extraction), and selective absorption (ion exchange). The production of precursor metal salts can be done by crystallization/precipitation or *via* metal deposition (by gas reduction or electrolytic reduction) and redissolution and crystallization.³

The main advantage of hydrometallurgical recycling over pyrometallurgy is the recovery of high purity pay metals, Ni, Co, Mn, Li, with high recoveries, greater than 99 percent, low impurity content and a lower energy consumption (Fig. 6).¹⁷ Lithium is only recovered with hydrometallurgy, as lithium carbonate. Another benefit of the hydromet processing route is that it can adapt to a mixed cathode feed stock, eliminating the need to separate the spent batteries based on chemistry.¹⁰ The pyrometallurgical processing route, can only recover Co, Ni and Cu as alloys. The alloys require further refinement using hydrometallurgy.²⁹

When recycling lithium-ion batteries, the most common hydrometallurgical method uses sulfuric acid and hydrogen peroxide. The following chemical equation, eqn (1), describes the leaching process.



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 weakens the M–O bond allowing for effective leaching. It is understood that the hydrogen peroxide, H₂O₂, behaves as a reducing agent which converts Co³⁺ into the soluble Co²⁺ metal ion. The addition of peroxide has improved the leaching efficiency to greater than 95 percent.³⁰ The by-product from the addition of H₂O₂ is water and oxygen gas. This reaction is graphically depicted in Fig. 7. This is a greener alternative than using other reducing agents such as sulfur dioxide, SO₂, which produces sulfurous acid.

Lithium leaching efficiency is directly correlated with the strength of acid. Displacement of Li⁺ with H⁺ allows for the lithium to become easily soluble during leaching.²⁹ Once the leached metals, Li⁺, Ni²⁺, Mn²⁺, Co²⁺, Cu²⁺, Fe³⁺, and Al³⁺, are in



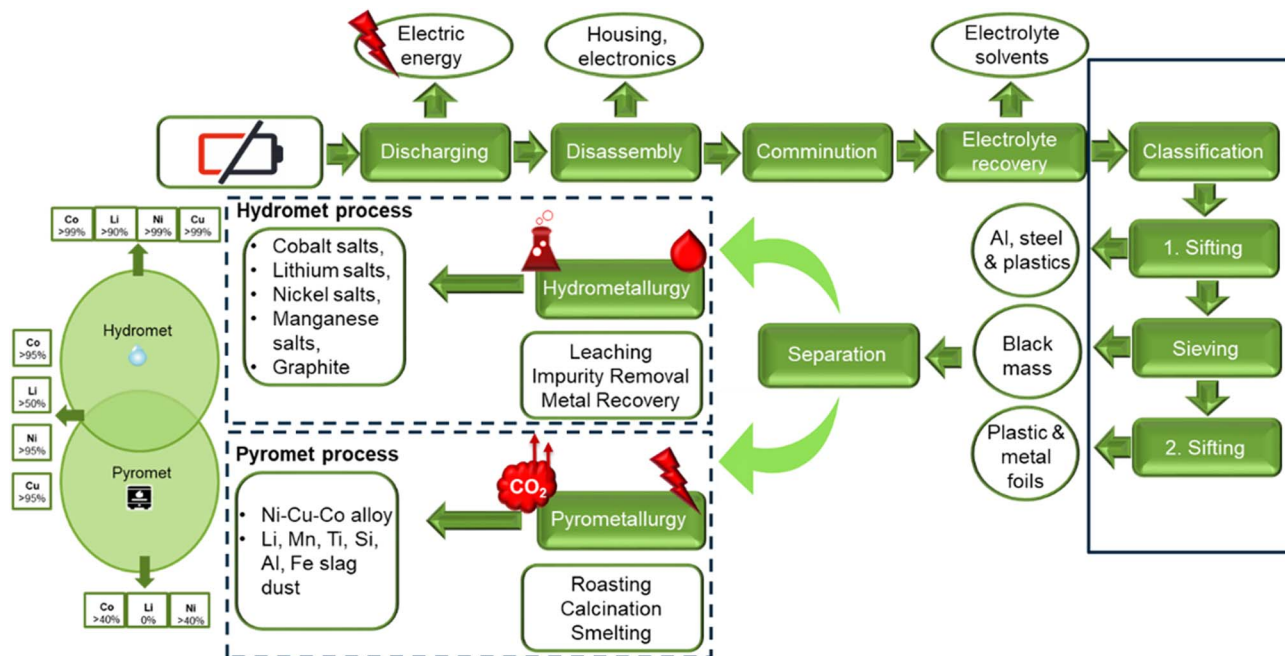


Fig. 6 Lithium-ion battery recycling flowsheet overview comparing hydromet and pyromet processes.

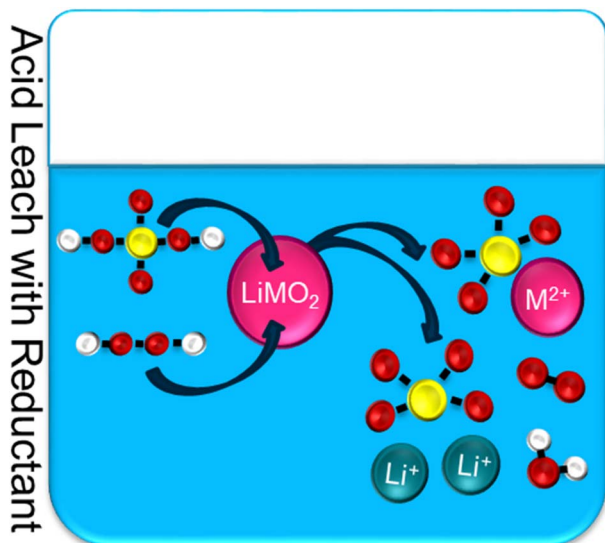


Fig. 7 Typical acid leach with reductant for NMC recycling, where yellow = sulfur, red = oxygen, white = hydrogen, M = metal (Ni–Mn–Co), M²⁺ = metal ions (divalent).

solution, they are selectively addressed in the impurity removal and purification stage. Typically, multiple precipitation and solvent extraction stages are used to separate and purify the solution prior to the recovery of the metals. Metals such as Cu, Fe and Al, are considered to be impurities in this process. These metals can co-precipitate with value metals. The solubility of metal hydroxides in the NMC leach solution can be evaluated with the help of solubility diagrams, Fig. 8a and b. Sequential hydrolytic precipitation of metal hydroxides may be brought upon by Incremental pH adjustments following the solubility

curves using a base, such as NaOH for example. The solution separation of Ni, Mn and Co is difficult to achieve using pH due to closeness of their respective solubility lines resulting in co-precipitation, and therefore a mixed metal hydroxide precipitate that requires further refinement by re-dissolution adding complexity and cost to the operation. Lithium hydroxide has a high solubility and thus often is precipitated with sodium carbonate, Na₂CO₃, as Li₂CO₃ (Fig. 8c and d). The fundamentals of metal ion compound precipitation from the standpoint of particle growth and cleanliness using supersaturation control methodologies are described by Demopoulos.³¹

The Ni–Mn–Co mixed metal solution following the impurity (Fe, Al, Cu) removal stage (by hydrolytic precipitation) is advanced to purification where the metals can be separated into individual purified solutions. Most hydromet processes use solvent extraction to separate the dissolved metals. The typical extraction reaction is given by, eqn (2), where (HA)₂ is the dimer form of an acidic extractant like D2EHPA. The reverse reaction represents stripping of the metal ions into an acidic solution from which metal recovery is affected.



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 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



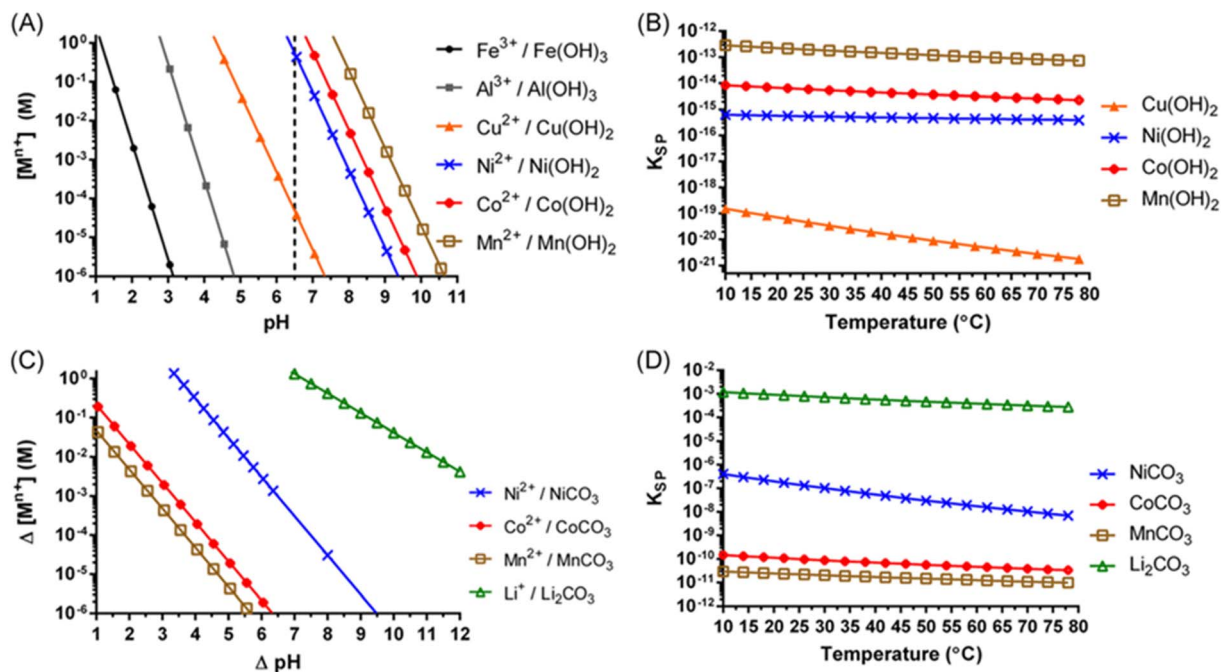


Fig. 8 Solubility diagram for metal hydroxides at 25 °C (A) temperature effect on metal hydroxide solubility (B) solubility diagram for metal carbonates at 25 °C (C) and temperature effect on metal carbonate solubility (D) (reproduced from ref. 30 with permission from ACS, copyright 2022).

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 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 (pK_a) 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 4.

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 Fig. 9.⁴²

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

Metal separations are often enhanced by using a blend of two extractants, as is the example shown in Table 4, where

a carboxylic acid extractant (Versatic 10, neodecanoic acid) was used in mixture with D2EHPA.⁴¹

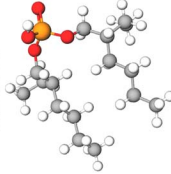
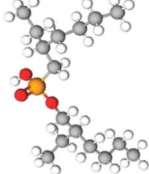
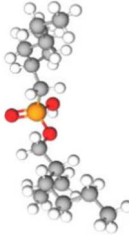
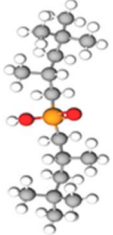
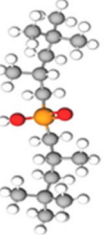
Commercial facilities

There are several commercial hydrometallurgical LIB recycling facilities in operation today. Selected process flowsheets are presented in the ESI.† Recovering valuable metals from spent LIBs started with the “Toxco” process in 1994, rebranded as Retriev Technologies company in 2013.^{45,46} The Toxco facility, located in Canada, treats the spent batteries with liquid nitrogen, -196 °C, to deactivate them (see ESI Fig. S1†). Once frozen, the batteries are shredded and then report to an aqueous solution with high pH.⁴⁵ 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. Lithium is recovered as lithium carbonate or lithium phosphate.³⁰ The overall process recycles 60 percent of the battery pack materials and has an annual capacity of 4500 tonnes.⁴⁷

On a pilot scale, Retriev has patented a process (Fig. S2†) 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. The metal oxides from the cathode material are recovered in the non-floated portion and regenerated with LiOH addition to correct lithium concentration and heating in a furnace (700–815 °C), milling and screening to achieve a particle size between 5



Table 4 Separation of Ni, Mn, and Co from spent NMC leach solutions using organophosphorus acid extractants (data sourced from ref. 32 and 33)

Category	Extractant	Applications	Solution composition (g L ⁻¹)	Extraction conditions	Extraction efficiency	Ref.
Organic phosphoric acid extractant	D2EHPA: 	<ul style="list-style-type: none"> Mn extraction and impurity ions Co-extraction Co–Ni–Mn from Li Separate Ni and Co 	Co: 0.175, Ni: 0.099, Mn: 5.269, Li: 1.248 Co: 6.438, Ni: 0.089, Mn: 6.312, Li: 1.602	T: 300 s, pH: 5, A/O: 0.5, 20% vol D2EHPA, 70–75% saponification T: 300 s, pH: 3.5, A/O: 1 : 1, 15% vol Mextral272P	Mn: 97% Mn: 97.1%	34 35
	PC88A: 	<ul style="list-style-type: none"> Separate Ni 	Ni: 2.54, Li: 4.82	pH: 6.5, A/O: 1, 0.15 M PC88 A	Ni: 99.9%	36 and 37
	P507: 	<ul style="list-style-type: none"> 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	38 and 36
Organic phosphinic acid extractant	Cyanex/Mextral 272P: 	<ul style="list-style-type: none"> 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%	39
	Cyanex 272P: 	<ul style="list-style-type: none"> 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	40
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	41



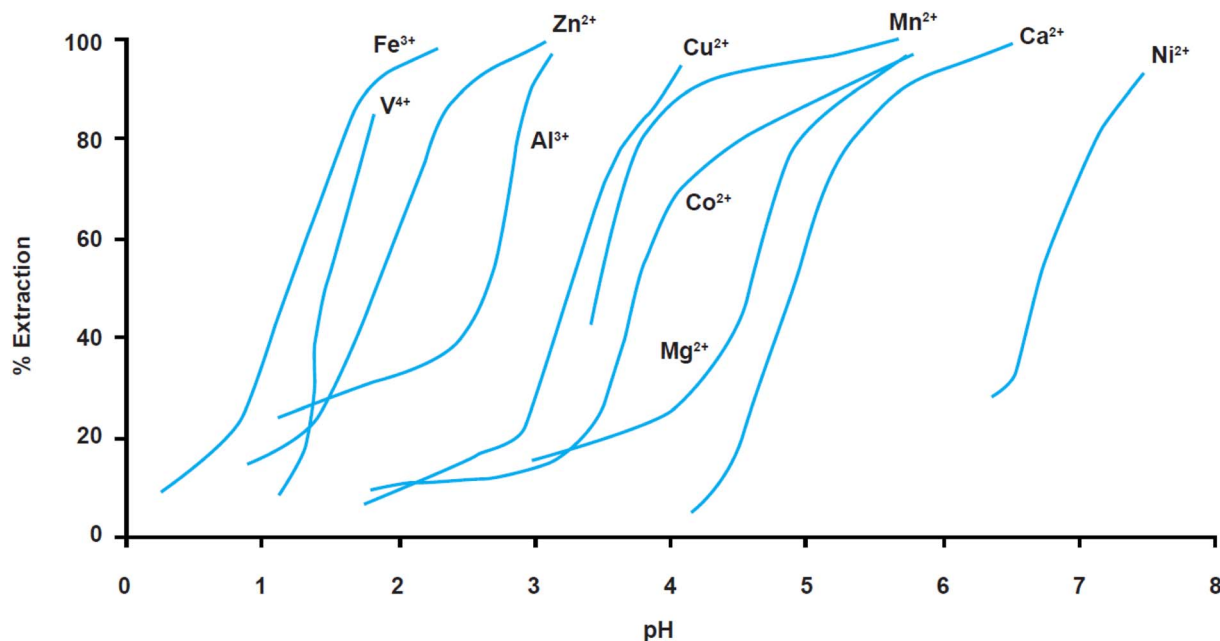


Fig. 9 Extraction equilibria of metals (in%) using cyanex 272 vs. pH in sulphate solutions (reproduced from ref. 43 with permission from KISTI, copyright 2015).

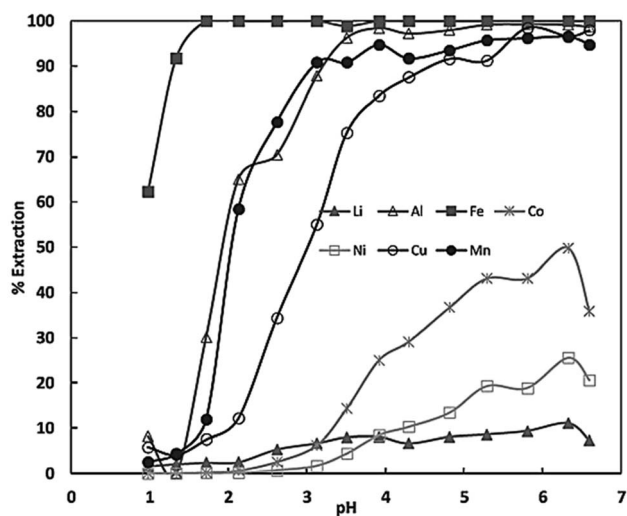


Fig. 10 Extraction equilibria of metals (in%) using D2EHPA vs. pH in sulphate solutions (reproduced from ref. 44 with permission from MDPI, copyright 2022).

μm and $25 \mu\text{m}$.⁴⁸ The purity of the reactivated cathode material has not been reported but judging from their latest development activities involving the addition of hydrometallurgical purification steps it is deduced that this was not battery-grade. The latest addition 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. There appears to be a two-stage leaching process (Fig. S3†) with the first

stage (H_2SO_4) serving to remove selectively iron and copper impurities and the second stage in HCl solution allowing the separation of Ni and Co into $\text{Ni}(\text{OH})_2$ and CoCl_2 products. A key environmental step of the Umicore process is the use of a high temperature step to treat waste gases, avoiding toxic emissions. Overall, the process seems to recover ~ 70 percent of the metals, 10 percent graphite and 15 percent of the plastics. The earlier grade of the recovered metals was not suitable for new battery manufacturing,⁴⁷ but this appears to have been overcome with process improvements reported from pilot scale testing.⁴⁸

Brup Recycling/CATL (China) process has an annual capacity to treat 30 000 t per year of spent LIBS.⁴⁸ The recycling process (Fig. S4†) includes discharging, thermal pre-treatment, mechanical treatment and complex hydrometallurgy (acid leaching with H_2SO_4 and HCl, solvent extraction for the separation of Ni and Co, crystallization of metal sulphate and chloride salts and a mixed intermediate hydroxide precipitate). The process, it is claimed to have a 99.3 percent metal recovery of nickel, cobalt and manganese, but this is difficult to verify. Additionally, it is unclear if the copper, aluminum and graphite is recovered in their process.

GEM Ltd, also known as Green Eco-Manufacturer Hi-Tech Co., Ltd, is located in China. The recycling company has an annual production of 5000 tonnes per year. The process begins with pre-treatment which sorts the major battery components using comminution. Metals such as, copper, aluminum, iron, cobalt and nickel, are separated by complex hydrometallurgical processing steps (of which little is known, Fig. S5†) and then synthesized into salts.⁶ The electrolyte is not recovered in this process.

Accurec (Germany) operates a LIB recycling process that includes thermal, mechanical, pyrometallurgy and



hydrometallurgy steps (Fig. S6†). The recycling plant treats 3000 tonnes of lithium-ion batteries annually. Accurec has new technology being implemented in the current recycling process that will allow for the recovery of lithium and graphite.⁶

Nickelhütte Aue GmbH (NHA) has been recycling Li-ion batteries in Germany since 2011.⁶ Thermal pre-treatment, pyrometallurgy processing, and hydrometallurgy methods make up the recycling process. The flow diagram, shown in Fig. S7,† depicts NHA's process.⁴⁹ The pyromet process smelts the spent batteries in a batch-wise-furnace to obtain Ni-Co-Mn matte product which subsequently is subjected to leaching to recover various metal salts. A rotary kiln is used to thermally pre-treat the batteries. Limited information is available regarding the specifics of the hydrometallurgy treatment. Unless there have been recent improvements the produced metal salts may not be of battery-grade but rather used in other fields like electroplating shops. The overall process capacity is 7000 tonnes per year.⁶

The Duesenfeld lithium-ion battery recycling process, LithoRec, completely discharges the battery packs before physical separation. As shown in Fig. S8,† 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 application. The mechanical recycling rate is 72 percent, the recovery of electrolyte and graphite bring the overall recycling efficiency to 91 percent. The separator film and high boiler portion of the electrolyte make up the unrecycled 9 percent. The process located in Germany has an annual capacity of 3000 tonnes.⁶

SungEel HiTech, located in Korea, have a recycling plant capacity that treats 8000 tonnes of spent LIBS annually. The process scheme, shown in Fig. S9,† follows the general approach encountered in the previous plants starting with mechanical separation and followed by hydrometallurgical purification. There is not specific information available on the hydrometallurgy operations but judging from the products listed in the published flowsheet (Fig. 16) that includes salts and metal ingots, it is expected to be a complex one ranging from leaching to solution purification and recovery of metal salts by crystallization and metals by electrolysis. The company announced in 2020, it will be expanding operations to a new site that will triple the current capacity to 24 000 tonnes per year.^{6,50}

Dowa Holdings Co. Ltd (Japan) currently treats 1000 tonnes of spent LIBs a year. The process includes disassembly, thermal pre-treatment (rotary kiln), pyromet and hydromet processing. Details regarding the process technology, efficiency and recovery rates are not available.⁶

New research developments

The life cycle analysis of pyro- and hydro-metallurgy recycling methods was compared to the direct recycling method by Argonne National Laboratory using the EverBatt model as shown in Fig. 11.⁵¹ The hydrometallurgy method consumed the highest energy, a result of high material throughput.¹⁰ Greenhouse gas emissions between pyro- and hydro-met were around 2 kg kg⁻¹ 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. Many of the new processes under development aim towards more efficient hydrometallurgy-based recycling technologies and in particular towards adoption of the new direct recycling approach. Advanced examples of such developments that have reached the pilot-plant stage are reviewed in this section.

New hydrometallurgy recycling technologies

France is home to Recupyl, now TES-AMM recycling company, this process uses a multi comminution approach. 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 Li₃PO₄ as by-product (see Fig. 12). Any remaining lithium can be precipitated as Li₃PO₄ using H₃PO₄. The process can also recover cobalt as a hydroxide or elemental cobalt *via* electrolysis.⁴⁸ The annual capacity of the Recupyl process is 110 tonnes.

In another development, Volkswagen (VW) adopted the LithoRec process from Duesenfeld and is now recycling LIBs on

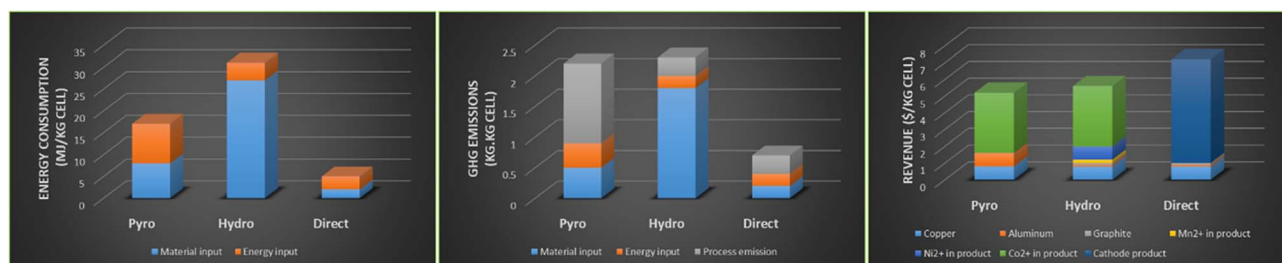


Fig. 11 Life cycle analysis for pyrometallurgy, hydrometallurgy and direct recycling (pyro, hydro, direct) (left) energy consumption, (middle) GHG emissions and (right) revenue from outputs, (reproduced from ref. 10 with permission from MDPI, copyright 2022).



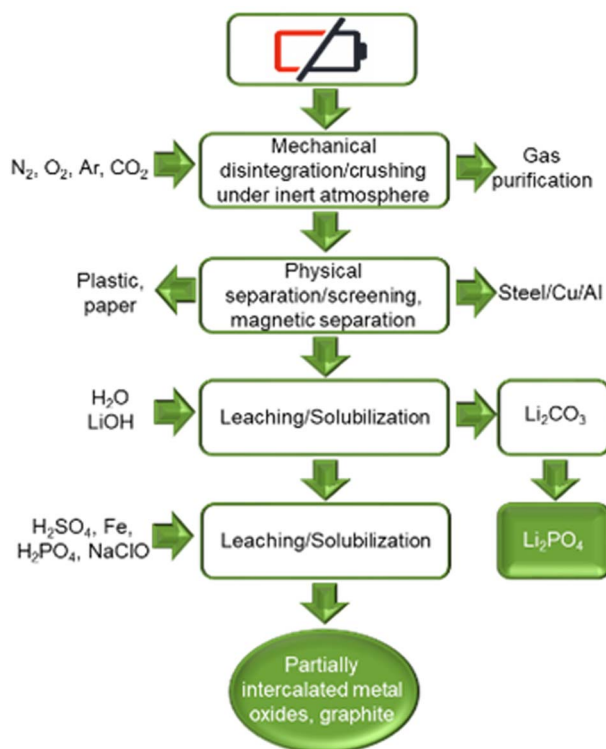


Fig. 12 Recupyl LIB recycling process (reproduced from ref. 48 with permission from MDPI, copyright 2021).

a pilot scale (Fig. S10†). 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 have a target to recycle over 90 percent of spent batteries at the Salzgitter plant in Germany.⁵²

Aalto University (Finland) has developed a comprehensive LIB recycling process that has been demonstrated in a laboratory scale (Fig. 13). The process targets 99 percent overall recovery using an improved pyro- and hydro-metallurgical method.⁵³ The process involves mechanical separation of spent LIBs followed by screening of cathode material from metal foils.⁷ 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 sulfates-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 section. An important feature of the Aalto process is the treatment of sodium hydroxide and its in-plant utilization for REE precipitation to improve the overall economic and environmental impact.⁵⁴

American Technology Company, located in the USA, uses the automated de-manufacturing of batteries (high separation of low-value by-products, targeted removal of contaminants), targeted hydrometallurgical proprietary chemical extraction train which extracts Li, Ni, Co and Mn and upgrades into battery grade (simplified IR, highly selective recovery of products, battery grade purity cathode products).⁵⁵ The commercial recycling facility is under construction. The facility will treat 20 000 tonnes of spent LIBs annually.

Lithion Recycling received \$125 M in funding to build the first LIB recycling plant in Quebec, Canada. Commercialization of the plant is expected to begin in 2023, following the

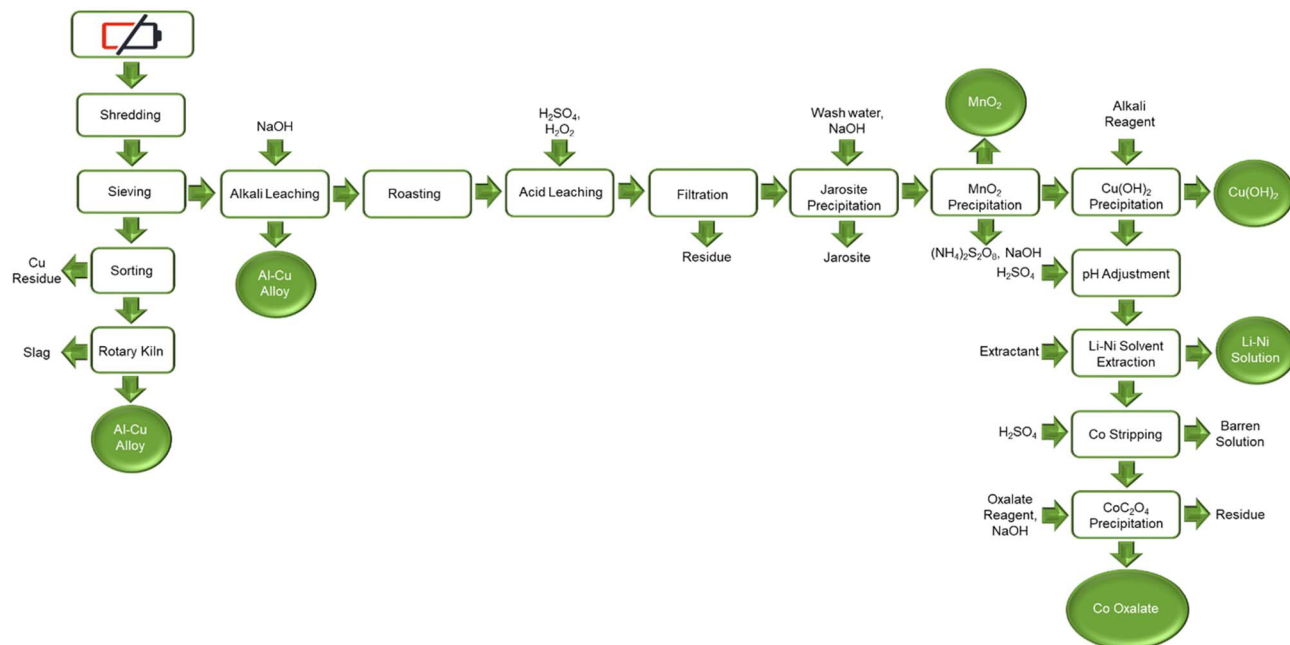


Fig. 13 Aalto University suggested NMC recycling process (reproduced from ref. 48 with permission from MDPI, copyright 2021).



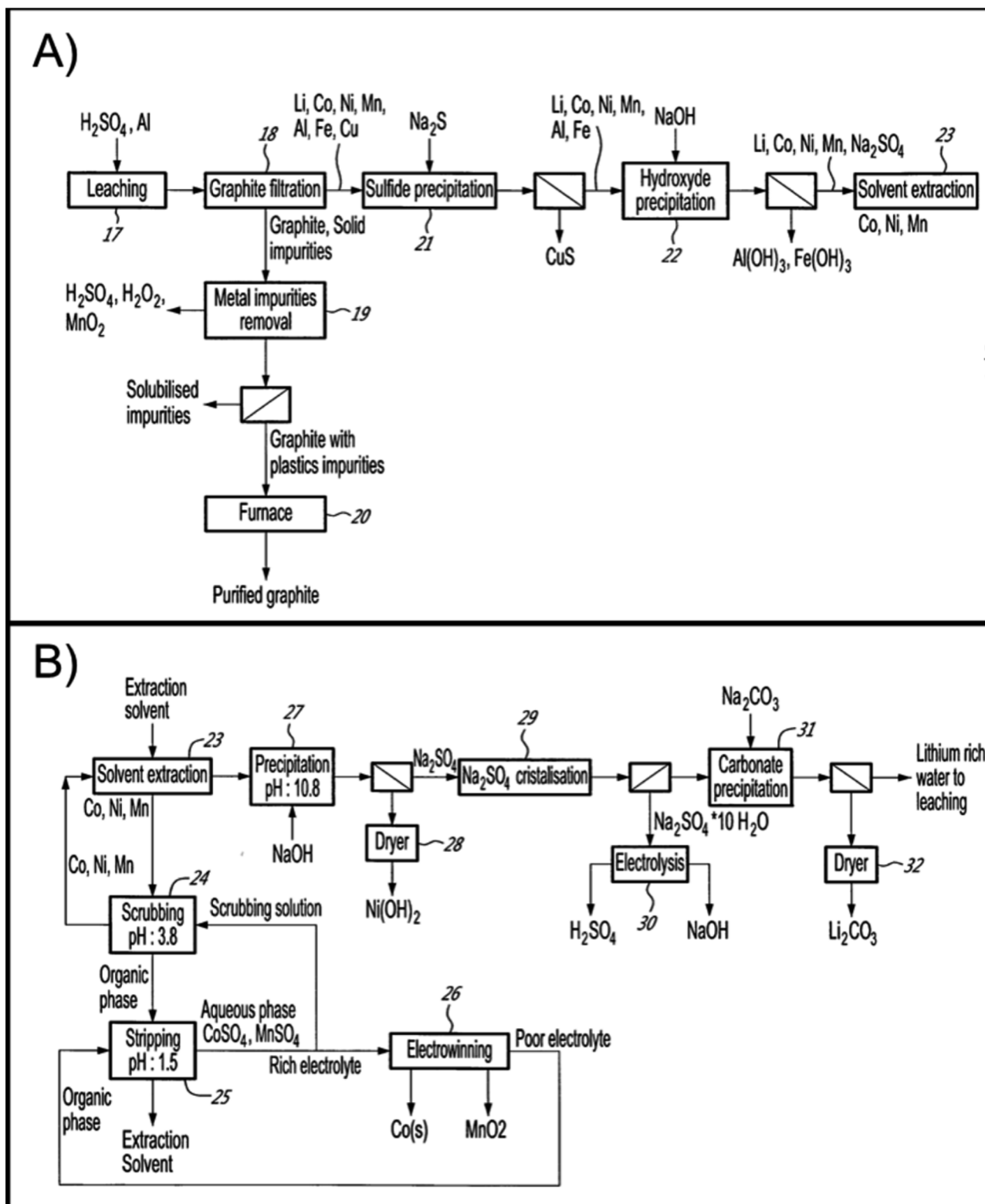


Fig. 14 Lithion recycling patented hydromet process (A) leaching circuit and (B) metal separation for recovery of all value metals and graphite from spent NMC.⁵⁷

successful demonstration plant. The hydrometallurgical process operations are outlined in Fig. 14A, the leaching circuit, and in Fig. 14B, the metal separation steps. 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. Following solution purification, the cathode metals are recovered as lithium carbonate (by crystallization), nickel hydroxide (by neutralization) and cobalt metal (by electrowinning). The company claims their hydrometallurgical technology, has a recovery rate of 95 percent battery metals, which are purified for re-entry into the battery production chain⁵⁶.

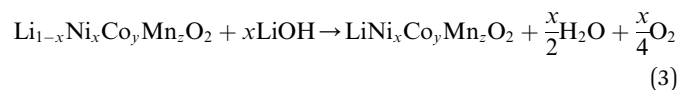
Li Cycle is another LIB recycling company located in Canada developing a spoke and hub operation for the North American market. The facility treats all types of LIBs and brings them from a charged state to inert product. A combination of mechanical separation and hydrometallurgical resource recovery techniques are used. The mechanical separation and size reduction produces a black mass free of foil components. Then the black mass follows a hydrometallurgical flowsheet 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 sulphate salts. Sodium sulphate is then recovered through the crystallization process. Finally, lithium is treated and crystallized as a carbonate. Li-Cycle plans to have seven spokes and one hub in North America and Europe by the end of 2023. The Li Cycle process will have greater than ninety five percent recovery rate according to their patent.⁵⁸

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 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.⁵¹ Sloop *et al.* first patented this concept in 2016.^{59,60} As per ReCell center's modeling work direct recycling has the lowest impacts for all cost and environmental categories.⁵¹ 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.⁶¹ Typically, direct recycling (Fig. 15) consists of three processing steps:¹ selective chemical de-lithiation (if NMC cathode in discharged state),² hydrothermal re-lithiation, and³ thermal processing/annealing.⁶²

Hydrothermal treatment to induce re-lithiation¹⁰ of the de-lithiated NMC cathode is done in an autoclave with lithium hydroxide solution, to bring the Li back to ideal stoichiometry, 1.0.⁶³ as per the following reaction (eqn (3)).



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.¹⁰

This method is non-destructive to the active NMC particles and regenerates their functionality in terms of lithium capacity and conductivity.⁶⁴

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, *i.e.*, 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 re-lithiated NMC material.⁶³ In the following section the latest hydromet-based direct recycling developments involving NMC cathodes are briefly introduced.

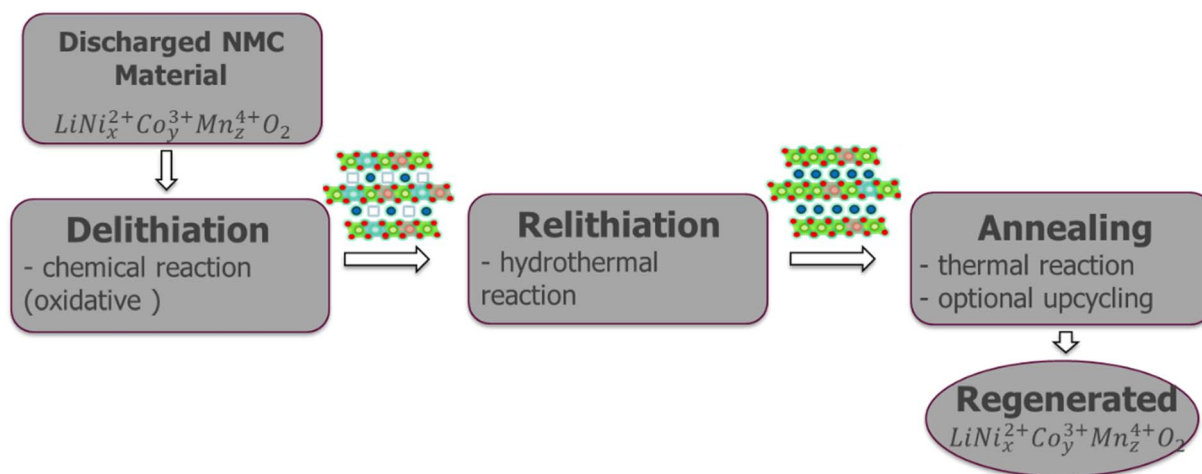


Fig. 15 Typical direct recycling process for NMC cathodes.



Direct recycling developments

American Manganese is a recycling company that is using a direct recycling/upcycling approach. The patented process, RecycLiCo™, has achieved up to 99 percent recovery of lithium, cobalt, nickel and manganese. The process comprises a leach stage, co-precipitation stage and a lithium recovery and regeneration stage. The cathode material is not decomposed/dissolved like other hydrometallurgical processes but is preserved in compound form and regenerated as cathode active material (CAM).⁶⁵ Lithium is recovered by electro dialysis. A three-compartment cell regenerates lithium hydroxide and sulfuric acid from lithium sulfate solution (Fig. 16). The Li^+ moves to the cathode compartment and the SO_4^{2-} moves to the anode compartment, as shown in Fig. 16. The upcycling method includes the conversion of spent NMC chemistry to the desired Ni-rich composition (ex. NMC 111 to NMC 622) and allows for a direct integration into the re-manufacturing of LIBS. The demonstration plant is located in Vancouver, Canada and has exceeded the original capacity of 500 kg of scrap NMC cathode material per day, with an impressive 99% extraction of valuable materials such as lithium, cobalt, nickel and manganese.⁶⁶ This will be the first hydrometallurgical cathode waste recycling and upcycling plant in North America.⁶⁷

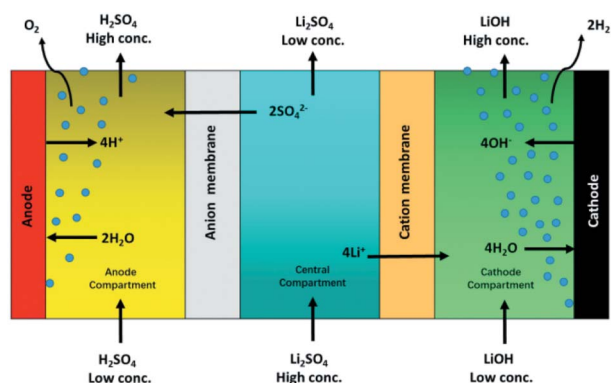


Fig. 16 American Manganese RecycLiCo™ process, a three compartment membrane electro dialysis cell for generating LiOH and H_2SO_4 (reproduced from ref. 67 with permission from Taylor and friends, copyright 2021).

Battery Resources, now Ascend Elements, opened a 154 000 square foot facility which can process 30 000 tonnes of LIBS waste per year in Georgia, USA.⁶⁸ Using a hydrometallurgical and direct recycling approach, the process has shown superior performance of recycled cathode materials.⁶⁹ The patented Hydro-Cathode™ process claims that upcycled battery materials have 50 percent longer cycle life and 88 percent higher power capacity.⁷⁰ The material from the lithium battery recycling stream undergoes an acid leach, which produces the leached solids. The solids are heated while being heated with a strong acid to remove any remaining cathode and separator components. By changing from aluminum oxide to aluminum sulfate, the strong acid eliminates any remaining aluminum oxide from the separator. Washing the acid-treated solids removes water-soluble impurities, such as aluminum sulfate formed when aluminum oxide and sulfuric acid interacted and produces graphite that is essentially pure (99%). The elemental composition of the cathode material is adjusted to suit industry needs. The process can either leave as a mixed NMC hydroxide (precursor), or a sinter (CAM) into various NMC chemistries (111, 532, 622, 811).⁷¹

OnTo Technology LLC has been a pioneer in direct recycling technology. Their patented process is called Cathode-Healing™ Direct Recycling. The process includes, extraction of electrolyte using supercritical CO_2 , shredding, mechanical electrode harvesting, flotation, Cathode-Healing™, and rebuilding cells using recycled cathode and anode materials.⁵³ The cathode healing method, classified as a direct recycling process, uses two-steps as described above, hydrothermal and heat treatment. The NMC cathode is regenerated by using lithium solution to add Li^+ back into the structure, as well as repair the microstructure defects using heat.⁶⁴ The regeneration mechanism of the cathode material structure is graphically illustrated in Fig. 17.

Discussion: challenges and trends

Currently the recovery of expensive materials, primarily cathode, has been the focus of commercial recycling companies using pyro- and hydro-metallurgy.¹⁷ With recent supply chain security issues, more companies are looking to improve the

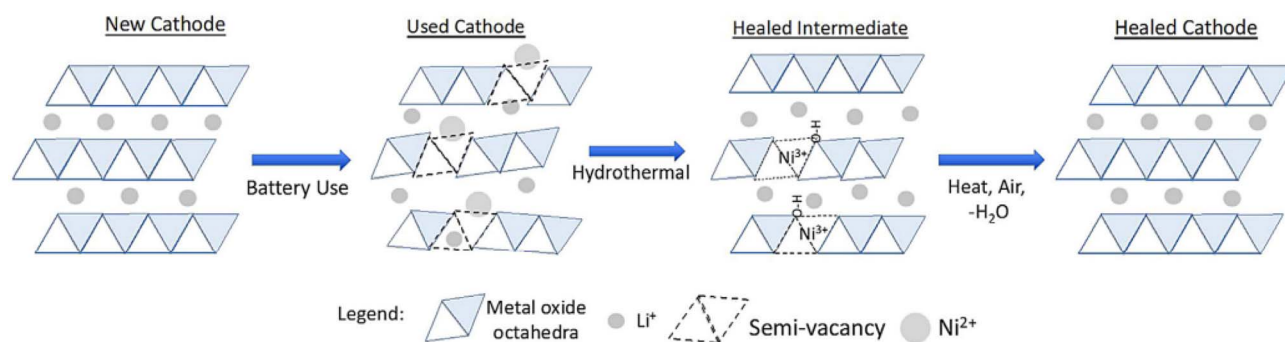


Fig. 17 OnTo technology's advanced battery recycling process for LIBS: cathode-healing™ impacts structure by mixing Ni^{2+} and Li^+ to regenerate the full layered structure (reproduced from ref. 64 with permission from Elsevier, copyright 2019).



Table 5 Summary of commercial hydrometallurgical lithium-ion battery recycling operations

Company	Location	Capacity (tonnes per year)	Method used to expose active materials	Method used to recover recyclable materials	Primary recovery material	Secondary recovery material	Lost material	References
Retriev technologies	Canada	4500	Wet mechanical treatment	Flotation, alkaline precipitation	Li ₂ CO ₃ , MeO	Steel, Cu, Co, Al, graphite	Plastics	48
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	48
Brunp/CATL	China	100 000	Discharging, thermal pre-treatment, mechanical treatment	Hydromet: H ₂ SO ₄ /H ₂ O ₂ , Na ₂ S, or NaHS reductive acid leaching, SX	Ni–Mn–Co hydroxides, Co–Ni sulfates, Co chloride	Unknown	Unknown	6
GEM Ltd	China	30 000	Sorting, comminution	Hydrometallurgy, high temperature treatment	Co, Ni, Cu, Al, Fe	Unknown	Electrolyte, binder	6
Accurec	Germany	4000	Sort, dismantle, milling, separation, agglomeration	Vacuum thermal treatment, reductive leaching H ₂ SO ₄	Li ₂ CO ₃ , Co-Alloy	Metallic alloy	Electrolyte, polymers, graphite	48
Nickelhutte Aue GmbH	Germany	3000	Thermal pre-treatment	Pyro- and hydro-metallurgical treatment	Ni, Cu, Co	Slags	Unknown	6
Duesenfeld	Germany	2000	Discharge, inert physical separation: two-stage crushing, air classification	Drying, calcination, leaching	Li ₂ CO ₃ , metal oxides	Al–Cu, plastics, electrolyte	Graphite	6 and 48
SungEel HiTech	Korea	8000	Mechanical pre-treatment in water	Hydrometallurgical process	Co, Mn, Ni, Li ₂ CO ₃	Cu, Al	Unknown	6
Dowa holdings	Japan	1000	Dismantle, thermal pre-treatment	Pyro- and hydro-metallurgical treatment	Co, Ni, Cu	Unknown	Unknown	6



Table 6 Summary of recent state-of-the-art lithium-ion battery recycling developments

Company	Location	Capacity (tonnes per year)	Stage	Method used to expose active materials	Method used to recover recyclable materials	Primary recovery material	Secondary recovery material	Lost material	Reference
Recupyl	France	110	Active	Dry mechanical treatment under inert atmosphere	H ₂ SO ₄ /H ₂ O ₂ reductive acid leach, selective precipitation	Li, metal oxides, graphite	Steel: Cu/Al, plastic	Unknown	31 and 32
Volkswagen	Germany	Unknown	Pilot scale	Physical separation, shredding, drying, sieving	Hydro-metallurgy	Co, Ni, Mn, Li	Steel, separator, Al, Cu	Electrolyte, plastics	19
Aalto University	Finland	Unknown	Concept laboratory process	Shredding, sieving	Al smelter, leaching	CoC ₂ O ₄ , Al-Cu Alloy	Jarosite, MnO ₂ , Cu(OH) ₂ , Li-Ni solution	Graphite, binder, plastic, Cu, water	48 and 21
American battery technology Lithion	USA Canada	20 000 5000	Under construction Under construction	Automated de-manufacturing process Physical separation, shredding, drying, sieving	Hydro-metallurgy: Impurity removal Hydro-metallurgy, distillation	Unknown Ni, Co, Mn, Li	Unknown Unknown	Unknown Unknown	22 23 and 24
Li-Cycle	Canada	5000	Planned	Mechanical separation, size reduction	Hydro-metallurgy	Ni, Co, Mn, Li	Steel: Cu/Al, graphite	Electrolyte, plastics	25
American manganese Battery resourceers	Canada USA	180 30 000	Planned Planned	Shred, separate Discharge, shred, mag sep, sieve, dense media, ambient	Direct recycling/ Hydro upcycling Hydromet/Direct recycling: NaOH, H ₂ O ₂ , H ₂ SO ₄ and Na ₂ CO ₃	NMC hydroxide, Li ₂ CO ₃ Li ₂ CO ₃ , cathode powder	Unknown Ferrous metals	Unknown Electrolyte	26 and 27 48
OnTo technology LLC	USA	Unknown	Unknown	Supercritical CO ₂ , physical disassembly	Hydromet/Direct recycling: Heat treatment, LiOH leaching	Cathode powder, Li ₂ CO ₃	Electrolyte, graphite, Fe, Al, Cu, plastics	Unknown	20, 30 and 33



required to produce battery-grade precursor salts in fewer steps in addition to embracing closed loop processing. The new direct recycling method is by far the most promising green recycling technology. The process is simpler and more effective in repairing the cathode materials, without causing structural changes, and restoring the original electrochemical performance. Hydrometallurgy is expected to play a key role in developing direct recycling technologies as are for example the lithiation and delithiation steps by adopting non-polluting reagents and hybrid low temperature treatments. There are currently no commercialized facilities for direct recycling. The challenge all current recycling methods face is the feed stock needs to be indiscriminate to the different LIB cathode compositions. A technology that is applicable to all battery chemistries has yet to be discovered.

In conclusion, the development of physical recycling processes, including stabilization, opening, and separation, is crucial for sustainable LIB recycling. Separating the black mass following cell disassembly enables direct recycling and reduces waste, contributing to a more environmentally friendly and efficient recycling approach.

Conflicts of interest

There are no conflicts to declare.

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