Recycling and Regeneration of Spent Lithium-ion Batteries

by

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Abstract

The exponential rise in demand for lithium-ion batteries (LIBs) in applications that include grid-level energy storage systems, portable electronic devices and electric vehicles, has led to logistical, and environmental challenges in the supply of raw materials required for its production and the management of end-of-life batteries. Lithium, cobalt, nickel and graphite are some of the raw materials critical to the production of LIBs and the primary source of these materials is mining operations which pose a multitude of environmental concerns as well as human rights concerns. Therefore, supplementing the supply chain of these raw materials via recycling from spent LIB can mitigate the above challenges to a certain degree while simultaneously providing a route for waste management in keeping with the principles of a circular economy. Hydro- and pyro-metallurgical techniques which are an extrapolation of extractive metallurgical methods are commercially employed presently to recycle the components of lithium-ion batteries in industrial scale. These conventional techniques currently employed for recycling LIBs are marred by environmental concerns due to their dependence on high temperatures and strong acids. These energy-intensive methods are known to produce harmful emissions and thus lack environmental friendliness. Moreover, the low purity of the recovered materials and low yields of the recovered metals render them inefficient. Given the exponential demand for LIBs and the resultant pressure on the environment, more sustainable and efficient recycling techniques are necessary to alleviate these environmental concerns and meet the needs of a growing market.

The first chapter of this thesis presents a literature review of the existing pre-treatment and recycling strategies employed for end-of-life batteries and discusses the advantages and disadvantages of each method. Additionally, the recent trends and progress in the domain are explored. The second chapter introduces the experimental work, results and discussion on the green approach designed to effectively and sustainably recycle the active materials in the electrode of a commercial spent LIB. Chapter 3 of this work details a partially successful attempt to directly regenerate spent NCM622 cathode material through the application of molten salt relithiation followed by hydrothermal treatment. In chapter four, a perspective on circular economies is presented with a focus on the incorporation of its principles for achieving a sustainable lithium-powered future. The challenges that currently hinder the development of a fully-realized circular economy for lithium-ion batteries are also discussed, along with ongoing efforts aimed at overcoming these challenges.

Preface

The content presented in Chapter 1 is adapted from a review article which has been accepted for publication in the Renewables Journal, published by the Chinese Chemical Society. The initial draft was prepared by me and subsequently refined with the assistance of Dr. Zhixiao Xu and Dr. Ge Li. The content in Chapters 2 and 4 is based on original manuscripts which are currently under review for publication. The experimental procedures and analysis were conducted by me. Dr. Xiaolei Wang made significant contributions to the conceptualization of the project, provided valuable supervision throughout its development, and contributed to the review and editing of all manuscripts.

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Chapter 1. Literature Review

1.1. Introduction

Advancements in electric devices and electric vehicles coupled with the digital revolution has catapulted the demand for lithium-ion batteries (LIB) in recent years. Additionally, the need for robust energy storage systems to accommodate the transition towards sustainable sources of energy has further increased the interest towards LIBs [1]. High energy density with tolerant operating conditions, long cycle life and comparatively lower self-discharge rates are the primary reasons behind the attention that LIB receives [2]. Moreover, global efforts towards the decarbonization of roads will further compound the demand for LIBs as they are the preferred choice to power electric vehicles (EV) owing to their aforementioned advantages. The surge in demand for LIBs can be aptly reflected by the growth in percentage of lithium consumption for battery related applications from 40% to 60% in the space of just 5 years (2015 - 2019) [3]. The increase in usage and subsequently burgeoning demand of LIBs results in three main challenges. These include constraints in the supply of the base metal lithium and other raw materials, logistical bottlenecks and the buildup of end of life (EOL) LIBs leading to environmental complications.

The bulk of exploitable lithium reserves as per the United States Geological Survey (USGS) is located in Chile, Australia and China which leads to a host of geographical and political limitations that could result in demand of the metal outpacing supply in addition to increasing the market price of the metal [4]. Therefore, reliance on mining alone to keep up with global requirements of lithium in the context of LIBs may not be an infallible strategy in the long term. Another major concern facing the LIB sector is the buildup of e-waste caused by EOL batteries entering the waste stream. The primary reason behind this trend is the sheer volume of electric vehicles entering the market as estimates point to global sales of EV breaching the 6 million mark in 2020 alone with notable increase in the following years [5], [6]. Hence, the accumulation of waste LIB is an imminent environmental concern which requires immediate action. Recycling and regeneration of spent LIBs is a potent strategy that can address both supply chain concerns while simultaneously mitigating the environmental impact of waste LIB. Additionally, the recovery of precious metals such as cobalt can be achieved over the course of LIB recycling process making it an economically advantageous endeavor for industries operating in the niche [7], [8].

Numerous strategies for LIB recycling have been developed with varying levels of commercial adoption ranging from pilot to industrial scale. However, much of the techniques employed for large scale LIB recycling suffers from low efficiency, process complexity and high energy requirement. Nascent techniques, such as direct regeneration, which are still in the laboratory stage are currently being explored to overcome the limitations of prevalent recycling strategies.

1.2. Importance of Recycling Infrastructure

Presently, most industrial initiatives are centered on sustainable practices as part of the global "green" efforts to reduce carbon footprints for the purpose of mitigating the effects of climate change as outlined by the Paris Agreement since 2015 [8]. Much of these endeavors involve transitioning towards renewable energy sources and away from fossil fuels. A key component to ensure successful transitions is the development of energy storage systems (ESS) and the technology is supported by LIBs owing to its intrinsic and characteristic properties such as long cycle life, high energy density and efficiency [9], [10]. Additionally, growth in consumer electronics and EVs have added to the global demand of LIBs. As mentioned earlier, much of the global lithium reserves are concentrated in a few geographical locations which makes it difficult to support demand solely by mining operations. Also, the environmental impact of mining, as outlined in subsequent sections, is quite significant. Therefore, an alternative method to substantiate lithium supply is critical and recycling is a suitable candidate with the potential to achieve the same.

1.2.1. Role in Energy Transitions

Energy transition is defined as the amount of time that elapses for a new energy source to achieve considerable share or even replace traditional energy sources such as fossil fuels [10]. The onus for the present energy transition rests on two renewable sources, namely solar and wind. The breakdown of global energy consumption by energy source is illustrated in figure 1. However, seasonal changes leading to intermittency is a challenge to the widespread deployment of renewably sourced energy and requires the support of grid-level energy storage systems. Grid-level ESS stores excess generated electrical energy and is used to stabilize electric power systems during peak loading intervals [11]. Grid-level ESS is supported by battery technology with LIBs serving as the first choice for these applications. This is evidenced by the large-scale usage of LIBs, in excess of 77% as of 2018, in USA's power storage systems [12].

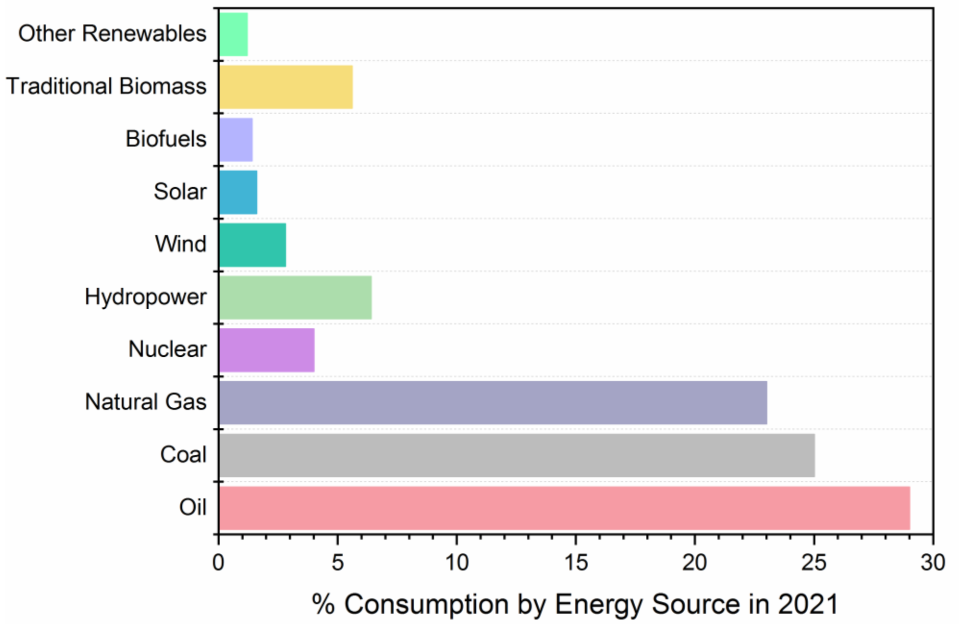

Figure 1: Breakdown of global energy consumption by source in 2021 [13]

Renewable energy sources are cost-effective compared to their fossil fuel counterparts and are not limited by supply constraints. The variables that are of interest in this regard are seasonal, temporal and geographical leading to unpredictability in power output. Wind turbine and photovoltaic solar farms need to be integrated with LIB energy storage systems for the purpose of peak shaving and frequency regulation. Peak shaving involves leveling out short-term spikes in energy demand while frequency regulation refers to providing frequency and voltage stability when there is a discrepancy between power generation and utilization. LIB's electrochemistry is ideally suited to handle both of these functions for extended periods due to its cycle life and efficiency [9]. Notable examples of LIB energy storage system deployments include a 32 MW/8 MWh in New York, 6 MW/10 MWh in the UK and a 40 MW/20 MWh in Japan [14]–[16]. The market for battery energy storage systems (BESS) is estimated to have a compound annual growth rate of 32.8 % from 2020 to 2025 which substantiates predictions that the trend for the proliferation of BESS is set to continue [17]. Taking the aforementioned information into consideration, it can be inferred that a marked increase in the demand for LIBs is imminent in the foreseeable future and emphasizes the need for a streamlined recycling infrastructure.

1.2.2. Electric Vehicle Shift

Decarbonization of roads is a central aspect of green initiatives and electric vehicles are currently touted to hold the key for its materialization. In addition to reducing the carbon footprint, electric vehicles provide an enhanced driving experience and offer an opening to break free of gasoline dependency which further drives its popularity. Being a critical aspect of the decarbonization drive, electric vehicles receive immense support from governments in the form of subsidies and tax incentives. Aggressive examples of the EV revolution include Norway's hybrid/fully-electric target by 2025 and Germany's 2030 goal to put a stopper on the internal combustion engine [18]. The primary impediment to amplified sales of EV is the high cost associated with them and much of it can be attributed to the LIB that powers these vehicles [19]. However, the combination of technological advancements and governmental intervention has made EVs more accessible to the public, thereby, encouraging its adoption in road transportation [20].

A study conducted by N. Rietmann et al. predicts that by 2032, the global share of passenger electric vehicles on roads will breach the 30% mark [21]. The researchers employed a logistic growth model with data collected using sales data from 26 countries over a 9-year period (2010 – 2018) to arrive at this conclusion. This significant rise in EVs will require the support of a corresponding number of LIBs to serve as the power source. The average composition of precious metals lithium and cobalt in these commercial LIBs are 1.6% and 9.4% respectively [6]. Furthermore, Marano et al. has estimated that the average life-span of a LIB used in electric vehicles is approximately 10 years or 150,000 miles under optimal operating conditions [22]. Therefore, the need for expensive and geopolitically scarce metals to manufacture LIBs for EVs as well as the volume of e-waste entering the waste stream because of end-of-life EV batteries obligates an alternative method to sustain uninterrupted use of the technology. Moreover, the spent batteries are also a source for precious heavy metals like lithium and cobalt. Recycling can, thereby, aid in waste management while simultaneously achieving reclamation of precious metals.

1.2.3. Demand and Supply Risk of Lithium

Lithium is an indispensable component for the manufacture of LIB electrodes and electrolytes. In recent years, the demand for LIBs have grown exponentially owing to an increase in demand for portable electronic devices, renewable energy integrations and electric vehicles. In 2019, 65% of lithium supply worldwide went towards the manufacturing of batteries [23]. This trend is expected to continue as low carbon technologies such as electric vehicles continue to gain a foothold in internationally significant markets [3], [23]. Despite being a relatively common metal, reserves with economically exploitable concentrations of lithium are limited with three countries holding in excess of 17% of global lithium reserves [24]. Naturally, there is potential for a supply-demand mismatch of lithium in the future with the demand of the heavy metal outpacing supply. In a risk assessment conducted by Helbig, C. et al. with respect to material supply for LIB battery production, three key risks were examined [25]. These include risk of demand increase, risk of supply reduction and political risk. Among all the metals evaluated in the study, the highest risk was associated with cobalt and lithium [25]. An important factor influencing the demand increase and supply reduction risk is the price of lithium. Higher demand could raise lithium prices as was the case from 2013 to 2018 while oversupply can cause the prices to plummet as evidenced in 2019 which would result in the reduction of lithium mining endeavors [23]. The price fluctuations interpose uncertainty in lithium extraction, consequently introducing challenges to steady supply of the metal to meet future demands. Additionally, the concentration of exploitable lithium reserves in a handful of countries such as Chile, China and Australia could lead to political tensions thereby detrimentally affecting the supply of the metal [4], [24]–[26]. Therefore, reliance on mining alone to satiate global lithium demand can significantly impede technological innovation and decarbonization drives involving the metal. This further illustrates the need for a secondary source for extraction and supply of lithium.

1.2.4. Closed-loop Recycling

As discussed in the earlier sections, recycling of spent LIBs is critical to overcome the outlined challenges and closed-loop recycling offers a systematic solution to tackle the same. Closed-loop recycling is a system that involves a product whose materials has been recycled to be used in the second iteration of its production with little to no degradation and wastage [26]. The defining characteristic of closed-loop manufacturing is that the end-of-life product does not reach the landfill. Closed-loop recycling is a key aspect for waste management and the creation of sustainable supply chains as it is a zero-waste system [27]. The value of adopting a closed-loop process can be illustrated through the example of EVs. A life cycle environmental assessment conducted by Majeau-Bettez, G. et al. revealed that PHEVs and EVs have a typical energy consumption for material production of 129 and 125 MJ/kg for the batteries with an associated cradle-to-gate greenhouse gas (GHG) emissions of 22 Kg CO_2/kg of battery [28]. Therefore, closed-loop recycling can contribute to lowering the energy consumption and GHG emissions involved in the manufacturing of subsequent versions of LIBs. An analytical study conducted by Dunn, J. B. et al. confirmed the same where the results indicated a reduced energy consumption of up to 48% over the course of the material production step in the case of a closed-loop setting [29]. A closed-loop recycling infrastructure is crucial for the sustainable prolonged use of LIBs. A mix of government initiatives, efficient collection of spent LIBs and economies of scale are the essential conditions that will govern the creation of a streamlined recycling infrastructure in this regard [30].

1.3 Environmental Impact of Lithium-ion Extraction

In addition to the logistical and economic facets, the primary extraction of lithium metal introduces an environmental concern as well. The majority of lithium deposits are found in one of two types - brine and hard rock. Brine reserves feature a water basin that is rich in lithium salts. Hard rock or pegmatite reserves are typical mineral ores that are accessed by drilling. For lithium extraction from brines, the brine is pumped into large evaporation ponds and left to evaporate by solar energy and the process could extend to several months. This is followed by a combination of chemical treatment and filtration. Extraction of brines is more prevalent than its counterparts and accounts for the bulk of global supply from South America. On the other hand, extraction from hard rocks is a more cost-intensive process that involves the removal of the ore from the earth and subsequently subjecting it to heat and size reduction operations. The powdered mineral is subjected to chemical reagents, filtered and evaporated to achieve the final form which is usually lithium carbonate [31], [32].

Lithium extraction and processing has been known to cause a host of deleterious effects to the environment, chief of it being the loss of water due to evaporative technology. Estimates indicate that 500,000 gallons of water are lost for every ton of lithium extracted leading to depletion of local water sources [33]. A notable example of the impact of evaporative technology used in lithium mining is the Salar de Atacama mines of Chile that upended the local farming community by consuming 65% of water available in the region [33]. In addition to the environmental impact, lithium mining also inflicts damage on biological systems. Lithium tends to build up overtime in storage ponds and pile tailings which ultimately makes its way to local ecosystems. Lithium causes adverse biophysical effects such as disrupting neurological systems in living organisms as well as changing soil ecology. Additionally, the reagents used for lithium extraction such as hydrochloric acid and sulfuric acid contaminate downstream effluents leading to the disruption of aquatic life by altering water pH [32]. Therefore, primary sources of lithium are not environmentally viable and emphasizes the need for secondary sourcing from recycling to supplement the supply chain.

1.4. Working Principle of Lithium-ion Battery

LIBs are an integral part of portable electronic devices and electric vehicles. The first LIB prototype was developed in 1985 by Akira Yoshino and was followed by commercialization of the technology in the subsequent decade by the Sony and Asahi Kasei corporations [34]. The four key components of a LIB are the cathode, anode, electrolyte and separator. Typical cathode materials include lithium cobalt oxide, lithium manganese oxide, lithium nickel cobalt manganese oxide and lithium iron phosphate. Commonly used materials in anode fabrication are graphitic carbon and lithium titanate and other viable anode materials in the development stage include hard carbon, metallic lithium, silicon-based materials and tin-based alloys. LiPF6-based carbonate electrolytes are commercially employed for LIB production and other viable electrolyte material, mostly in the development stage, include $LiClO_4$, $LiAsF_6$ and $LiCF_3SO_3$ [34]. The working principle of a LIB is illustrated in figure 2a and involves oxidation and reduction reactions occurring at each electrode [50]. Figure 2b depicts the composition of a typical Lithium Cobalt Oxide (LCO) battery [35]. During charging, the Li+ ions de-intercalate from the cathode layer and are transferred to the anode where they intercalate between the anode layers [36]. The reverse process occurs during discharging and the transfer of electrons through the external circuit powers the connected system. The typical half reactions that occur in a LCO battery are shown below:

Cathode: $LiCoO_2 \rightleftharpoons CoO_2 + Li+ + e^-$ (equation 1)

Anode: $C_6 + Li^+ + e^- \rightleftharpoons LiC_6$ (equation 2)

Full Reaction: $LiCoO_2 + C_6 \rightleftharpoons LiC_6 + CoO_2$ (equation 3)

Due to the increasing demand for alternative technologies in line with global efforts to reduce carbon footprint, the production and use of LIB have increased drastically. In order to ensure efficient e-waste management and minimize environmental impact through circular economies, recycling and regeneration of spent LIBs is essential. Prior to implementing these techniques, pretreatment operations must be executed for safe and efficient recycling.

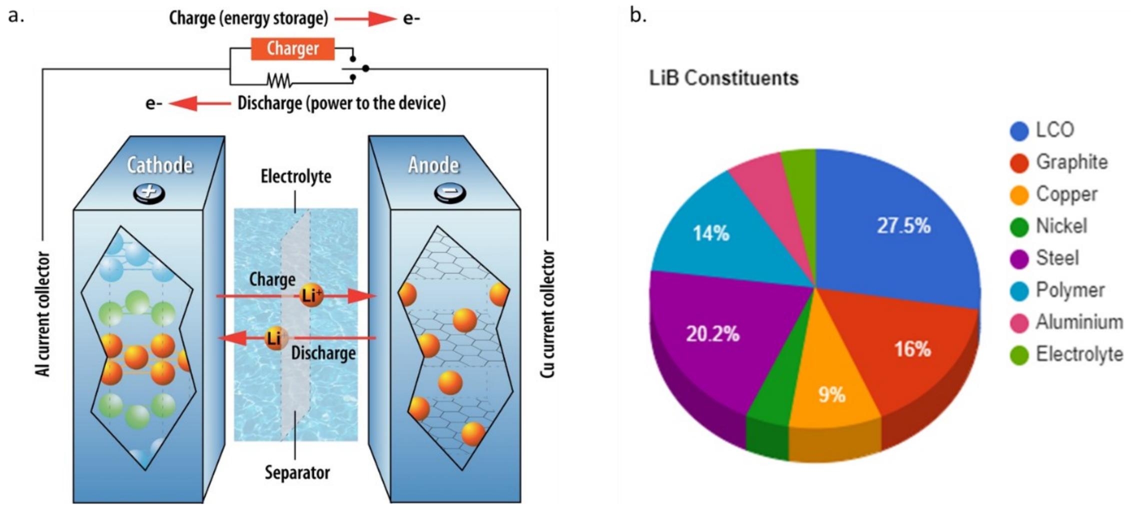

Figure 2: (a) Working Principle of a lithium-ion battery ("How a lithium-ion battery works" © Argonne National Laboratory, CC BY-NC-SA 2.0) (b) Typical Composition of Portable LIB

1.5. Pretreatment

LIB recycling can be conducted by both physical and chemical means. In either case, the spent batteries need to undergo certain pretreatment operations prior to being subjected to recycling techniques. Pretreatment is an indispensable step of the recycling process and aids in improving the recycling efficiency of both these methods while ensuring process safety. The major pretreatment processes are Discharging, Disassembly, Size reduction, Classification, Separation, Dissolution and Thermal treatment [37], [38].

An EOL battery can hold up to 20% of its available energy in reserve [38]. This means that, although these batteries cannot work at peak capacity, a substantial quantity of residual charge remains. Therefore, the risk of explosion during disassembly or size reduction is significant due to the thermal runaway effect [39]. Thus, it is absolutely critical to completely discharge EOL batteries prior to any mechanical separation. The most common method to completely discharge a battery is to use a salt solution with good electric conductivity. The schematic for a typical salt solution discharge is show in figure 3. Numerous studies have shown that NaCl solution is ideally suited for this purpose with the only caveat being a higher degree of corrosion [39], [40]. Alternatively, efficient chemical discharging can also be achieved with $MnSO_4$ and $FeSO_4$ at lower levels of corrosion albeit at a higher cost as they are comparatively more expensive than NaCl. A parameter determining the choice of salt for chemical discharging is the discharging efficiency. Discharging efficiency is described in terms of the Active Discharge Time (ADT) of the system where lower ADT is indicative of higher discharging efficiency [39]. However, high discharge efficiency is often accompanied by negative environmental impact due to the galvanic corrosion of the battery's metallic shells and the leaking of organic material leading to secondary pollution [39]. A study conducted by Song et al. (2015) discovered $MnSO_4$ to be the most environment-friendly option compared to its counterparts, albeit possessing a lower discharge rate [41]. Other discharging techniques include physical discharging and cryogenic freezing. Physical discharging is executed using metal powder; however, it can result in sharp temperature spikes which introduces safety considerations. On the other hand, cryogenic freezing eliminates this safety concern but the technique is expensive due to high equipment and maintenance cost and is not typically preferred in industry [42]. To conclude, the choice of discharging technique needs to strike the ideal balance between efficiency, safety and cost in a manner conducive to the final purpose.

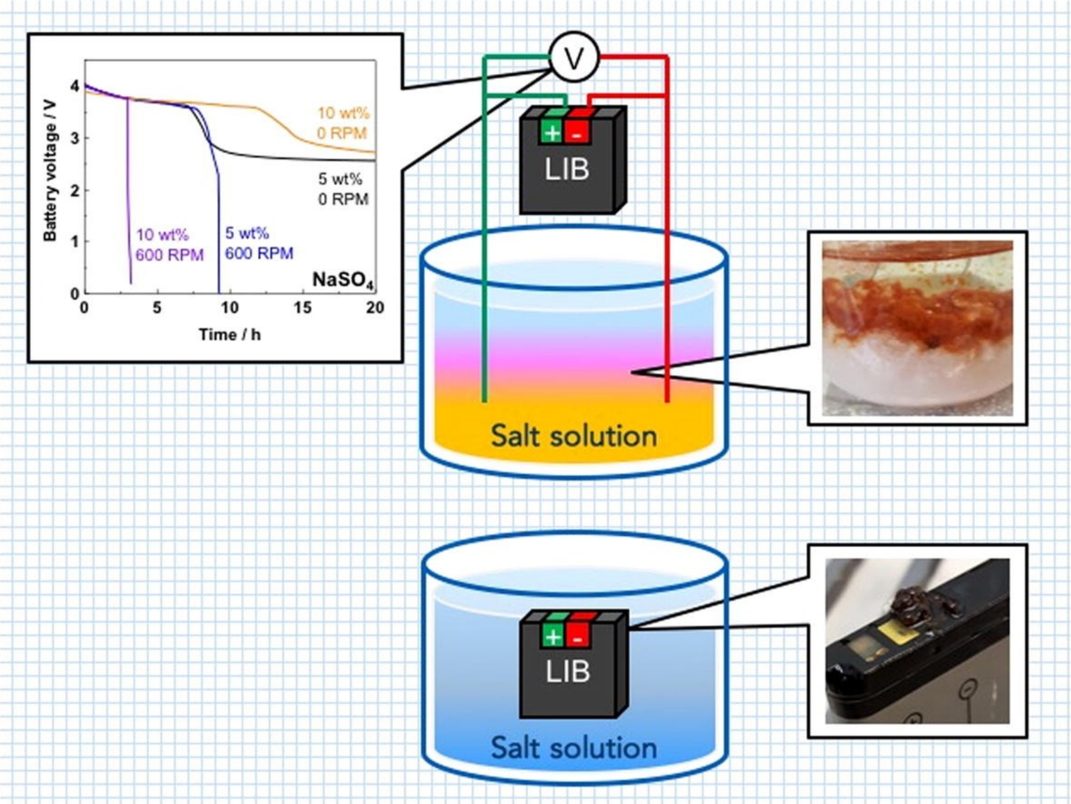

Figure 3: Schematic of salt solution discharge of spent lithium-ion battery. Reprinted from ref. [43]*, copyright 2018 Elsevier*

Following discharging, spent batteries need to be disassembled into its constituents for efficient recycling. Manual dismantling of LIB is possible for laboratory purposes but not feasible on an industrial scale. Moreover, LIB components include toxic materials and prolonged exposure can be harmful. Therefore, crushing is employed in large scale operations for separating spent LIB components [39]. Li et al. (2019) designed an automation line system prototype, shown in figure 4, for the disassembly of EOL lithium-ion pouch cells [44]. The automated system was able to successfully liberate the anode and cathode sheets, separators and polymer-laminated aluminum film housing while preserving the cathode sheet integrity [44]. Another body of work by Schafer et al. proposed a novel re-manufacturable battery module and automated remanufacturing station on the basis of investigations on joints in battery modules[45]. The major hurdle for the proposal was that battery joints were not capable of being non-destructively removed. It can be inferred from the aforementioned research works that battery design needs to be adjusted to facilitate non-destructive dismantling in order to avoid the destructive crushing process and improve recycling efficiency.

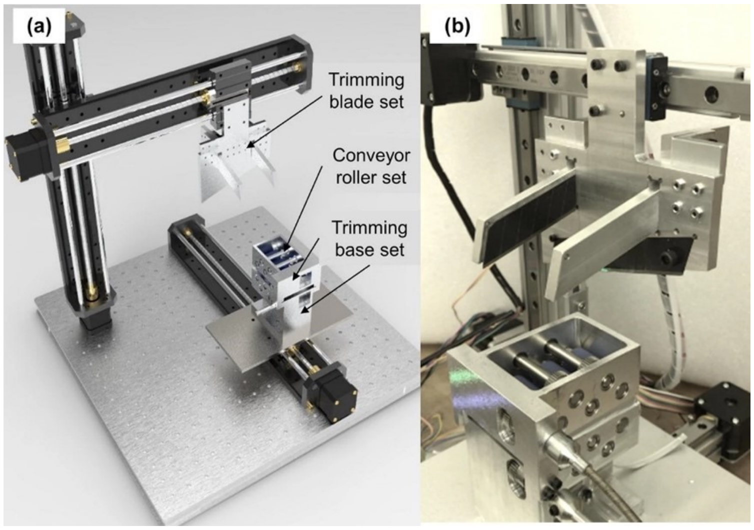

Figure 4: (a) CAD design and (b) prototype of the automated pouch removal module designed by Li et al. Reprinted from Ref. [60], copyright 2019 Springer

The primary purpose of recycling is to liberate the constituent components of LIBs. Size reduction in the form of mechanical crushing or comminution is often the preferred method to achieve the liberation of electrode materials [39]. This step is integral to hydrometallurgical processing. There are many forms of comminution depending on the equipment used but they fall under the two general categories, shredding and milling. Shredding utilizes high torque rotary blades to achieve size reduction typically at low speeds. Milling uses the impact of machines such as hammer mills and shear crushers to comminute spent LIBs [46]. Both types of size reduction are often executed in series to achieve the desired size for liberation. For instance, the Recupyl process uses a two-step crushing process where the first step employs a low-speed rotary mill and followed by a high-speed impact mill for secondary crushing [47]. The multi-step approach optimizes electrode powder recovery. Size reduction operations for LIBs can be carried out in both wet and dry conditions. Water is fed into the crusher inlet during wet crushing operations to form a slurry which is eventually sieved [37]. Zhang et al. (2014) studied both wet and dry recycling methods and concluded that dry crushing offered optimal liberation of electrode material from corresponding copper and aluminum foils without over crushing other battery components [48].

The subsequent step after crushing is to sort the size-reduced materials. Shin et al. (2005) designed a process to recover lithium and cobalt from spent LIB and the classification following crushing was carried out using 106 µm, 200 µm and 850 µm size- sieves [49]. Carbon and lithium cobalt oxide was obtained as undersized products while separators, plastic packaging, steel casing, aluminum and copper foils made up the oversized products. Successive sieving can ensure relatively homogeneous compositions suitable for recovery methods such as acid leaching and solvent extraction [49]. The coarser particles such as the casing, copper and aluminum foils can be separated out from non-metallic components using electrostatic separation due to the conductivity difference. Another separation technique employed by Bi et al. utilized eddy current separation to separate nonferrous metals like aluminum from lithium-iron phosphate batteries and achieved a separation rate of 100% [50]. Another important constituent that requires separation are the electrolytes. Electrolytes are volatile and direct exposure can have detrimental effects on the body. A separation strategy that preserved the organic solvent composition in the electrolyte was introduced by Liu et al. which employed supercritical CO_2 for electrolyte extraction in spent LIB with an extraction yield of 85.07 ± 0.36% [51]. In addition to the high yield and separation efficiency, this method is environment-friendly and requires mild operating conditions.

The pretreatment methods discussed in the previous sections may not be able to completely liberate the active materials in the spent LIBs. This could be due to either agglomeration of active materials following classification and separation or attachment of active materials to current collectors [37]. The phenomenon occurs because of the binders present in spent LIB. Polyvinylidene fluoride (PVDF) is the most commonly used binder in LIBs. The dissolution of these binders is achieved by using appropriate solvents. He et al. (2015) employed N-Methyl-2-pyrrolidone (NMP) for the dissolution of PVDF to liberate the active material from the cathode layer [52]. The liberation was achieved using a combination of dissolution and ultrasound cavitation. A peel-off efficiency of 99% was recorded under conditions of 240 W ultrasonic power and a process temperature of 70 ^{0}C. The ultrasonication was conducted for a duration of 90 minutes [52]. Although the solvent is proven to be highly efficient, NMP is expensive compared to other solvents resulting in Dimethylformamide (DMF) and Dimethylacetamide (DMAC) being considered as alternatives. Zhou et al. conducted dissolution experiments involving all 3 solvents and DMAC demonstrated highest solubility of PVDF at ambient and elevated temperature [53]. NMP demonstrated low solubility of PVDF at temperatures below 50 ^{0}C but was comparable to DMAC at 70 ^{0}C. DMF showed higher solubility than NMP at lower temperatures. All three solvents demonstrated higher solubility at elevated temperatures [53].

Active material and carbon conductive agents are affixed to electrodes using binder materials. These binders can be removed using thermal treatment methods in lieu of or following solvent dissolution. Aerobic roasting is an effective method for removing binders to obtain cathode powders while maintaining its structure and phase [39]. However, aerobic roasting is not an environmentally suitable method and can also result in the loss of organic material present. Lee et al. devised another effective strategy that combines mechanical and thermal treatment to obtain concentrated electrode active materials in powdered form [54]. The first thermal treatment was done at a temperature of 100 - 500 ^{0}C for a duration of 30 minutes followed by size reduction operations. The second treatment is done at the temperature range of 300 - 500 ^{0}C for an hour. Finally, calcination was done at 700 - 900 ^{0}C for another hour. The results indicated complete removal of the binders and carbon present [54]. For recycling organic material in spent LIB, pyrolysis technology involving a tube furnace is more appropriate. Zhang et al. combined pyrolysis and flotation technology and achieved cathode and anode liberation efficiency of 98.23% and 98.89% without changing the phase characteristics of electrode materials [55]. Froth flotation was used to separate the anode and cathode material as they are hydrophobic and hydrophilic respectively. By using pyrolysis technology, the organic components can be recycled using condensation or with the help of an exhaust gas collection system.

1.6. Hydrometallurgy

The composition of LIBs includes heavy metals and organic compounds which are detrimental to the environment and human life. In addition to ecological ramifications, e-waste also leads to the loss of precious metals and other materials found in spent LIB. Therefore, sustainable recovery of these materials will help to mitigate the environmental impact whilst providing the means for continued use of the metals through recycling. The primary recycling techniques for spent LIB can be broadly classified into mechanical, hydrometallurgical and pyrometallurgical methods. Hydro- and pyro-metallurgy are extractive techniques in metallurgy used to obtain various minerals and the methodology for the same is repurposed for metal recovery in spent LIBs. Pyrometallurgy delivers high recovery percentages but the high temperatures involved in its operations could lead to substantial capital investments and secondary pollution. Therefore, a combination of mechanical and hydrometallurgical methods is preferred for the recovery of valuable metals from spent LIB.

Leaching is a common technique employed in both conventional metal extraction and spent battery recycling. Following the completion of pretreatment steps, the active materials are subjected to leaching for recovering the metals present. Leaching can be executed using chemical reagents or reductants and with microorganisms. Reagents used in chemical leaching include organic acids, inorganic acids and alkalis along with reducing agents such as H_2O_2, SO_2, ascorbic acid, ethanol and $NaHSO_3$. Bioleaching is conducted using microorganisms such as bacteria or by utilizing microbial metabolites for indirect leaching.

Inorganic or mineral acids such as H_2SO_4, HNO_3, HCl and H_3PO_4 are commonly employed to recover valuable metals like cobalt, lithium, manganese, and nickel from spent LIB. The composition of a typical LIB in terms of these metals are 5-7% of lithium, 5-20% of cobalt, and 5-10% of nickel [56]. Numerous studies have been conducted to investigate the leaching efficiency and determine the optimal conditions for the mineral acids mentioned above. Zhu et al. investigated the leaching of lithium and cobalt from LIB using sulphuric acid [57]. The researchers were able to leach 96.3% and 87.5% of Co and Li respectively using a mixture of 2 mol/L H_2SO_4 and 2 volume % H_2O_2 (reducing agent) at a temperature of 60 ^{0}C with a residence time of 2 hours. Cobalt was recovered as $CoC_2O_4 \cdot 2H_2O$ by the addition of ammonium oxalate and lithium was precipitated as Li_2CO_3 using sodium carbonate [57]. Chen et al. conducted experiments to determine the optimal conditions for the leaching of active materials in HNO_3 [58]. They were able to achieve near 100% leaching efficiency of Li, Mn, Co, and Ni at conditions of 0.5 mol/L of HNO_3 and ascorbic acid (reducing agent) at a temperature of 85 ^{0}C with a residence time of 10 minutes. Wang et al. (2009) developed a method to recover Co, Mn, Ni and Li using 4M HCl at 80 ^{0}C with a residence time of 1 hour [59]. Under these conditions, the researchers were able to achieve a leaching efficiency of 99%. Pinna et al. attempted to leach $LiCoO_2$ from spent LIBs using H_3PO_4 to recover lithium and cobalt [60]. They achieved optimum dissolution efficiency of 88% and 99% for lithium and cobalt metals respectively at 90 ^{0}C with a residence time of 1 hour at H_3PO_4 and H_2O_2 concentrations of 2% v/v [60]. The optimal conditions for leaching using mineral acid are summarized in Table 1 and their efficiency for leaching Li, Co, Ni and Mn are shown in figure 5.

Table 1: Optimal conditions for mineral acid leaching

No.	Mineral Acid	Reducing Agent	Acid Conc.	Leaching time	T/ ^{o}C	Solid-liquid ratio	Dissolution efficiency	Ref.
1	H_2SO_4	H_2O_2 2% v/v	2 M	2 hours	60	33 g/l	96.3% Co, 87.5% Li	[57]
2	HNO_3	Ascorbic acid 0.5 M	0.5 M	10 minutes	85	20 g/l	Li, Mn, Co, Ni ~100%	[58]
3	HCL	-	4 M	1 hour	80	0.02 g/l	Co, Mn, Ni, Li ~99%	[59]
4	H_3PO_4	H_2O_2 2% v/v	2% v/v	1 Hour	90	8 g/l	Li 88%, Co 99%	[60]

As can be observed from table 1, the dissolution efficiency of inorganic acids is quite high which makes them suitable for large scale operations. In terms of cost economics, the ideal leaching technique should possess lower residence time, higher dissolution efficiency, median temperatures and lower concentration of leachant [61]. However, this contrasts with operational feasibility as dissolution efficiency increases at higher acid concentration, higher temperatures and longer leaching times. Majority of the research conducted in this area focuses on optimizing these parameters. The use of reducing agents to enhance the leaching efficiency of acids have shown the most promise in this regard. Aaltonen et al. investigated the effect of the reducing agents glucose, hydrogen peroxide and ascorbic acid when used alongside sulphuric acid for the reduction of valuable metals on spent LIB cathodes [62]. The addition of reducing agents demonstrated a significant increase in the recovery of lithium, cobalt and nickel. Among the three reducing agents, glucose (12% g/gscraps) demonstrated the highest increase in leaching efficiency followed by hydrogen peroxide (2% v/v) and ascorbic acid (10% g/gscraps). All three were able to achieve near 100% leaching efficiency. It should be noted that increasing the concentrations of the reducing agents above the value listed earlier showed minimal impact on metal recovery [62].

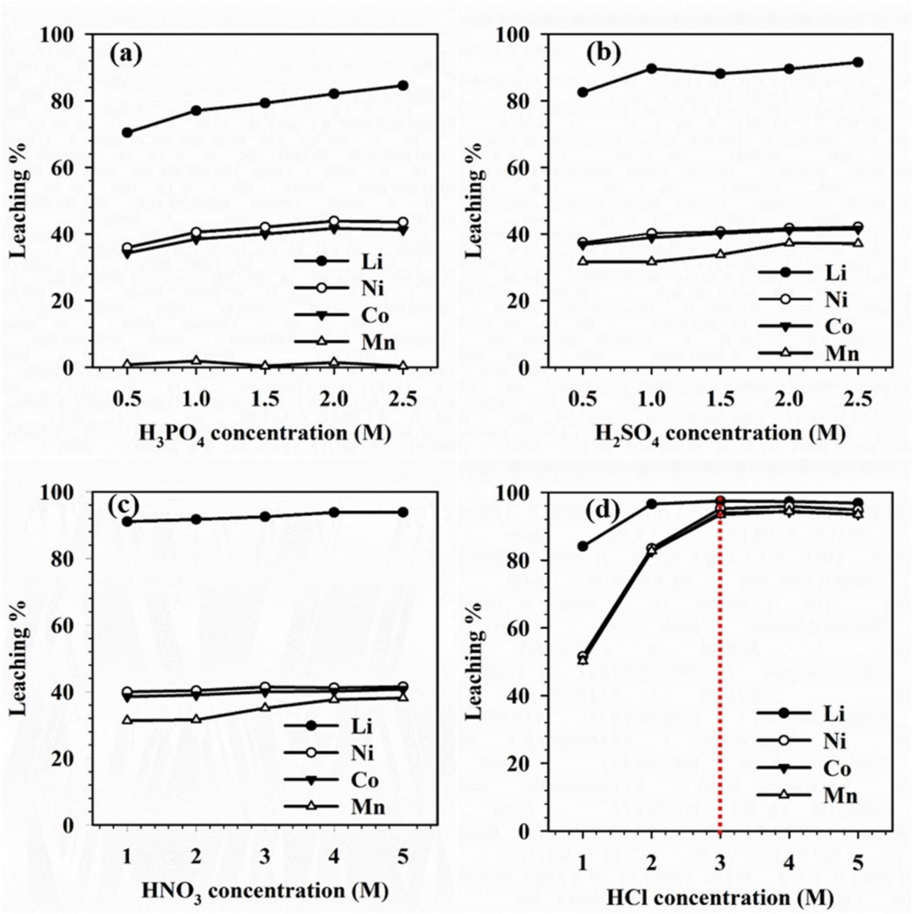

Figure 5: Different inorganic acids of (a) H3PO4 (b) H2SO4 (c) HNO3 (d) HCl on the leaching efficiencies of Li, Ni, Co and Mn from NCM battery cathode materials. Reprinted from ref. [63]*, copyright 2021 Elsevier*

Organic acids are an eco-friendlier option as compared to mineral acids to recover valuable metals in spent LIB. Since they are a natural constituent of biological systems and are produced by microorganisms, their impact on the environment is minimal [64]. Organic acids are biodegradable which mitigates the risk of secondary pollution. Moreover, organic acids do not release toxic gasses like their inorganic counterparts and continuous exposure does not result in any harmful effects to humans [65], [66]. Additionally, organic acids are more stable and they can be easily recycled. Organic acids also offer an economic advantage to industries in terms of handling and storage as they are notably less corrosive [67]. These advantages make organic acids a more appealing choice to mineral acids. However, organic acids are yet to be used in large scale operations as they are still being investigated to understand their potential for scaling up. Golmohammadzadeh et al. performed a review on the utilization of organic acids as leaching agents [66]. They examined and compiled the results of studies regarding leaching performances of organics acids on spent LIBs conducted by various researchers. The results are summarized in table 2. As can be observed, when used in tandem with a reducing agent, some of these organic acids exhibit greater recovery of cobalt and lithium than sulphuric acid and hydrochloric acid. An interesting trend that can be noted is that greater leaching efficiency is shown by organic acids with a higher number of carboxylic groups [66], [68]. Organic acids such as ascorbic acid can also act as reducing agents making a combination of organic acids an efficient method for leaching. Nayaka et al. used a combination of Tartaric and Ascorbic acid to dissolve nearly 100% of Li and Co from spent $LiCoO_2$ [69]. In their studies, it was concluded that the optimal concentration to achieve maximum leaching was 0.4 M tartaric acid and 0.02 M ascorbic acid. Mineral acid concentrations to achieve comparable leaching efficiency ranges from 0.5 M to 2 M as indicated in the earlier section. Therefore, lower concentrations of organic acids achieve the same result which gives them an additional economic advantage over inorganic acids [66], [68], [69].

Table 2: Leaching Performance of Organic Acids on Spent LIB [66]

Leaching agent	**Reducing agent**	**Amount of reducing agent**	**Recovery without reducing agent (%)**		**Recovery with reducing agent (%)**	
			Li	Co	Li	Co
Lactic acid	H_2O_2	0.5 Vol.%	59	34	98	99
Ascorbic acid	Ascorbic acid	1.25M	Not reported	Not reported	98	95
Iminodiacetic acid	H_2O_2	0.02 Vol.%	Not reported	Not reported	99	91
Succinic acid	H_2O_2	4 Vol.%	20	42	100	96
L-Aspartic	H_2O_2	4 Vol.%	1	1	60	60

acid						
DL-Malic acid	H_2O_2	2 Vol.%	54	37	99	93
Citric acid	H_2O_2	1 Vol.%	54	25	99	92
DL-malic acid	H_2O_2	2 Vol.%	Not reported	Not reported	91	84
Citric acid	H_2O_2	1.25 Vol.%	Not reported	Not reported	92	84
Tartaric acid	Ascorbic acid	0.02M	Not reported	Not reported	>95	>95
L-tartaric acid	H_2O_2	4 Vol.%	31	17	99	99
Citric acid	H_2O_2	1 Vol.%	Not reported	~35	Not reported	99
Citric acid	H_2O_2	0.6 g g−1	61	36	99	98
Citric acid	Tea waste	0.4 g g−1	61	36	98	96
Citric acid	Phytolacca Americana	0.4 g g−1	61	36	96	83
Citric acid	H_2O_2	1 Vol.%	54	25	100	90
Citric acid	H_2O_2	1 Vol.%	50	23	98	90
Citric acid	H_2O_2	0.55 Vol.%	Not reported	Not reported	100	96

Citric acid	H_2O_2	3 Vol.%	Not reported	Not reported	100	100
Citric acid	Ascorbic acid	20 mM	Not reported	Not reported	100	80

Bio-metallurgy is a novel addition to conventional hydrometallurgy and utilizes the concepts of biotechnology to recover metals from waste electrical and electronic equipment including LIB. Biometallurgical processes are executed by two methods namely bioleaching and biosorption [70]. Biometallurgy employs acidophilic iron and sulfur oxidizing microorganisms to mimic mining processes involved in metal transformation. As opposed to typical metal leaching practices involving chemicals as lixiviants, bioleaching uses microorganisms or microbial secondary metabolites to facilitate the leaching process [70], [71]. In a study conducted by Boxall et al., biogenic ferric iron and sulfuric acid were used to execute bioleaching for spent LIBs with comparable success [72]. Although batch leaching achieved less than 10% leach yields, researchers were able to obtain higher yields by conducting multi-step leaching. The bioreagents facilitated the yields of 60% Li, 53% Co, 49% Ni, 82% Mn and 74% Cu. Xin et al. (2016) conducted a similar study by utilizing biogenic sulfuric acid and achieved 95% extraction efficiency of Ni, Co, Li and Mn [73]. High rates of metal recovery were achieved by maintaining the pH at 1 by adding exogenous sulfuric acid. Biosorption is another method of biometallurgy that utilizes microbial biomass to concentrate and adsorb valuable metals. It is a nascent technique and its potential in the recycling of WEEE is currently being investigated [70].

From an absolute comparison of bioleaching with traditional leaching methods, it can be concluded that the extraction percentage and recovery rate of valuable metals from LIB by bioleaching is noticeably lower [70]–[73]. Moreover, bioleaching is still in the experimental stage and is yet to achieve industrial-scale commercialization. The major advantage of bioleaching over conventional acid leaching is the cost economics of operation. Mineral acid leaching typically requires temperatures in the range of 60 - 80 ^{0}C. In contrast, bioleaching processes can be successfully carried out in ambient temperature conditions [70], [72]. Moreover, mineral acids such as sulfuric acid required to supplement the bio-leaching process are in the range of 100 mM while inorganic acid leaching using standalone sulfuric acid needs 1.5 - 2 M sulfuric acid [57], [72]. Bioleaching is also an environmentally benign operation with minimal toxic gas emission and effluent release. Therefore, bioleaching possesses the edge over traditional acid leaching in terms of cost economics, environmental friendliness and energy consumption [70], [72].

In the hydrometallurgical methods outlined in the earlier sections, the metals are recovered in leaching solutions or as precipitates. Additional separation and purification steps are required to obtain the metals for reuse. The challenge and ultimate goal of chemical precipitation is to achieve selective separation of constituent metals. Wang et al. employed sodium hydroxide (NaOH) to precipitate Mn, Ni an Co from the leach liquor following acid leaching [59]. Lithium cannot be precipitated using this method as it does not react with hydroxide ions. This is advantageous as it allows for selective removal of the metal. The most common technique is to use sodium carbonate to precipitate lithium as lithium carbonate. The method involves concentrating the leached solution containing lithium following removal of other metals and addition of saturated sodium carbonate solution. The final precipitate is reclaimed through evaporation [74]. Lithium can also be selectively precipitated by following a similar methodology using Na_3PO_4 and NaF [75], [76]. The selective removal of Fe ions is another consideration in hydrometallurgical metal recycling of spent LIB. Pakarinen et al. examined various methodologies for the precipitation of iron from leach liquor and identified that oxidative precipitation SO_2/O_2 gas mixtures was the most appropriate for continuous Fe precipitation in terms of cost economics [77]. Other precipitants such as $KMnO_4$ and $C_4H_8N_2O_2$ can be used to selectively leach Mn and Ni respectively [59].

Despite being able to be carried out in relatively reasonable temperature and pressure conditions, hydrometallurgical recycling methods possess their fair share of disadvantages [78]. Chief among them is the water requirement to execute hydrometallurgical processes. Although exact data for the water consumption for various hydrometallurgical recycling processes is currently not available, similar methods used in the hydrometallurgical extraction of lithium indicate that nearly 500,000 gallons of water are required to recover 1 ton of lithium [32]. Moreover, large amounts of wastewater generated over the course of the process requires complex purification methods prior to safe disposal [78], [79]. The use of mineral acids and other corrosive chemicals further compound the cost of hydrometallurgical methods in terms of transport, storage and maintenance. Further downstream, hydrometallurgical processes produce sizable quantities of leach residue which require additional separation steps [78], [80]. Additionally, the process time for hydrometallurgical recycling is quite large and is not suitable in terms of industrial sustainability in the long term. Another complication of hydrometallurgy is that the various chemicals used in hydrometallurgical recycling methods result in the release of toxic gasses such as oxides of sulfur and nitrogen [80]. Hydrometallurgical processes also tend to release concerning amounts of greenhouse gasses. The same was quantified in a study on various battery recycling methods conducted by Ciez et al. The researchers estimated that hydrometallurgical recycling emitted 7 - 9 kg CO_2/ kg of battery recycled [81]. Hydrometallurgy enables recovery of metals with high levels of purity and the techniques used to execute these processes are well established. However, it can be inferred from the drawbacks discussed above that hydrometallurgical recycling is not an environmentally sustainable process in the long run [80].

1.7. Pyrometallurgy

Recycling methods dominated by pyrometallurgy are robust battery recycling techniques and are currently used in commercial scale. Pyrometallurgy is a straightforward technique capable of accommodating a wide variety of battery feeds and is relatively easy to scale up. The technique employs high temperatures to implement recovery of valuable metals from spent LIB through a combination of physical and chemical transformations [82]. External energy input is required to achieve the elevated temperatures required for pyrometallurgical operations and the process is governed by the processing time, purge gas used, flux addition and the temperature. Thermal pretreatment is employed to prepare the batteries for extractive metallurgy through incineration and pyrolysis. Subsequent extraction steps include roasting or smelting. Roasting involves the heating of the cathode material with carbonaceous reducing agents such as charcoal and coke. The primary advantage of the method is the reduction of lithiated compounds to low valence states which promotes separation in the later stages. Smelting is more suited for high-volume operations to achieve better metal recovery. In this method, spent batteries are directly fed into a furnace and heated at temperatures above the melting point of battery materials. The carbon and aluminum present in the battery act as reducing agents. The pyrometallurgical products are subjected to leaching for metal recovery or directly regenerated to be used in next generation batteries [82], [83].

The conventional technique that is commercially employed for pyrometallurgical recycling of LIB is the Umicore VAL'EAS™ process developed by Belgian company Umicore NV. A combination of pyrometallurgical and hydrometallurgical processes are employed in this method and does not involve any significant pretreatment operations. The absence of complex pretreatment makes the process relatively easier to replicate and expand. The process flowsheet for this method is shown in figure 6a [84]. The main disadvantages of the Umicore process are the high consumption of coke and the loss of lithium ion in the slag [84], [85]. An emerging pyrometallurgical technique that was initially developed for nickel-cadmium battery recycling, the Accurec process designed by the Accurec GmbH® company in Germany is gaining popularity in LIB recycling. This method is usually executed in batches and utilizes a combination of mechanical, pyrometallurgical and hydrometallurgical techniques to aid in metal recovery. The process flow for the Accurec process is shown in figure 6b [84]. Li is precipitated as Li_2CO_3 in the Accurec process with a lithium recovery of 90%. Although the active material chemistry is maintained in this process and it is more in line with the closed-loop recycling concept, the electrolyte, binder, and conductive additives are lost during the course of the process [84].

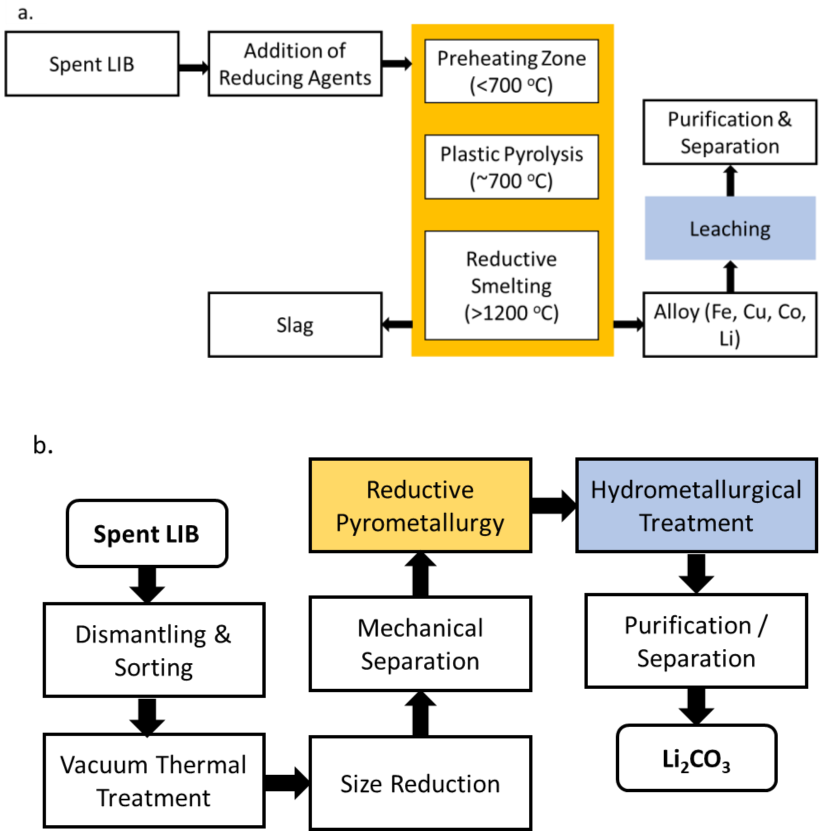

Figure 6: (a) Schematic of Umicore VAL'EAS™ process (b) Process flow of Accurec process

Pyrometallurgical strategy is an established technique and accounts for about 17% of global battery treatment and recycling processes [82]. However, the method is not attuned for environmental sustainability and economic profitability as compared to hydrometallurgical and direct regeneration methods. The high temperature requirement of pyrometallurgy calls for substantial energy consumption and also results in considerable emissions of greenhouse gasses. Moreover, high temperatures come with associated safety concerns while compounding handling and maintenance costs. Pyrometallurgical processes also pose the risk of persistent organic pollutants release such as dioxins and furans. Although pyrometallurgical processes are capable of handling heterogenous feed, the recovery efficiency declines drastically at low volumes. Furthermore, lithium, manganese and aluminum tends to get into the slag following pyrometallurgical treatment and the purification steps tend to get extremely tedious. Due to these drawbacks, direct regeneration and hydrometallurgical-dominant techniques are being preferred over pyrometallurgical dominant ones [79], [85]–[87].

1.8. Direct Regeneration

As established in section 1.6, hydrometallurgical processes are highly efficient in terms of metal recovery percentages and operating conditions but possess high maintenance, handling and environmental costs. Direct recycling is a novel strategy that has been adopted recently to mitigate the disadvantages posed by hydrometallurgical methods. The method directly addresses the reasons for capacity fade in LIBs and seeks to directly regenerate them for extended use. The three main reasons behind capacity fade in LIBs are the formation of solid electrolyte interface (SEI), loss of active lithium to side reactions or lithium ions becoming trapped in electrolytes and the deposition of cyclable lithium ions in the anode [88]. Traditional recycling methods such as hydrometallurgy and pyrometallurgy utilizes chemicals or higher temperatures to break the bonds in the active cathode material and subsequently regenerate them which requires high energy inputs. Direct recycling adopts a more straightforward and non-destructive approach to regenerate the cathode active material by healing or reversing the effects mentioned above that arise during battery operation. Due to the nature of the process, direct recycling is more economically viable and leaves minimal environmental impact as compared to its counterparts [89]. Some of the recent research and innovations in this domain are discussed below.

Xu et al. devised a novel strategy, schematic shown in figure 7a, for direct recycling of spent LIB through targeted healing [90]. The strategy involved a combination of aqueous solution relithiation and rapid post-annealing. Commercial lithium iron phosphate (LFP) cells were used in the study and the relithiation was achieved with the help of 0.2 M LiOH and 0.08 M citric acid solutions. Following relithiation, the LFP powders were mixed with excess Li2CO3 and subjected to thermal annealing. The electrochemical performance of relithiated LFP demonstrated an initial capacity of 159 mAh/g while pristine LFP (reference) demonstrated a capacity of 161 mAh/g at 0.5 C. This method was able to achieve a near complete recovery of the electrochemical performance of pristine LFP at low energy consumption and GHG emissions [90]. Zhang et al. developed an effective electrochemical method for the relithiation of spent Lithium cobalt oxide (LCO) cathode materials [91]. This direct regeneration strategy, depicted in figure 7b, utilized an electrochemical device with an anode plate made of platinum and waste Li_xCoO_2 from cycled LCO as the cathode immersed in a Li_2SO_4 solution. Li+ insertion was achieved by the application of a constant cathodic current followed by annealing to restore the crystal structure. By utilizing the electrochemical regeneration technique, the researchers were able to achieve a charge capacity of 136 mAh g^{-1} which is comparable to a commercial LCO electrode charge capacity of 140 mAh g^{-1} [91].

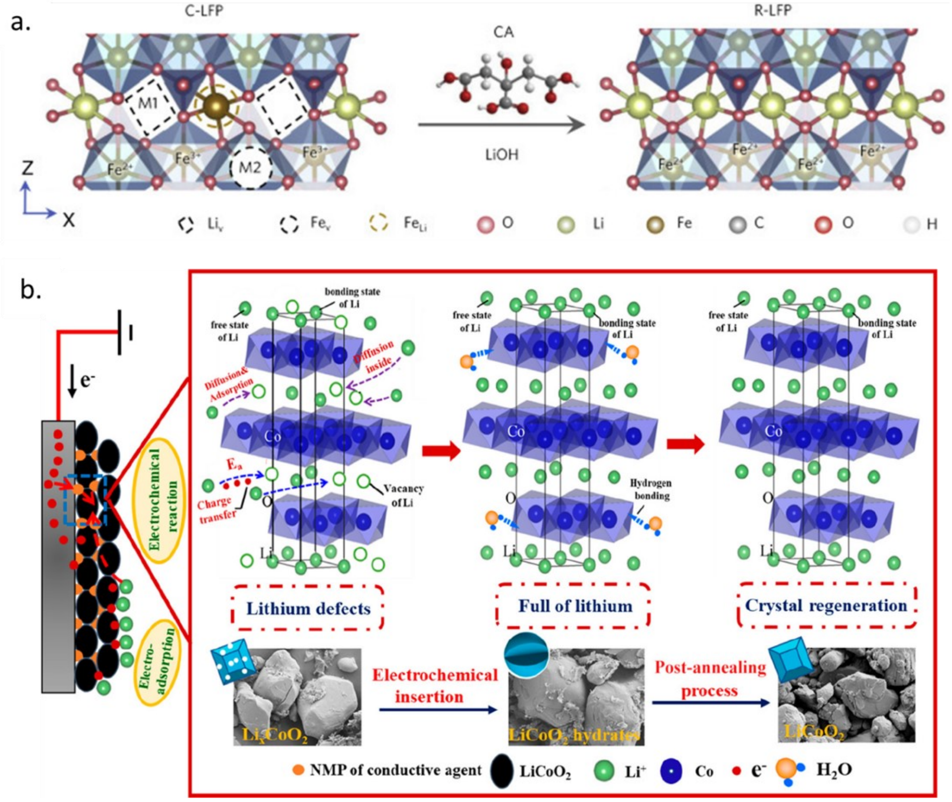

Figure 7: (a) Schematic representation of the solution relithiation process employed by Xu et al. reprinted from ref. [90], *copyright 2020 Joule (b) Schematic of the direct regeneration mechanism for electrochemical insertion of Li+ ions into spent LixCoO2 electrode employed by Zhang et al. Reprinted from ref.* [91], *copyright 2020 ACS.*

One of the main advantages of direct regeneration methods is that it bypasses the multiple complex steps involved in traditional recycling methods. This paves the way for process simplicity which is a critical parameter for scaling up operations from lab to industrial scale. The work conducted by Gao et al. is an ideal representation of this advantage [92]. The researchers designed a one-step hydrothermal relithiation method to successfully replenish the loss of active lithium in the cathode. The method utilized LiOH to relithiate spent LMO cathodes using an autoclave at a temperature of 180 ^{0}C. The method was able to restore the electrochemical properties of the regenerated LMO to that of the pristine ones. The authors also performed a life cycle analysis and were able to confirm the economic and environmental viability of the process in keeping with the closed-loop recycling concept. The only caveat of this process is that the relithiation time extended to around 6 - 12 hours [92]. Wu et al. adopted a similar relithiation strategy but replaced the relithiation agent with polycyclic aryl−lithium compounds [93]. The researchers were able to achieve 100% relithiation ratios in the order of minutes. The major drawback of using organolithium compounds like polycyclic aryl−lithium is that they can lead to overlithiation and consequent structural damage due to irreversible crystal collapse [82], [93]. The schematic of a typical direct relithiation technique is shown in figure 8.

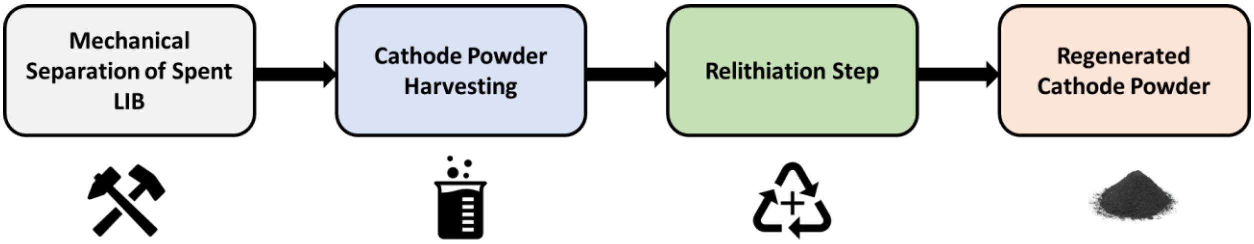

Figure 8: Process flow of direct relithiation method

Eutectic molten salt mixtures have been explored recently in place of lithium-based solutions to directly regenerate spent LIB cathode material. Eutectic molten salt mixture is a homogeneous system made of multiple salts whose melting point is lower than that of its constituents at normal pressure conditions [94]. Shi et al. employed eutectic solutions for the direct relithiation of spent $Li_xNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ ($0<x<1$) (LNCMO) at ambient pressure conditions [95]. $LiNO_3$ and LiOH at a molar ratio of 3:2 was used to make the salt mixture. Degraded LNCMO was added to the salt mixture and heated at 300 ^{0}C to achieve relithition. The strategy was able to restore the cycling stability, rate capability and Li storage capacity of the degraded cathodes to original levels via the molten salt approach by achieving their original composition and crystal structure at ambient pressure and relatively low temperatures conditions [95]. The results for capacity restoration using eutectic molten salt lithiation strategy is shown in figure 9. Qin et al. adopted a ternary molten salt method to achieve efficient regeneration of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode in spent LIB [96]. The hybrid ternary molten salt was made using $LiNO_3$, $LiOH \cdot H_2O$, and $CH_3COOLi \cdot 2H_2O$ (LNO, LOH, CCL) at a molar ratio of 9:6:10. The ternary approach offered lower eutectic points, lower density and larger volume which promotes the chemical reaction and reduces the amount of salt for the regeneration process. The method was able to restore the electrochemical performance of the degraded cathodes to that of fresh materials [96]. The molten salt approach is facile, efficient and environment friendly. The major drawback of this technique is that excess Li salts are required to implement it leading to wastage of the metal [79], [95]–[97]. Despite this disadvantage, eutectic salt mixtures show immense potential for direct regeneration applications.

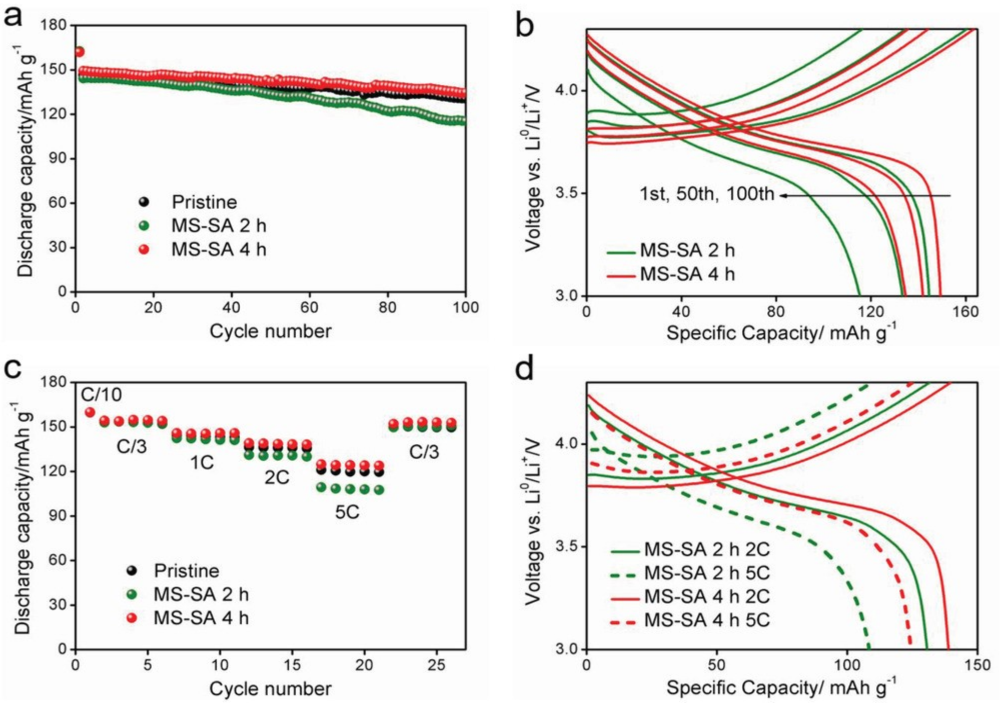

Figure 9: Electrochemical performance of directly regenerated LIB cathodes using eutectic molten salt (MS) solutions. (a) Cycling performance of pristine (reference) and regenerated cathode (MS-SA) (b) Charge-discharge profiles of regenerated cathodes subjected to Molten Salt solution relithiation for 2 (MS-SA 2h) and 4 (MS-SA 4h) hours (c) Rate performance of pristine and regenerated cathodes (d) Charge-discharge profiles of regenerated cathodes at various C-rates. Reprinted from ref.[95]*, copyright 2019 Wiley.*

1.9. Comparison of Hydrometallurgy, Pyrometallurgy and Direct Regeneration Techniques

Hydrometallurgical, pyrometallurgical and direct regeneration methods have been extensively explored to promote the recycling of spent LIB and avoid the issues with e-waste accumulation and contamination. Each of these methods have their fair share of pros and cons and the most suitable method is typically determined by feed size, composition and volume of operations. The long-term feasibility of a process is determined by its environmental impact, efficiency, capital expenditure and profitability [6], [98]. In terms of recycling, the aforementioned considerations are expressed in terms of the recycling method's ability to be part of the circular economy concept [84].

Xu et al. performed a life cycle analysis of the direct recycling method described in section 9 with reference to existing hydrometallurgical and pyrometallurgical techniques. The analysis was done using the EverBatt Model [90], [99]. Most of the energy input in pyrometallurgical techniques, almost 55 %, is focused on the maintenance of high temperatures during smelting. On the other hand, almost 88% of the energy required for hydrometallurgical techniques is consumed in the production of chemicals required to implement the process. So, hydrometallurgical and pyrometallurgical methods require 30.6 and 18.4 MJ per kilogram of LFP cells respectively. In contrast, the direct recycling technique developed by Xu et al. used only 3.5 MJ to recycle 1 kilogram of LFP cells. In terms of GHG emissions, the direct regeneration method released less than 28% of greenhouse gasses compared to the other two methods. Direct recycling also had a lower cost and was able to generate a profit of $ 1.04 per kilogram of spent LIB that was recycled [90]. The summary of their energy consumption, gas emission, and economic analysis is shown in figure 10.

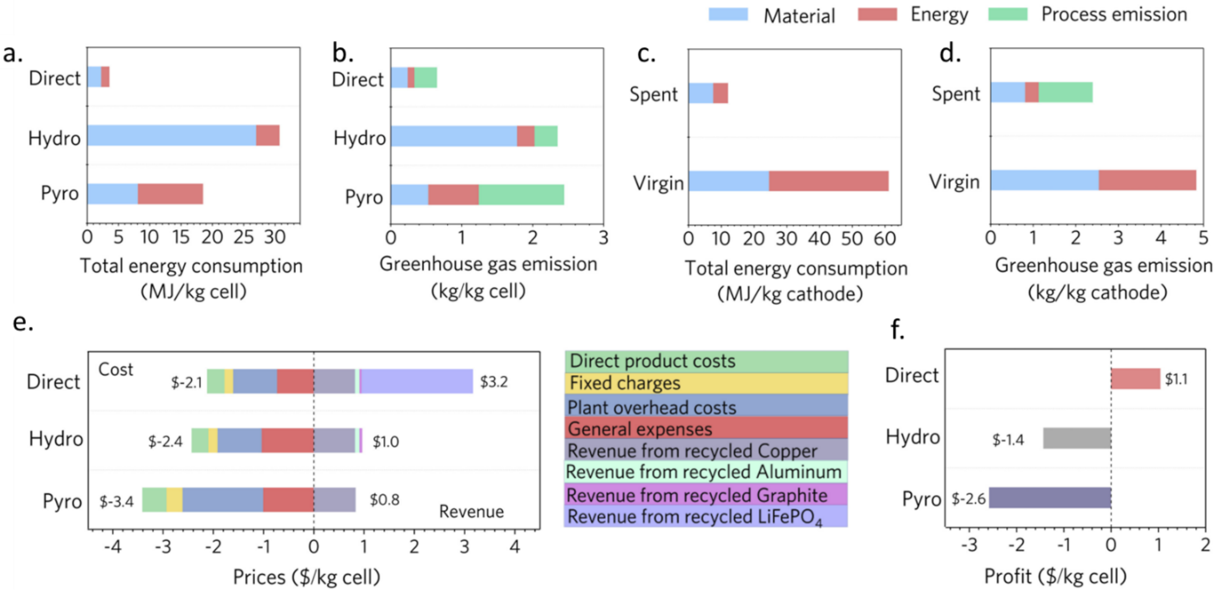

Figure 10: Summary of Economic and Environment analysis of the three recycling methods performed by Xu et al. (a) Total energy consumption per kg of spent cell of recycling. (b) GHG emissions per kg released during recycling. (c) Total energy consumption of manufacturing 1 kg cathode from virgin and recycled materials. (d) GHG emissions of manufacturing 1 kg cathode from virgin and recycled materials. (e) Cost and revenue per kg of spent LFP batteries recycled by pyrometallurgical, hydrometallurgical, and direct recycling. Cost: $ -3.4 (Pyro); $ -2.4 (Hydro); $ -2.1 (Direct). Revenue: $ 0.8 (Pyro); $ 1.0 (Hydro); $ 3.2 (Direct). (f) Profit of recycling 1 kg of spent LFP batteries with pyrometallurgical, hydrometallurgical, and direct technology, respectively. Profit: $ -2.6 (Pyro); $ -1.4 (Hydro); $ -1.1 (Direct). Reprinted from ref. [90], *copyright 2020 Joule.*

Gao et al. performed a similar life cycle analysis on the one-step hydrothermal relithitiation technique discussed in previous sections and compared it to existing hydrometallurgical and pyrometallurgical methods [92]. The researchers used the EverBatt model to perform the analysis on the basis of GHG emissions, energy consumption, operation cost and net profit [99]. As per their estimates, 18.5 MJ per kilogram are required for pyrometallurgical methods and 30.7 for hydrometallurgical methods. These values are similar to the results obtained in the life cycle analysis conducted by Xu et al. [90]. In contrast, the direct recycling process developed by Gao et al. required only a paltry 4.1 MJ per kilogram of spent batteries. In terms of GHG emissions, this direct recycling method releases just 20% of traditional hydrometallurgical and pyrometallurgical methods. The cost of recycling per kilogram of spent batteries was estimated to be \$2.43 for pyrometallurgy, \$1.3 for hydrometallurgy and \$0.94 for the direct recycling method discussed. The direct recycling strategy also generated the highest profit amongst three methods as well [92].

From the drawbacks mentioned in earlier sections and the life cycle analysis discussed here, it can be inferred that direct recycling offers a significant advantage over conventional pyrometallurgical and hydrometallurgical methods in terms of cost, profitability and environmental impact. However, direct regeneration is a relatively new technique and is yet to be implemented on an industrial scale. Hydrometallurgical and pyrometallurgical methods dominate commercial LIB recycling and a survey of 11 recyclers was conducted by Boyden et al. to understand the environmental impact and effectiveness of each method [35]. For the study, the researchers estimated the typical composition of a portable LIB. Among the 11 recyclers surveyed, pyrometallurgical methods were able to recover 5 of the materials in a typical LIB while hydrometallurgical methods or a combination of the two recovered 6 of these materials. The recycling efficiencies of the methods utilized by the companies, excluding carbon, were estimated and summarized in table 3. It can be observed that hydrometallurgical methods or a combination of the two methods demonstrated the highest efficiencies. The researchers also examined the environmental impact of hydrometallurgical and pyrometallurgical methods in terms of global warming potential (GWP) over a 100-year timeframe, terrestrial ecotoxicity potential (TETP) and human toxicity potential (HTP). The results are summarized in table 4. The results of the chosen sample size of 11 companies indicate that the environmental impact of both methods is of approximately the same order, however, the impact of transportation and electricity generation is heavily dependent on location and the results could vary significantly by company [35].

Table 3: Calculated recycling efficiencies of companies employing Hydrometallurgical and Pyrometallurgical methods [35]

Company	**Location**	**Method**	**Estimated Efficiency**
1	Europe	Pyrometallurgical	55.6%

2	Europe	Pyrometallurgical	31.1%
3	Asia	Hydrometallurgical	65.3%
4	North America	Hydrometallurgical	57.5 %
5	Asia	Hydrometallurgical	55.6%
6	Europe	Combination	50.1%
7	Europe	Combination	69.6%

Table 4: Life Cycle Assessment Summary of Hydrometallurgical and Pyrometallurgical Methods

Process	**GWP 100 (kg CO_2 eq)**	**HTP (kg DCB-eq)**	**TETP (kg DCB-eq)**
Pyrometallurgy	$1.63e^{-11}$	$1.37e^{-12}$	$8.61e^{-14}$
Hydrometallurgy	$3.16e^{-11}$	$9.95e^{-13}$	$7.35e^{-13}$

**DCB - Dichlorobenzene*

1.10. Conclusions and Perspectives

The transition to renewable energy, electrified road transport and the proliferation of portable electronics contribute towards the exponential rise in demand for LIBs. Due to the environmental and ethical concerns surrounding mining of valuable metals essential for the manufacturing of LIBs, an alternative approach is required to ensure the continuous supply of raw materials for battery production. Additionally, the accumulation of Waste from Electrical and Electronic Equipment, of which LIB is a major constituent, raises environmental and safety concerns, thereby, highlighting the need for safe waste management. A closed-loop recycling system conducive to the creation of circular economies is being extensively explored to overcome the challenges posed by the explosive growth in the LIB industry. A collaborative effort by battery manufacturers and recyclers coupled with policy regulations for spent LIB sourcing is required to implement a sturdy circular economy capable of promoting green and sustainable development.

The present study comprises four distinct projects with the overarching goal of facilitating the realization of a circular economy for LIBs. The first project pertains to the pretreatment of LIBs using salt solutions to enable complete discharge of the battery to ensure safe disassembly. The first project aims to optimize the pretreatment of spent batteries by utilizing alternative salt solutions that not only enable complete battery discharge for safe disassembly but also mitigate the drawbacks of Sodium Chloride solutions, the most commonly employed solution for battery discharge, such as chlorine gas generation and high corrosion. This project is further complemented by a bow-tie analysis to provide a risk management framework to ameliorate hazards associated with thermal runaway during pretreatment operations in industrial recycling by focusing on novel techniques for preventive and recovery controls. The second project deals with recovery and regeneration of active materials in the electrodes of spent LIBs by adopting a green approach. For the cathode, a combination of organic acids along with hydrogen peroxide as a reducing agent is employed to achieve near perfect recovery of lithium from spent NCM 622 cathode materials. The methodology devised provides comparable lithium reclamation to that of mineral acids while circumventing the disadvantages associated with the usage of inorganic acids such as high corrosion, high handling and transportation costs and release of toxic gases. Additionally, the reducing agent, H_2O_2, used enhances the leaching rate while being environmentally benign as it decomposes into water and oxygen. The second part of this project involves recovering and purifying spent graphite in the anode of an LIB by replacing the conventional sulfuric acid curing-leaching strategy with a more eco-friendly methodology. In the devised methodology, sulphuric acid is replaced with citric acid and the final graphitization at 1200 – 1400 ^{0}C is replaced with a calcination step at 900 ^{0}C to improve the interlayer spacing of the graphite to allow for better intercalation and de-intercalation of lithium when used for practical applications. The devised methodology makes the purifying process less energy intensive and more cost effective. Additionally, the structural defects in the purified graphite are repaired using carbon-tailoring while enhancing its electrochemical performance in the process. The final project deals with an examination of circular economies for lithium-ion batteries while pinpointing the challenges hindering the establishment of a robust circular economy.

Chapter 2. Recycling of Spent Lithium-ion Battery

2.1. Pretreatment for Safe Disassembly of Lithium-ion Batteries

2.1.1. Introduction

As mentioned in earlier sections, a spent battery can hold up to 20% of its energy in reserve [38]. Therefore, the probability of explosion due to thermal runaway during the disassembly and dismantling of spent LIBs is substantial. The high energy and power density of LIBs can lead to the rapid and uncontrolled release of stored electrical energy in the event of physical damage. This release of energy causes exothermic chemical reactions due to the presence of free lithium ions, a phenomenon known as thermal runaway. In order to avoid thermal runaway and ensure the safe dismantling of spent LIBs, the batteries should be discharged to a voltage below 2 V [100]. There are numerous methods to discharge LIBs safely and effectively. Discharging by immersion in a salt solution is the strategy that is widely used in a laboratory setup as it provides the fastest means of discharge. Placing a LIB in a salt solution can cause the lithium ions to move from the anode to the cathode through the electrolyte, generating an electrical current and discharging the battery. This technique is referred to as "electrolyte gating" and is considered to be a straightforward and inexpensive method for discharging LIBs [101]. Additionally, the salt solution may also inhibit the development of dendrites, which are thin protrusions that can develop on the surface of lithium metal electrodes and may cause short circuits, thermal runaway, and fire hazards. Prior to dismantling for all experiments discussed subsequently, salt solution discharge was employed. 3 wt% of salt solution was employed to discharge the battery [102]. The cycled commercial Samsung 26F ICR18650 was completely immersed in the salt solution and left overnight in a fume hood. Sodium chloride was typically used for discharge. Other salts, not widely investigated, were investigated in comparison to NaCl to identify the most efficient choice in terms of discharge efficiency and price.

2.1.2. Salt Solution Discharge

NaCl is typically used for performing salt solution discharge. However, it poses issues such as high degree of corrosion [43]. NaOH, K_2SO_4, Na_3PO_4 and CH_3COONa were trialed as alternatives for NaCl. The salts were chosen on the basis of availability and due to the lack of comprehensive investigations employing these salts. Initially, 3 wt% of NaCl was prepared and the commercial LIB cylindrical cell was immersed in it overnight and left in a fume hood. The change in mass following immersion and the degree of corrosion were observed. The battery was then dismantled and the amount of heat released during that time was given a temperature rating of 5 on a scale of 1 to 10. A similar procedure was followed for other salt solutions and a temperature rating was assigned to it with NaCl solution was used as reference. The results are summarized in table 5. Additionally, the change in voltage was measured at 6 hour and 12-hour intervals using a multimeter to gauge the discharge efficiency of each salt solution.

Table 5: Summary of salt solution discharge observations

Salt	**Before Discharge**	**After Discharge**	**Change in Mass**	**Temp. Rating**	**Cost/kg (aprox.)**	**Remarks**	**Initial Voltage**	**Voltage after 6 Hours**	**Voltage after 12 Hours**
NaCl	46.4 g	45.9 g	0.5 g	5	$5	Visible Corrosion	3.9	3.2	2.7
NaOH	46.9 g	46.8 g	0.2 g	6	$10	No visible corrosion	3.9	3	2.5
K_2SO_4	46.6 g	46.5 g	0.1 g	2	$154	Minimal Corrosion	3.8	3.5	3.1
Na_3PO_4	45.6	45.3	0.3 g	5	$156	Visible Corrosion	3.9	3.1	2.4
CH_3COONa	45.6	45.5	0.1g	6	$160	No Visible Corrosion	3.8	3.5	3.2

From the table, it can be surmised that K_2SO_4 shows minimal visible corrosion and shows the lowest change in mass following immersion. However, the salt is comparatively expensive and has lower discharge rates. On the other hand, Na_3PO_4 demonstrated the best discharge efficiency although the degree of corrosion and change in mass was substantial. Additionally, it is not an economic alternative. NaOH solution optimized all parameters and demonstrated ideal balance between cost, degree of corrosion and discharge efficiency and was, therefore, selected for all subsequent pretreatment steps for experimental studies.

2.1.3. Bowtie Analysis

Bowtie analysis is a risk management technique that uses a visual representation to identify and analyze potential hazards and the measures put in place to prevent them. The bowtie diagram is comprised of two key components - the threat, which refers to the source of danger, and the control, which refers to the safeguard put in place to mitigate the risk. This approach is widely used across various industries, particularly the oil and gas sector, for the assessment and management of risks in complex systems [103]. By providing a comprehensive and structured approach to risk analysis, bowtie analysis plays a crucial role in enhancing the safety and security of critical infrastructure. A risk that is always present during the disassembly of spent LIBs prior to pretreatment is thermal runaway. Thermal runaway refers to a process in which a rise in temperature sets off a chain of further temperature increases, leading to uncontrolled heating. This can happen in various systems, including batteries, chemical reactions, and electrical equipment. When it comes to batteries, thermal runaway can be initiated by internal or external factors, such as a short circuit or overheating. The sudden increase in temperature can cause the release of hazardous or flammable substances, potentially leading to fire or explosion[100], [102]. To ensure the safe operation of systems and avoid potential dangers to individuals and the environment, it is critical to prevent or manage thermal runaway effectively. Thermal runaway in spent lithium-ion batteries (LIBs) during recycling operations refers to a situation where the internal temperature of the battery increases rapidly and uncontrollably. This phenomenon is often caused by internal short circuits, which can occur as a result of damage to the battery during handling or processing. Due to their high energy density and the presence of flammable electrolytes, LIBs are particularly vulnerable to thermal runaway incidents [104].

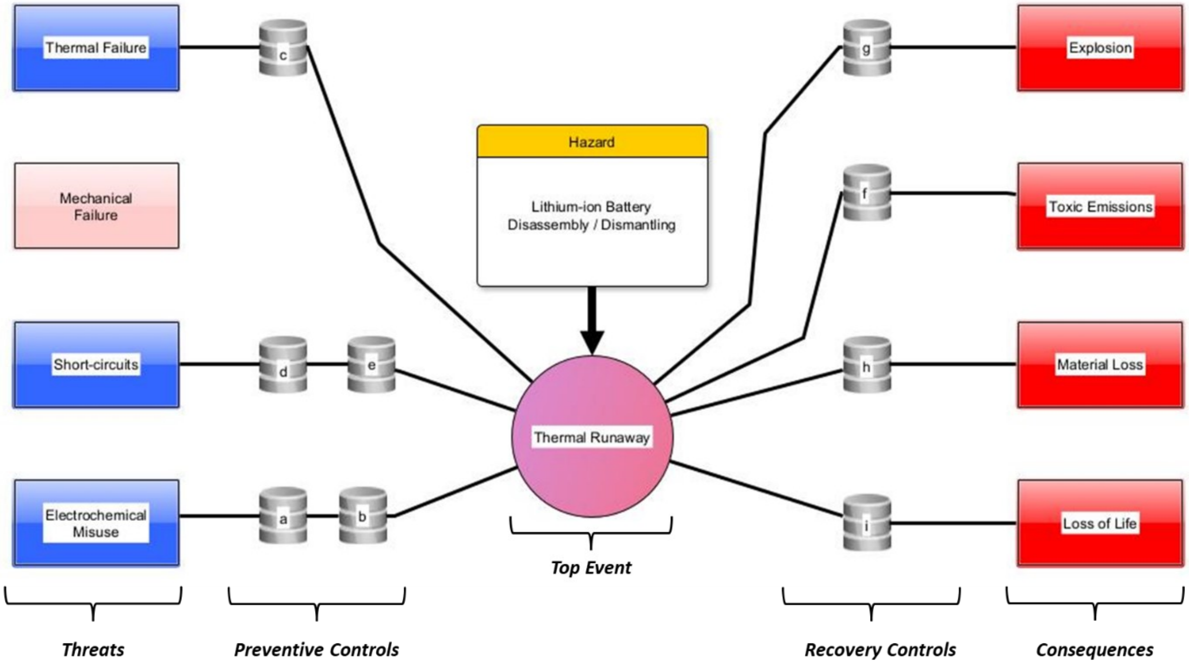

Figure 11: Bow-tie analysis schematic

During the disassembly or dismantling process of spent lithium-ion batteries (LIBs) for recycling, several factors can contribute to thermal runaway, including thermal failure, mechanical failure, short-circuits, and electrochemical misuse [105].

1. Thermal failure: The process of breaking down used lithium-ion batteries can produce heat that increases the internal temperature of the batteries. If the temperature rises above the maximum safe limit, it can result in thermal failure, which can cause thermal runaway.
2. Mechanical failure: The spent lithium-ion batteries being recycled can experience physical stress during the disassembly and dismantling process, for example, from being dropped, punctured, or subjected to high force. This can cause mechanical failure and damage the internal structure of the battery, potentially leading to short-circuits and subsequent thermal runaway.
3. Short-circuits: During the process of dismantling spent lithium-ion batteries, internal short circuits can occur. These short circuits can stem from either physical damage resulting from the dismantling process, or from preexisting faults in the manufacturing or battery management system. The large amount of current generated from the short circuits can

cause a quick increase in the internal temperature of the batteries, leading to thermal runaway.

4. Electrochemical misuse: Before being processed for recycling, spent lithium-ion batteries (LIBs) may have undergone electrochemical misuse, such as overcharging, deep discharging, or exposure to high temperatures. These actions can create instability within the batteries and trigger thermal runaway during the disassembly stage.

The present bowtie analysis is focused on exploring the recent advancements in research to identify effective preventive and recovery controls for the identified threats and consequences. The bowtie is summarized in figure 11 and the legend is shown in table 6. It should be noted that preventive controls for mechanical failure is not feasible owing to the nature of the dismantling operation.

Table 6: Bow-tie legend

	Preventive Controls	**Description**		**Recovery Controls**	**Description**
a.	Cryogenic Cooling *(electrochemical misuse)*	Solidifies electrolyte and reduces reactivity of metallic lithium	f.	Ventilation/Purge Units *(toxic emissions)*	Units to vent off toxic gases released and sensor-assisted purge units involving flame retardants
b.	Electrolyte extraction *(electrochemical misuse)*	Use supercritical CO_2 to recover electrolyte. Benefit of explosion prevention and avoiding toxic emissions	g.	Inert gas reduction *(explosion)*	Suppression gas to inhibit combustion and explosion and reduce explosion intensity

c.	Unroll/Dismantle under water *(thermal failure)*	Avoids contact with air. Heat of reaction results in dissolution of the binder and prevents fluorine emission	h.	High intensity Ultrasonication *(Material Loss)*	Cavitation at the electrode interface enables rapid and selective breaking of the adhesive bond, enabling efficient electrode delamination
d.	Solution discharge *(short circuits)*	Electrochemical discharging of batteries using salt solutions	i.	Sensor monitoring and alarm systems *(loss of life)*	Timely warning systems and robust evacuation protocols along with automated purging
e.	Electrical discharge *(short circuits)*	Remove residual charges by discharging using conductive Loads			

The first strategy suggested to prevent thermal runaway owing to electrochemical misuse is cryogenic cooling. Recent studies subjected LIBs to cryogenic grinding under nitrogen atmosphere to prevent thermal runaway. The method employed by the researchers allows for facile implementation and easy separation of constituents in subsequent recycling steps. By cooling the battery to cryogenic temperatures, the internal reaction rates within the battery slow down, reducing the risk of thermal runaway. Additionally, size reducing a LIB under nitrogen atmosphere can also prevent thermal runaway, as nitrogen is an inert gas that does not react with the battery components. The primary disadvantage of this process is that it is expensive and, consequently, difficult to scale up [106]. The second strategy used in this regard is the removal of electrolytes by supercritical CO_2 extraction. Supercritical CO_2 extraction is a process in which carbon dioxide is brought to a state of supercriticality (i.e., between a gas and a liquid) to extract a target substance. The risk of thermal runaway due to electrochemical misuse is reduced because the removal of electrolytes eliminates one of the key components that can lead to thermal runaway [51], [107], [108].

In order to mitigate the threat of thermal failure, the precise separation method introduced by Zhao et al. is suggested [109]. The method separates the components in water, which helps to avoid uncontrolled reactions from the anode and burning of the electrolyte. This results in minimized material cross-contamination and reduces the need for excessive energy and chemical consumption. The effective limitation of uncontrolled reactions and electrolyte burning through this precise separation technique helps to prevent thermal failure and the risk of thermal runaway during the disassembly of LIBs for recycling [109]. Solution discharge and electrical discharge are used to prevent short-circuits from causing thermal runaway. Solution discharge involves discharging the spent lithium-ion batteries using a conductive solution, such as a salt solution discussed in the previous section. Electric discharge involves applying a controlled electrical discharge to the spent lithium-ion batteries. By applying a controlled electrical discharge, the voltage across the battery is gradually reduced, reducing the risk of current concentration and hot spots that can cause thermal runaway. The discharge current also helps to dissipate any residual heat in the battery, further reducing the risk of thermal runaway [110], [111].

Recovery controls are measures that are implemented to prevent or mitigate the consequences of an undesired event in a bowtie analysis. The consequences part of the right side of a bowtie analysis lists the potential negative outcomes that may occur if the undesired event is not prevented or mitigated by the recovery controls. The most probable consequences of a thermal runaway event in this regard are Explosion, Toxic Emission, Material Loss and Loss of Life. Ventilation purge units and sensor-assisted purge units involving flame retardants can be used as recovery controls during the toxic gas emission. Inert gas reduction is another recovery control that can be used in case of an explosion caused by thermal runaway. The utilization of an inert gas, such as nitrogen, to substitute or displace the atmospheric air in an enclosed area constitutes the process of inert gas reduction. This method aims to establish a low-oxygen concentration environment, thereby decreasing the likelihood of combustion and explosion [104], [110], [112]–[114]. An economic consequence of thermal runaway is the loss of materials. Lei et al. devised a high-intensity ultrasonication method which uses high-intensity ultrasonic waves to effectively disintegrate the batteries, thereby reducing the potential for material loss caused by thermal runaway [115]. Sensor monitoring and alarm systems can serve as a recovery control to mitigate loss of life during thermal runaway during spent lithium-ion battery dismantling. The sensors detect any signs of thermal runaway and trigger an alarm to alert workers, allowing them to take prompt action to prevent or mitigate harm [113], [114], [116], [117].

2.1.4. Conclusion

The safe and effective discharge of spent LIBs prior to their dismantling is critical to avoid thermal runaway and ensure safety during the recycling process. Through experimenting with various salt solutions, the use of NaOH salt solution was found to provide the ideal balance between cost, degree of corrosion, and discharge efficiency, and was selected for all subsequent pretreatment steps in this study. The bowtie analysis further highlights the potential dangers associated with thermal runaway during the disassembly of spent LIBs, and the need to prevent or manage this risk effectively. The factors that can contribute to thermal runaway, including thermal failure, mechanical failure, short-circuits, and electrochemical misuse, should be taken into consideration and addressed appropriately to ensure the safe operation of systems and protect individuals and the environment. Further research is needed to refine and optimize the pretreatment processes such as the discharge method and to ensure the safe and sustainable recycling of spent lithium-ion batteries.

2.2. Electrode Active Material Recycling

2.2.1. Introduction

In order to minimize the impact of the challenges involved with the wide-spread use of LIBs discussed in chapter 1, recycling of spent batteries has been investigated with metal reclamation using acid leaching techniques being adopted at an industrial scale. However, the current strategy involves using inorganic mineral acids such as H_2SO_4, HCl and HNO_3 which poses certain limitations despite possessing more than 99% recovery efficiency [124]. Firstly, minerals acids are highly corrosive and, hence, incur high maintenance and handling costs. Additionally, they can damage equipment and structures which gives rise to numerous safety constraints. Secondly, during acid leaching, toxic and hazardous gases such as chlorine and oxides of sulfur and nitrogen will be released. They can lead to pervasive environmental impact and disrupt ecosystems[125]. A concerted effort has been made in recent years to move away from mineral acids. Organic acids have been employed as an alternative to leach lithium from spent cathode materials and have achieved various degrees of success [68].

On the anode side, graphite is commonly employed as the active material and poses similar environmental, logistical and waste management concerns as that of lithium in cathodes [126]. Extracting graphite can have detrimental effects on the environment, releasing pollutants and damaging ecosystems. Recent investigations have found that mining practices can lead to the emission of harmful substances, such as sulfur dioxide and nitrogen oxides, which can negatively impact air and water quality [127][128]. Furthermore, such operations can result in the destruction of habitats and displacement of nearby communities[129]. An effective means of ameliorating these impacts is through the recycling of graphite, which has the potential to diminish the reliance on mining activities to supply graphite and thereby minimize its environmental footprint. Moreover, the practice of recycling graphite can enhance the security of the supply chain of LIBs by decreasing the reliance on imported sources of graphite. Recycling graphite requires less energy than mining new graphite, which can help to reduce greenhouse gas emissions and other environmental impacts associated with energy production [129]. Studies conducted in recent years indicate that the utilization of recycled graphite in production processes can result in energy savings of up to 85% when compared to the energy required for mining new graphite [130] [131].

This study presents a green approach to recycle the active materials in the electrodes of NCM622 commercial cylindrical batteries in keeping with the principles of a circular economy. A combination of organic acids, citric and oxalic acids, are employed to recover lithium from spent cathode materials and achieve high recovery percentages. Previously reported studies have investigated the use of organic acids alone or in conjunction with a reducing agent [68]. This study employs a double organic acid system in conjunction with a reducing agent to investigate the recovery efficiency of lithium from spent cathode materials. On the anode side, the graphite was recovered, purified and regenerated. In this study, the acid curing-leaching strategy developed by Gao et al. was adopted and modified to enhance its environmental compatibility [132]. Gao et al. employed sulfuric acid and this study has replaced sulfuric acid with citric acid. Additionally, the 1500 ^{0}C high-temperature calcination step was replaced with 900 ^{0}C graphitization. In order to circumvent the high-temperature requirement for the final step used by Gao et al., the recovered and purified graphite was subsequently subjected to carbon-tailoring to repair surface defects caused by lithium intercalation and improve its electrochemical performance.

2.2.3. Experimental Section

Materials & Reagents: Analytical reagents sulfuric acid (H_2SO_4) at 98.3% concentration, citric acid ($C_6H_8O_7$) at >= 99.8% purity and oxalic acid ($C_2H_2O_4$) at 98% purity were used for the curing and leaching of spent electrode active materials. Spent electrode active materials were obtained from commercial Toshiba LGR18650P cylinder cells. Commercial graphite flakes at 99% carbon basis were used as reference. Hydrogen peroxide solution (30 % (w/w) in H_2O) was used as a reducing agent. 1-Methyl-2-pyrrolidinone (NMP) at 99% purity was used for cathode material recovery. 1-Methyl-2-pyrrolidinone at >=99% purity and Polyvinylidene Fluoride (PVDF) were used to prepare the electrode slurry for the recycled graphite. Commercial Lithium Cobalt Oxide (LCO) was used as cathode active material to make full cells. Glucose was used as a precursor for carbon tailoring.

Recovery of Active Materials: Commercial cylindrical Toshiba LGR18650P cells, with active material NCM 622 at the cathode and graphite at the anode, were cycled for 500 cycles to simulate spent cells. The cells were immersed in NaCl solution at 3 wt% to completely discharge the battery by electrolyte gating in order to prevent thermal runaway during dismantling. The cells were manually disassembled and the cathode and anode rolls were separated. The cathode rolls were cut into smaller pieces and immersed in NMP and sonicated for 15 minutes. This enables the separation of cathode active material from the aluminium foil. The active material was recovered by centrifugation and subjected to calcination at 700 ^{0}C for 2 hours to eliminate any residual organics like PVDF and carbon. Graphite was obtained by manual scraping from the copper current collector.

Li Reclamation: The cathode black mass following calcination was subjected to acid leaching via chemical dissolution in a 300 ml aqueous mixture containing citric and oxalic acids. H_2O_2 at 2 vol% was used as a reducing agent. The solution, containing 0.4 g of cathode material, was subjected to stirring on a conventional magnetic hot plate and the temperature of the system was maintained at 80-90 ^{0}C using a water bath. The concentration of Oxalic and Citric acids was varied from 0.2 to 1 M. Samples were collected at regular intervals using a syringe and insoluble residues were removed by filtration. The recycling strategy followed for lithium recovery by dissolution is shown in figure 12.

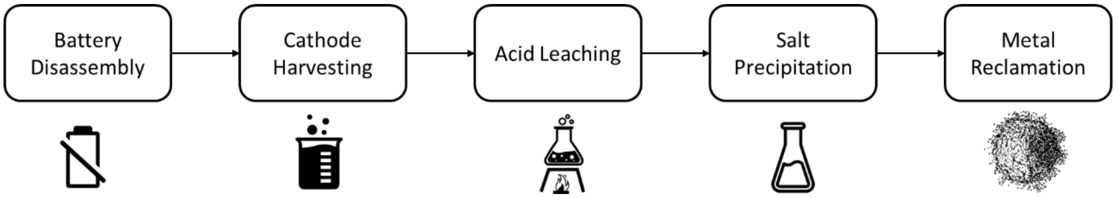

Figure 12: Schematic of recycling strategy for Li reclamation through organic acid leaching

Graphite Regeneration: The spent graphite was separated from the copper current collector by manual scraping and ground to a fine powder using a mortar and pestle. The acid curing-leaching combined strategy employed by Gao et al. was replicated with sulfuric acid to act as a reference and citric acid to facilitate an eco-friendly alternative. Following acid curing, the sulfuric acid-cured graphite and citric acid-cured graphite were obtained by centrifugation and subjected to low-temperature calcination at 400 ^{0}C for 1 hour. The sulfuric acid-cured graphite and citric acid-cured graphite were subjected to acid leaching in sulfuric acid and citric acid respectively at 80 ^{0}C for 4 hours. The sulfuric acid-leached graphite, S-graphite, and citric acid-leached graphite, C-graphite, were recovered and pH balanced through centrifugation and dried in a hot-air oven for 6 Hours. Subsequently, S-graphite and C-graphite were subjected to high-temperature calcination at 900 ^{0}C for 3 hours. The citric acid to graphite mass ratio was maintained at 1 for curing and leaching. The experimental process flow for graphite purification and regeneration is summarized in figure 13.

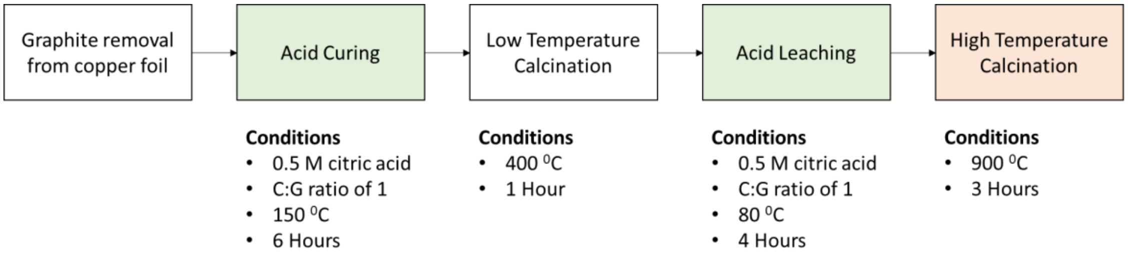

Figure 13: Process flow for graphite purification and regeneration using acid curing-leaching strategy

Carbon-tailoring: The C-graphite, following high-temperature calcination, was subjected to water bath carbonization to tailor the carbon in order to remove surface defects and repair the structure. 0.4 g of glucose was dissolved in water by ultrasonication. 2 g of C-graphite was added to the solution and was again ultrasonicated for 15 minutes under mild heat. The solution mixture was then vigorously stirred in a water bath for 1 hour at 80-90 ^{0}C. The tailored graphite, T-graphite, was obtained by evaporating the solvent. Finally, the T-graphite was carbonized under a nitrogen atmosphere in a tube furnace at 800 ^{0}C for 1 hour.

Materials Characterization: The crystal structure of C-graphite and S-graphite were tested using XRD (Bruker XRD D8 Discover) at a scanning speed of 5 ^{0}/min. The carbon-coating on the T-graphite was studied using Scanning Electron Microscopy (Zeiss Sigma FESEM w/ EDX & EBSD). ICP-optimal emission spectroscopy was used to determine the dissolution of Li during metal reclamation from cathode material and for verifying the purity of graphite during acid curing-leaching. ICP-optimal emission spectroscopy was used in tandem with XRD analysis to verify the purity of the purified graphite as the detection limit of metals during XRD is around 1%.

Electrochemical Tests: Each of the active materials, S-graphite, C-graphite and T-graphite were mixed with PVDF binder and Super P conductive agent in a mass ratio of 8:1:1 and the electrode slurries were formed by homogenizing in N-methyl-2-pyrrolidone. The homogenized slurries were uniformly coated on a copper foil using a doctor's blade and dried overnight at 60 ^{0}C to form the working electrode. The active material loading was maintained at around 1 mg.cm^{-2}. Coin cells were assembled in a glovebox under argon atmosphere with lithium discs and Celgard 3501 membrane used as counter electrode and separator respectively. A 1 M solution of $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate in a 1:1:1 ratio by weight was utilized as the electrolyte. The half-cells were experimentally tested by galvanostatic charge/discharge at a voltage window of 0.01-1.5 V on a Neware Battery Measurement System

(Neware, China) at room temperature. Electrochemical impedance spectroscopy (EIS) at a voltage amplitude of 1 mV with a frequency range of 10^5 to 10^{-2} Hz and cyclic voltammetry (CV) at a sweep rate of 0.1 mV/s and voltage range of 0.001 to 2.5 V was conducted on a BioLogic electrochemical workstation.

2.2.4. Results and Discussion

Li Reclamation: 6 trials were performed and the conditions and Li recovery percentages are summarized in table 7. In trial I, H_2O_2 as a reducing agent was not introduced and the recovery percentage was less than 5%. This can be attributed to the Co and Mn in the NCM 622 molecule ($LiNi_{0.6}Co_{0.2}Mn_{0.2}O$). The reducing agent brings down the oxidation number of Co and Mn from their stable states, 3+ and 4+ respectively, and the higher oxidation state allows for better dissolution of these metals [133]. Although Li's oxidation state is not affected, its dissolution is correspondingly influenced as it is part of the same chemical compound as that of Co and Mn. The chemical reaction of Li dissolution in oxalic and citric acid is complex and involves multiple intermediate reactions. The most probable overall reactions are shown in equations 4 and 5. Additionally, the effect of H_2O_2 concentration on the leaching rate was studied and the optimal concentration was found to be 2 vol %. It was also observed that leaching rates greater than 4 vol% lead to lower dissolution due to the H_2O_2 acting as an oxidizing agent instead of a reducing agent at lower pH [134] . The results of the correlation between H_2O_2 concentration and leaching rate are summarized in table 8. More than 98 % recovery of lithium was achieved in trial VI using 1 M of Oxalic and Citric Acid. The dissolution profiles for each trail are shown in figure 14. Thus, an environmentally benign combination of organic acids can be effectively utilized to recover lithium from spent NCM 622 cathode material.

$Li + C_6H_8O_7 \rightarrow LiC_6H_5O_7$ (Li citrate) (equation 4)

$Li + 2\ C_2O_4^{2-} \rightarrow LiC_2O_4$ (Li oxalate) (equation 5)

Table 7: Summary of Conditions and Results from Acid Leaching Experiment

	Trial I	**Trial II**	**Trial III**	**Trial IV**	**Trial V**	**Trial VI**
Experimental Conditions	80 ^{0}C,	90 ^{0}C,	90 ^{0}C,	90 ^{0}C,	90 ^{0}C,	90 ^{0}C,

	0.2 M Citric Acid, 0.2 M Oxalic Acid	0.2 M Citric Acid, 0.4 M Oxalic Acid, 2 vol% H_2O_2	0.3 M Citric Acid, 0.6 M Oxalic Acid, 2 vol% H_2O_2	0.3 M Citric Acid, 1 M Oxalic Acid, 2 vol% H_2O_2	0.5 M Citric Acid, 1 M Oxalic Acid, 2 vol% H_2O_2	1 M Citric Acid, 1 M Oxalic Acid, 2 vol% H_2O_2
Li recovery %	2.4%	42.7	51.1	81.3	94.8	98.9

Table 8: Summary of the correlation between H_2O_2 concentration and leaching rate at 30 minutes for 1M citric and oxalic acid

	Trial I	**Trial II**	**Trial III**	**Trial IV**	**Trial V**
H_2O_2 Concentration	0 vol %	5 vol %	4 vol %	3 vol %	2 vol%
Leaching rate (mg/L*min)	1.2	2.3	2.4	4.5	4.8

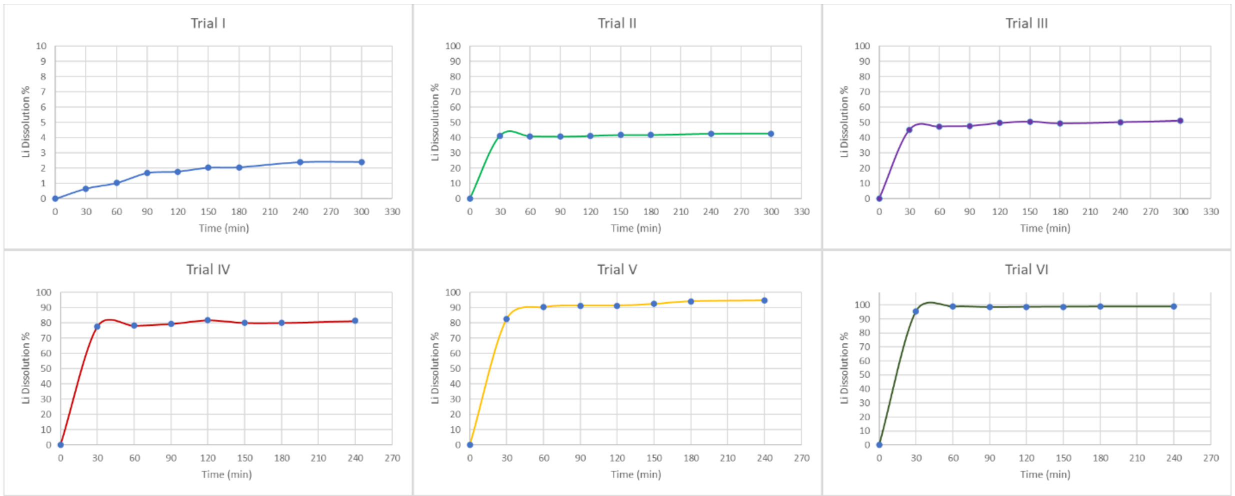

Figure 14: Dissolution profiles of Li under each trial

<u>Graphite Purification and Regeneration</u>: C-graphite was subjected to ICP-OES analysis before and after purification; the results are summarized in table 9. As can be seen from table 9, there is a significant decrease in impurity content, particularly that of lithium which drops from 183.9 ppm to 0.02 ppm. The other impurities present such as Cu, Fe and Co are almost completely removed. Therefore, this confirms the validity of the organic acid curing-leaching method and demonstrates its ability to produce comparable results to sulfuric acid, making it a suitable substitute for the methodology developed by Gao et al. [132]. To corroborate these results XRD analyses were done

on C-graphite and S-graphite. The results are summarized in figure 15. The X-ray diffraction (XRD) analysis of the sample revealed a diffraction pattern that was in agreement with the ICDD reference data for graphite (PDF #41-1487). The characteristic peaks at 2θ angles of 26.5° ± 0.5° and 44.3° ± 0.5° for the (002) and (100) planes, respectively, were observed, further confirming the presence of graphite in the sample and the absence of impurities. Importantly, our results showed that the peaks for C-graphite were identical to those of S-graphite, demonstrating that the organic acid substitution is a viable and environmentally friendly alternative to conventional methods.

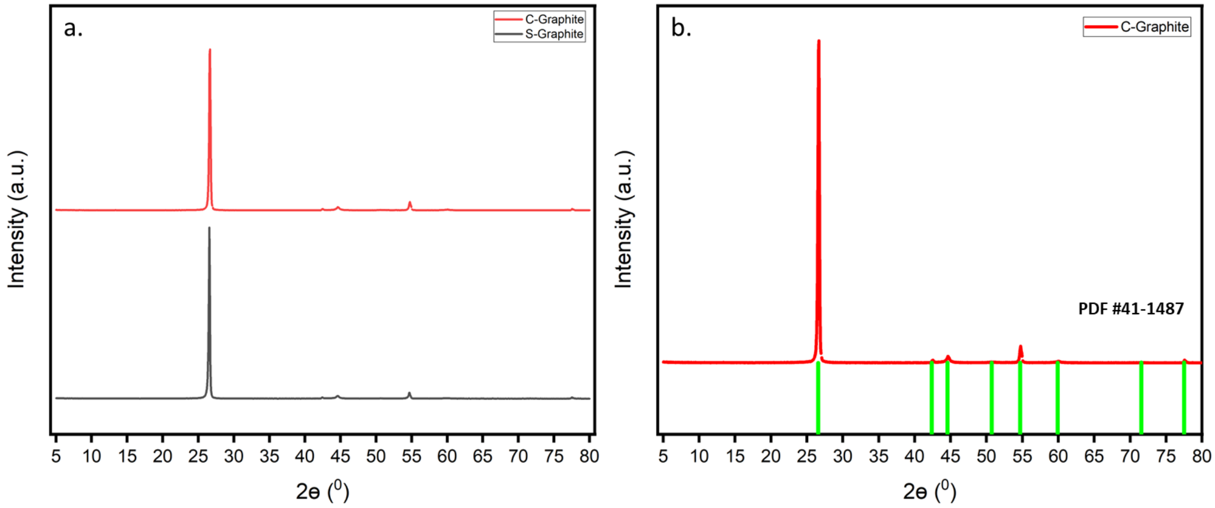

Figure 15: (a) XRD patterns of S-graphite and C-graphite (b) XRD patterns of C-graphite compared with the ICDD reference data for graphite (PDF #41-1487, green line)

Table 9: Composition of recovered graphite before and after purification

	Li	Cu	Fe	Al	Mn	Ni	Co
Before Purification using Citric Acid (ppm)	183.9	4.6	1.1	0.83	0.02	0.03	0.08
After Purification using Citric Acid (ppm)	0.02	0.01	0	0.04	0.01	0.01	0

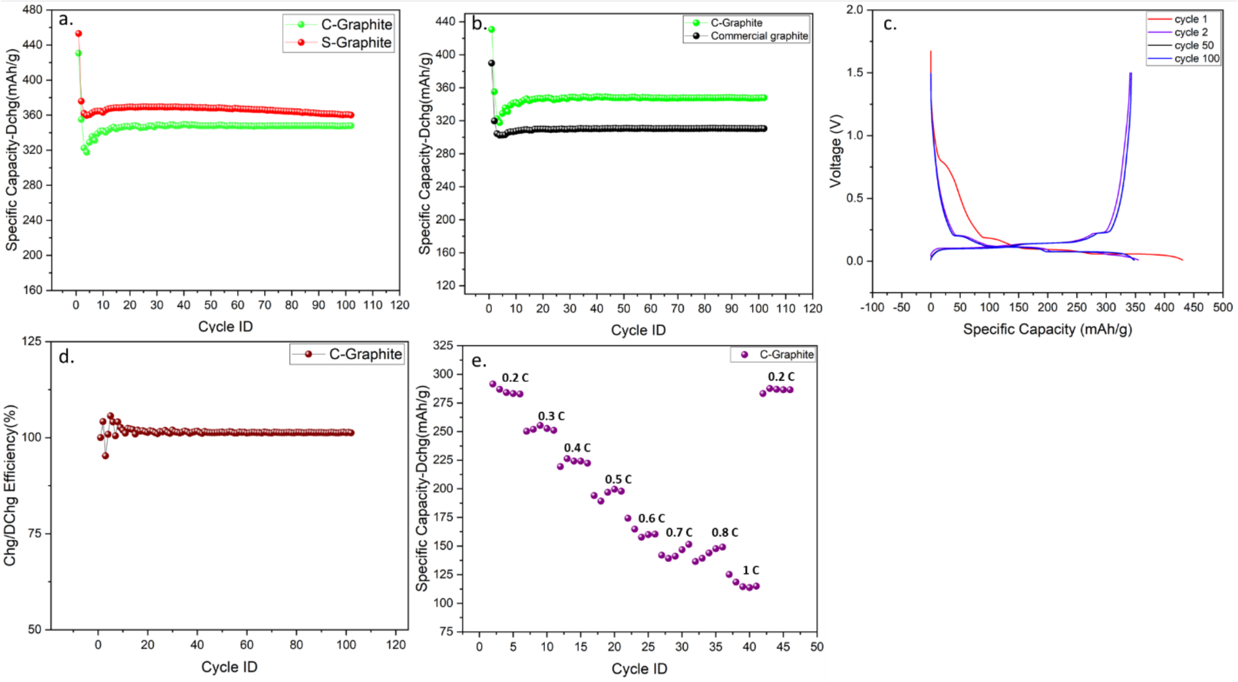

Figure 16: (a) Cycle performance of C-Graphite and S-Graphite (b) Cycle performance of C-graphite and Commercial Graphite (c) Charge/Discharge curve of C-graphite 1st, 2nd, 50th and 100th cycle (d) Charge/Discharge efficeincy of C-graphite (e) Rate capability of C-graphite

Electrochemical Performance: The electrochemical performance of S-graphite, C-graphite and commercial graphite at a rate of 0.1 C (1 C = 371 mAh/g), with an initial activation cycle of 0.05 C, is shown in figure 16. The cycling performance of S-Graphite and C-graphite after 100 cycles is shown in figure 16a. The specific capacity of C-graphite stabilizes around 340 mAh/g while that of S-graphite achieves 360 mAh/g after 50 cycles. The electrochemical performance of S-graphite and C-graphite is almost similar and further confirms that it is viable to replace sulfuric acid curing-leaching with organic acid curing-leaching. Figure 16b compares the electrochemical performance of C-graphite against that of commercial graphite. C-graphite achieves more than 30 mAh/g of discharge capacity than commercial graphite. The better electrochemical performance of regenerated graphite as compared to commercial can be attributed to its higher purity and more consistent structure enabled by the final calcination step. High temperature calcination increases the interlayer spacing, making it easier for lithium ions to intercalate between the graphite layers [135] [136]. This enhances the performance of LIBs by improving their rate capability, capacity, and stability. The regenerated graphite demonstrated an outstanding charge-discharge efficiency, shown in figure 16d, with a value close to 100%. This efficiency was measured by monitoring the amount of charge stored in the graphite during charging and the amount of charge retrieved during discharge. The near-perfect efficiency indicates that the regenerated graphite is highly suitable for use as an electrode material in LIBs and can serve as an alternative to commercial graphite. The rate capability of C-graphite was examined and the findings are presented in Figure 16e. The study showed a marked decrease in the discharge capacities of the C-graphite electrode with increasing current densities, which can be attributed to the increased rate of lithium ion diffusion within the electrode at high current densities. This results in reduced efficiency in lithium ion intercalation and deintercalation processes, leading to decreased discharge capacities [137][138]. The specific capacity of C-graphite was found to be recoverable upon reducing the current densities, due to the slowing of lithium ion diffusion and the corresponding improvement in the efficiency of the lithium ion intercalation and deintercalation processes [138]. The galvanostatic charge-discharge curve for C-graphite is shown in figure 16c. C-graphite shows good capacity retention of more than 98% after 100 cycles.

Figure 17 shows the CV and EIS spectra of C-graphite. The CV curve, shown in figure 17a, was obtained after three cycles. In the first cycle, the formation of a solid electrolyte interface (SEI) was observed, which was indicated by a deviation from the expected voltammogram. The SEI formation resulted in a shift of the reduction peak potential towards more negative values, and a decrease in the peak current compared to subsequent cycles [139]. After the SEI formation, the reduction peak indicated the electron transfer process at the electrode-electrolyte interface and lithium intercalation into the graphite lattice, forming LiC_x. The overlapping of the reduction and oxidation peaks in the second and third cycles indicated reasonable reversibility for the recycled graphite, suggesting good stability and performance for practical applications. The shape of the peaks was symmetrical, indicating a homogeneous electron transfer process. The peak current increased linearly with an increasing sweep rate indicative of a diffusion-controlled process. The peak potential remained relatively unchanged with an increasing number of cycles, indicating a stable electrochemical interface. The EIS spectra of C-graphite is shown in figure 17b. The high-frequency semicircle is related to the diffusion and migration of lithium ions through the SEI film within the graphite electrodes, which can be seen as the capacitive behavior of the system. On the other hand, the second semicircle represented in the medium-frequency region results from an interfacial charge transfer of Li^+/Li and can be seen as the resistive behavior of the system. The large resistance observed can be attributed to the formation of a thick SEI film due to the structural defects present in the regenerated graphite [139][140].

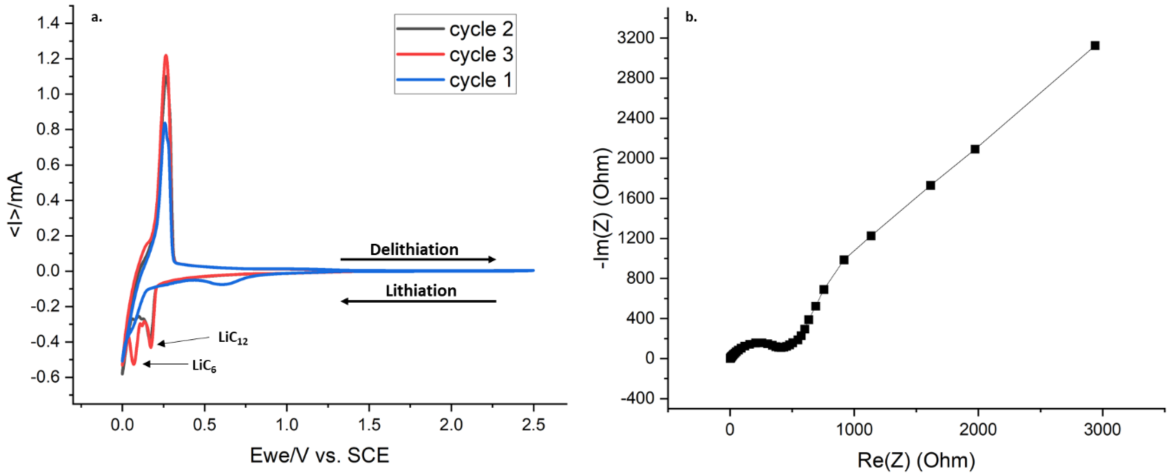

Figure 17: (a) CV curve of C-Graphite half-cell (b) EIS Spectra of C-Graphite half cell

Carbon-tailored Graphite: The C-graphite was subjected to water bath carbonization in order to repair the structural defects caused by lithium intercalation and improve the electrochemical performance of the graphite. The electrochemical performance of T-graphite is shown in figure 18. From figure 18a, it can be observed that the T-graphite stabilizes at around 420 mAh/g and its cycling performance is significantly better than C-graphite and commercial graphite. This can be attributed to the formation of amorphous carbon on the C-graphite during carbonization in tube furnace [141]. Carbon-rich films form on the C-graphite due to the decomposition of glucose in addition to repairing the structural defects. During the thermal treatment, the carbon-rich film undergoes a structural rearrangement, leading to the formation of amorphous carbon. Amorphous carbon has a higher surface area and porosity compared to crystalline graphite, which can increase the accessibility of lithium ions to the active material and improve the rate of lithium-ion insertion and extraction. Additionally, amorphous carbon can also have improved electrical conductivity compared to crystalline graphite, reducing the resistance and increasing the rate of charge transfer. Furthermore, amorphous carbon can also have a more homogeneous and uniform structure compared to crystalline graphite, which can improve the stability and cyclability of the material [141], [142]. Additionally, the carbonization process can also lead to the formation of various intermediate species, such as carbon nanotubes, graphene, and graphitic carbon, which can further affect the final structure and properties of the amorphous carbon [143]. The specific effects of amorphous carbon on the electrochemical properties of graphite depend on various factors such as the carbonization conditions, the type and amount of glucose used, and the initial state of the graphite. Further research is needed to fully understand the mechanisms behind the effects of amorphous carbon on the performance of graphite. The coulombic efficiency, in figure 18b, is almost 100% and consistent for 100 cycles. The galvanostatic charge-discharge profile is shown in figure 18c and T-graphite has a capacity retention of more than 98% from 2nd to 100th cycle.

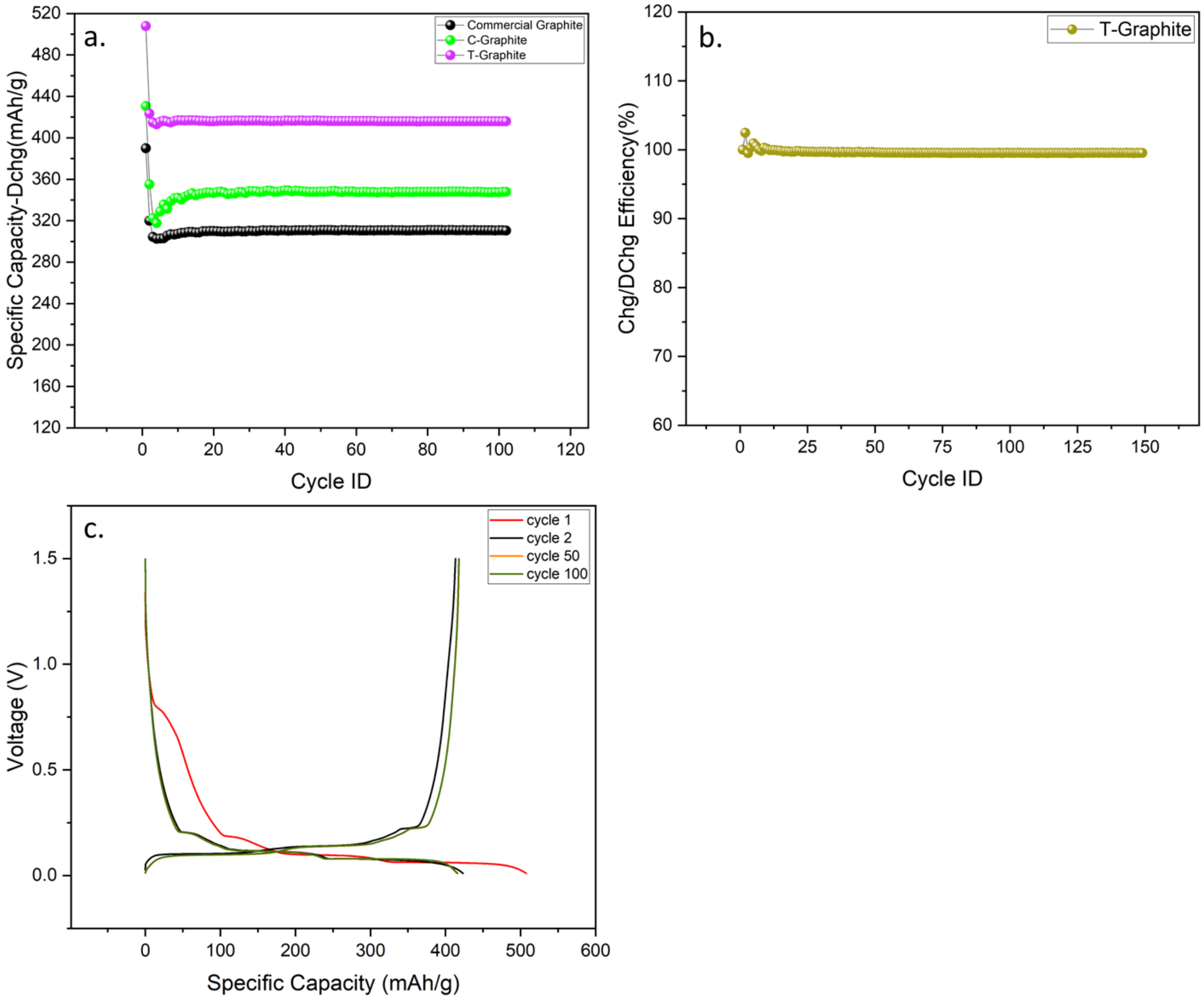

Figure 18: (a) Cycle performance of commercial graphite, C-Graphite and T-Graphite (b) Charge/discharge efficiency of T-Graphite (c) Charge/Discharge curve of T-graphite at 1st, 2nd, 50th and 100th cycle

The SEM images of the T-graphite is shown in figure 19. The images show that the T-graphite has a potato-shaped structure with flake-like particles dispersed on it. The SEM images of the regenerated graphite also reveal a lack of metallic impurities which highlights the efficacy of the purification process. The presence of amorphous carbon can be confirmed by the SEM images shown in figure 19c and, as discussed earlier, serves as the reason behind the elevated performance of T-graphite [142][144]. The SEM images also reveal porous surface and exposed edge planes. Exposed edge planes in graphite can affect its electrical conductivity by disrupting the smooth flow of electrons due to aggregation at the edges or by acting as electron scattering centers[145],

[146]. This reduced conductivity can lead to higher resistance and could potentially be another reason behind the high resistance indicated in EIS measurements.

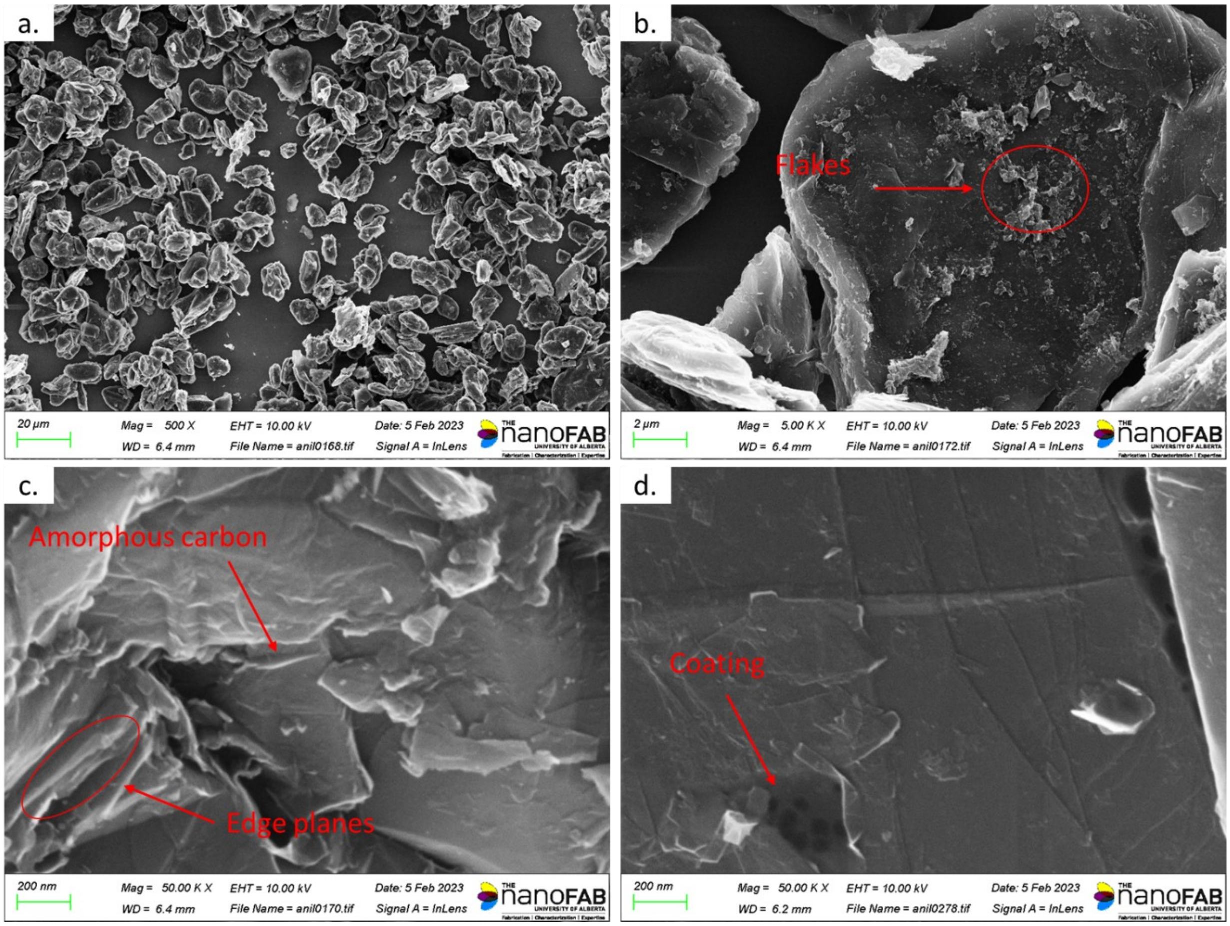

Figure 19: SEM images of T-Graphite at a magnification of (a) 500 X (b) 5.00 K X (c) & (d) 50.00 K X

Full Cell Test: The full cell test was done using C-graphite as anode active material and commercial LCO as the cathode active material to demonstrate the commercial viability of regenerated graphite. Initially, the half cells were prepared directly and achieved a maximum initial capacity of 100 mAh/g. In order to improve the electrochemical performance, direct contact prelithiation was done. Direct contact prelithiation is a method of preparing the graphite anode by pre-doping it with lithium ions prior to its assembly in the cell. The process used in this work involves direct contact between the graphite anode disk and a lithium metal foil in order to introduce lithium ions into the graphite. Direct contact prelithiation can result in a more homogeneous distribution of lithium ions throughout the graphite, reducing the risk of lithium clustering and improving the stability of the anode during charge and discharge cycles. Additionally, direct contact prelithiation can also lead to improved rate performance and energy efficiency of the full cell, as the pre-doping of the graphite can reduce the activation energy required for lithium-ion insertion and extraction. Furthermore, direct contact prelithiation can also reduce the formation of solid SEI on the surface of the graphite, which can limit its electrochemical performance. By reducing the SEI formation, direct contact prelithiation can improve the overall cycle life and stability of the full cell [147][148]. The initial specific capacity increased to 120 mAh/g following prelithitaion and the cycling performance and galvanostatic charge/discharge curves are shown in figure 20.

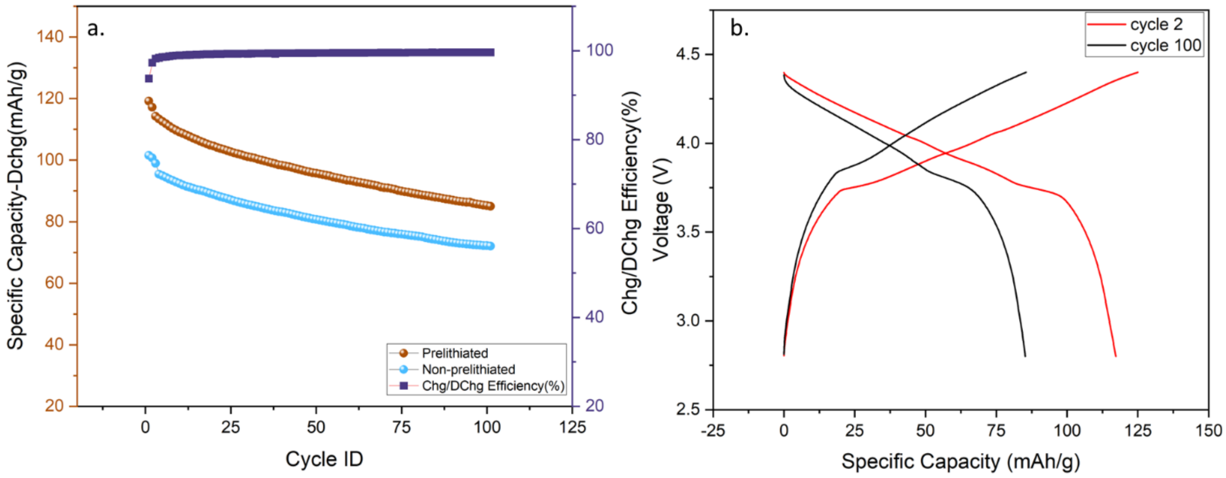

Figure 20: (a) Charge/Discharge efficiency and Cycle performance of prelithiated and non-prelithiated C-Graphite full cells (b) Charge/Discharge curves of prelithiated C-Graphite full cell at 2nd and 100th cycle

2.2.5. Advantages of the Green Recycling Strategy

The use of inorganic mineral acids, such as sulfuric acid, for the hydrometallurgical recovery of lithium from spent lithium-ion batteries has several disadvantages [149]. Firstly, the high reactivity of these acids causes significant corrosion of reactor equipment and other operational components, leading to increased maintenance and replacement costs. Secondly, the use of mineral acids generates toxic and corrosive waste streams that require proper handling and disposal, resulting in environmental and health hazards and potential regulatory restrictions and penalties. Thirdly, the high operating temperatures and pressures required for effective lithium extraction using mineral acids result in high energy consumption and elevated production costs, while also requiring specialized reactor equipment and process control systems, adding to the capital investment costs [125][150]. Finally, the efficiency of lithium extraction is influenced by the presence of other metals that can complex with lithium, reducing solubility and extraction yield and increasing process complexity and cost.

Organic acids such as citric and oxalic acids have emerged as promising alternatives to inorganic mineral acids in the hydrometallurgical recovery of lithium from spent lithium-ion batteries. These organic acids have several advantages over their inorganic counterparts. Firstly, they are biodegradable and non-toxic, making them more environmentally friendly and reducing the risk of regulatory penalties. Secondly, they are less corrosive and operate at lower temperatures and pressures, resulting in lower energy consumption and reduced production costs. Thirdly, they have been shown to effectively dissolve lithium, while minimizing the complexation with other metals, resulting in improved lithium recovery yields. Overall, the use of organic acids such as citric and oxalic acids offers a more sustainable and cost-effective alternative to inorganic mineral acids for the hydrometallurgical recovery of lithium from spent lithium-ion batteries [68], [123].

The hydrometallurgical leaching method presented in this study for the recovery of lithium from spent batteries using a mixture of 1 M oxalic and citric acid achieved near complete lithium recovery. Unlike previous studies where one of the acid mixtures acted as a reducing agent and the other served as the leaching agent, both acids functioned solely as leaching agents in this study. Furthermore, previous studies using individual acids required 1.2-1.4 M citric acid for more than 90% lithium dissolution, while 1 M oxalic acid only achieved less than 70% dissolution [68]. The presented method, therefore, offers economical benefits due to its reduced acid concentration requirements. Additionally, this study effectively leached NCM622, a more complex compound, whereas prior leaching studies focused mostly on LCO. The acid curing-leaching method to recycle graphite presented in this study offers an environmentally sustainable and cost-effective alternative to the procedure introduced by Gao et al. by utilizing citric acid in place of sulfuric acid and a reduced temperature for the high temperature calcination step. Furthermore, the carbon tailoring step eliminates the requirement for high temperature calcination and rectifies the structural damage caused by lithium intercalation, thus enhancing the electrochemical performance of the regenerated graphite.

2.2.6. Conclusion

In this work, facile and eco-friendly alternatives to recycle the electrode active materials of spent LIBs are developed. Li reclamation by utilizing organic acid mixtures provides an efficient and reliable pathway to recover lithium from spent cathode material and provides recovery yields comparable to that of inorganic mineral acids. Additionally, this method provides economic benefits by avoiding mineral acid handling, storage and transportation complications. The organic acid curing-leaching process recovers and purifies spent graphite to the same degree as the sulfuric acid-curing leaching process investigated by Gao et al. Additionally, the high-temperature calcination step is carried out at a lower temperature and carbon tailoring is employed to repair the structure and fully regenerate the graphite while simultaneously enhancing its electrochemical performance. The methods proposed in this study are easy to execute with readily available lab equipment which demonstrates the potential for lab scale upscaling. Moreover, the reagents used are cheap and readily available. There is almost no wastewater generation as well. The novel procedure developed in this study is in keeping with the principles of a circular economy and can help mitigate the socioeconomic and environmental implications of the global rise in LIB demand. The results obtained by carbon-tailoring which enhances the electrochemical performance beyond the theoretical capacity of graphite demonstrate the upcycling potential of the study.

Chapter 3. Direct Regeneration of Spent Cathode Materials

3.1. Introduction

As discussed in chapter 1, traditional recycling methods such as hydrometallurgy and pyrometallurgy utilize chemicals or higher temperatures to break the bonds in the active cathode material, which requires high energy inputs and may have adverse environmental impacts. In recent years, direct recycling or regeneration has emerged as a novel approach to mitigate the drawbacks of traditional recycling methods. Direct recycling aims to regenerate spent LIBs for extended use by directly addressing the reasons for capacity fade that arise during battery operation. This approach is more straightforward and non-destructive, making it more economically viable and environmentally friendly compared to traditional recycling methods. Direct recycling methods are distinct from conventional recycling methods as they aim to restore or undo the effects of battery usage rather than breaking down the cathode material. In direct recycling of spent LIBs, recent research has demonstrated positive outcomes, utilizing techniques such as electrochemical regeneration, one-step hydrothermal relithiation, and aqueous solution relithiation [90]–[93], [95], [96], [152]–[156]. A molten salt relithiation is discussed in this work

Direct regeneration of spent LIBs cathodes using molten salt treatment shows potential in the field of battery recycling. This process involves mixing a molten salt with the spent cathode, which allows for the replenishment of lithium lost during cycling [96], [156]. Subsequently, the cathode is heated to a high temperature to enable lithium ion diffusion into the cathode and achieve full relithiation. Unlike traditional recycling methods, this approach restores the performance of spent cathodes without breaking them down. Molten salt treatment also has the advantage of being performed at a lower temperature, making it a more energy-efficient and cost-effective method for LIB cathode regeneration. LiOH was used as a molten salt in this study to directly address the reason behind capacity fade, loss of active lithium, and replenish the lost lithium in tandem with a hydrothermal treatment. However, the attempts were only partially successful. Hence, it was not possible to formulate a cogent and comprehensive plan utilizing the following methodology.

3.2. Experimental Methodology and Mechanism

Cathode active material was recovered from spent commercial LIB cylindrical battery using the same methodology discussed in chapter 2. The recovered NCM 622 cathode material was uniformly mixed with LiOH using mortar and pestle. The mixture was transferred to a furnace boat and heated in a tube furnace. A two-step heating strategy was utilized to enable uniform lithiation. The mixture was heated to 500 ^{0}C and held at that temperature for 1 hour to enable the formation of molten salt. The temperature was subsequently ramped up to 800 ^{0}C with residence time of 6 hours to facilitate molten salt lithiation. The relithiated black mass was recovered and mixed in a solution containing an excess of LiOH and Li_2CO_3 to form a uniform mixture. The mixture was subjected to hydrothermal treatment in a Teflon-lined autoclave at 180 ^{0}C for 12 hours. The salt was recovered by centrifugation and dried overnight. The dried powder was calcined at 400 ^{0}C for 1 hour to remove any residual lithium salts and water. Electrode slurry was prepared using the regenerated cathode material, Super P conductive agent and PVDF as binder in a 8:1:1 ratio. Coin cells were assembled using lithium foil as counter electrode to evaluate their cycling performance. Coin cells were also assembled using spent cathode material prior to relithiation to act as reference. The cells were cycled at 0.5 C (1 C = 180 mAh/g) within a voltage window of 3 to 4.2 V.

During the molten salt treatment, lithium metal nanoparticles formation is elicited by the reduction of lithium ions at the cathode surface. The nanoparticles serve as sites for the initiation of the precipitation of a lithium-rich phase on the surface of the cathode. The restoration of the electrochemical activity of the cathode involves the diffusion of lithium ions from the molten salt into the cathode material to replenish lost lithium ions. This ion exchange process is expedited by the high temperature and molten state of the salt, enabling fast diffusion of the ions [96], [156], [157]. For the hydrothermal treatment, the cathode material's surface reacts with the lithium salt precursor solution which also results in the formation of lithium compound nanoparticles. These nanoparticles function as nucleation points for the formation of a lithium-rich phase on the cathode surface. As a result, the lost lithium ions are replenished allowing for the restoration of electrochemical activity [154].

3.3. Results and Conclusion

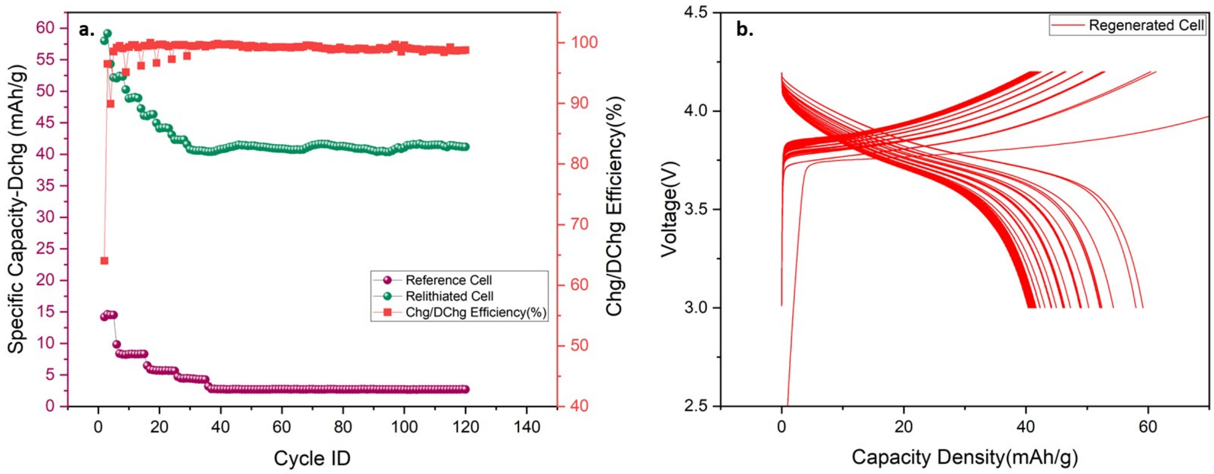

Figure 21: (a) Cycling performance of reference and relithiated cells and charge/discharge efficiency of relithiated cell. (b) Charge/Discharge profiles of regenerated cell

The cycling performance of the reference and relithiated cells and the charge/discharge efficiency of the relithitated cells is shown in figure 21a. The galvanostatic charge/discharge curve is shown in figure 21b. It can be observed that the molten salt and hydrothermal direct regeneration strategy was only able to restore around 60 mAh/g of capacity while the theoretical capacity of NCM 622 is around 277 mAh/g with a practical capacity of around 170 to 190 mAh/g. Although, direct relithiation strategy employed here was able to restore the capacity to a certain extent when compared to the spent reference cell, it is unable to achieve even 50 % of the expected capacity. Moreover, the capacity retention of the relithiated cell remained below 70% after 100 cycles, rendering the approach unviable for further investigations in this project. A range of operational parameters, such as furnace temperature, heating time, lithium salt type, etc. were systematically evaluated to identify the optimal conditions for the highest achievable performance restoration. The reported results in figure 21 illustrate the parameters that led to the maximum restoration of capacity. Cycling performance of additional attempts at direct recycling are included in Appendix A.

Although molten salt relithiation has demonstrated considerable potential in reviving the capacity of discharged lithium-ion batteries, it is essential to acknowledge that the efficacy of this approach can be significantly influenced by the chemistry and structure of the cathode material. NCM622 has a complex composition comprising mixed transition metal oxides, which poses a greater challenge in terms of regaining the lost capacity compared to less intricate cathode materials like LCO. In addition, the layered structure of NCM622 exhibits a significant level of structural ordering, which may impede the diffusion of lithium ions within the cathode material during cycling and the molten salt treatment [158], [159]. As a result, the distribution of lithium within the cathode particles may become uneven, which can constrain the capacity restoration during the relithiation process. Another possible reason would be the diffusion of lithium ions into the cathode material can be hindered by the formation of a stable SEI layer on the cathode surface during cycling. As a result, the restoration of capacity during the molten salt treatment may be limited because the lithium ions in the molten salt may not be able to penetrate the SEI layer and reach the cathode surface [34], [36], [82], [156][160].

Chapter 4. Circular Economies for Lithium-ion Batteries

4.1. Introduction

The exponential increase in global energy demands, brought about by developments in technology, an upward trend in the global standard of living, and an increasing population, has thrust the need for sustainable development into the spotlight. The use of fossil fuels to meet the burgeoning energy demand promotes a multitude of detrimental and pervasive consequences for the environment [161]. The utilization of carbon-based fuels is a major contributor to the emission of greenhouse gases and is a primary factor driving the phenomenon of climate change [162], [163]. International agreements such as the Kyoto Protocol and Paris Climate Accords have been signed by multiple member nations to ensure a coordinated global effort to reduce greenhouse gas (GHG) emissions in order to mitigate the effects of climate change [8], [164]. The success of such undertakings is governed by numerous factors and energy transitions form an integral part of the endeavor [165]. Weaning away from fossil fuels and reducing dependency on non-renewable energy sources is the strategy that is currently employed to mitigate the impacts of climate change and climate overshoot [119]. Solar, wind, biomass fuels and geothermal energy have been explored as alternatives to supplement grid requirements with varying levels of success [166]. However, the intermittent nature of these renewable sources and the lack of robust infrastructure in terms of storage and transportation of the energy generated hampers the large-scale deployment of these technologies [19]. In order to circumvent this issue, energy storage systems (ESSs) are being employed particularly to enable peak shaving and support grid stability. There are various techniques to store energy using ESS and the point of interest in this work is electrochemical energy storage. Electrochemical Energy Storage Systems are backed by battery technology with lithium-ion battery technology supporting a major chunk of such applications [167]. This is evidenced by the USA’s reliance on LIBs for its ESSs where, as of 2018, approximately 77% of the nation’s power storage systems employ LIBs [9]. Another facet of energy transitions is the decarbonization of the transportation sector by switching to electric vehicles which are predominantly powered by LIBs as well. Additionally, the rise in popularity of consumer technology, which has a projected Compound Annual Growth Rate (2022 - 2025) of 7.2%, powered by LIBs further highlights the importance of the energy storage device in the future [168]. As a result, it can be inferred that LIBs play a crucial role in the energy transitions and sustainable development endeavors of the future. Given their importance, the production and lifecycle management of LIBs have become a paramount concern, warranting thorough consideration.

As a vital aspect of the upcoming energy transition, LIBs are all set to witness a surge in demand. The burgeoning demand and concomitant expansion of production give rise to a plethora of questions pertaining to the viability and ecological soundness of the undertaking. To utilize LIBs in a sustainable manner and minimize their impact on the environment, recycling techniques that promote resource optimization must be adopted for spent LIBs [169]. This includes the recovery of metals, regeneration of spent active materials and creation of a system for the second use of spent batteries. Owing to the importance of LIBs in energy systems, multiple strategies have been proposed to optimize the structure of a LIB's life cycle and the most effective of these is the creation of a Circular Economy. The circular economy concept was first proposed in 1988 and has been partially adopted by numerous manufacturing value chains. The core concept of this model is the recycling and reuse of existing materials in a product and keeping it in the manufacturing supply chain for as long as possible [170].

4.2. Circular Economy

The circular economy concept has garnered renewed attention recently as the environmental impact of industrial activities are being heavily scrutinized. The term "circular economy" was first coined in late 1980s, however, the concept embodying all the relevant principles had been suggested prior to the conception of the term. Most authors credit David Pearce and R. Kerry Trainer for introducing the concept in their book Economics of Natural Resources and the Environment (1989) [171]. The book explores neoclassical environmental economics starting from the post-war era and the influence of natural resources on the economy. The authors describe a circular economy by establishing the dependence of the economy on the environment and comparing it with traditional linear economies, depicted in figure 22a. Without factoring in the environment, a traditional economy starts with the input of natural resources followed by production and eventually consumption with each stage generating waste. Naturally, this form of economic model is not sustainable when dealing with finite resources, particularly when it comes to non-biodegradable waste [171]. The authors utilized Kenneth Boulding's spaceship model to arrive at the concept of circular economy [172]. A recycling step along with an environment waste sink, as indicated in figure 22b, was added to close the loop. As can be observed, waste cannot be completely recycled due to two main factors – entropic losses and losses due to scale. The sheer number of components in a finished product puts the recycling of each component beyond feasibility limits. Typically, the high-value and polluting or non-biodegradable components are given priority for recycling operations. Another reason is that the technology might not exist to perform certain recycling tasks for a particular material. Entropic losses are governed by the second law of thermodynamics. The waste that enters the environment is considered reasonable as long as the assimilative capacity, the amount of waste the environment is capable of reabsorbing while not incurring any detrimental effects, is not exceeded [170], [171], [173]. LIB recycling, as discussed in subsequent sections, revolve around the aforementioned limitations as well. A LIB is composed of various components ranging from cathodes, anodes, binders, current collectors, etc. and formulating selective recycling operations for each component is not viable [174]. High-value components such as the electrode active materials are often prioritized for recovery and second use applications for this reason.

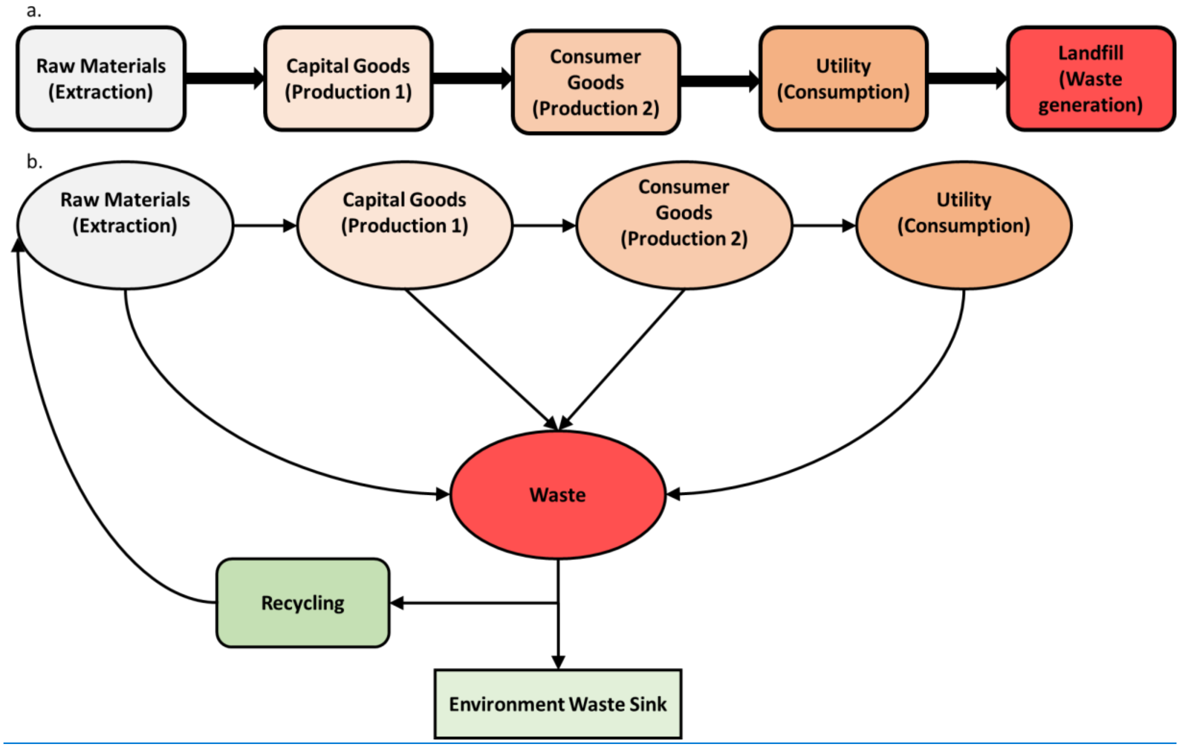

Figure 22: a. Linear Economy following "take-make-waste" approach. b. Circular Economy model with an environment waste sink

Multiple definitions have been put forth to describe the concept but the regenerative aspect remains central to its definition. Yuan et al. defined circular economies with reference to China's development plan [175]. The Chinese central government in 2002 had set a development goal for 2020 that involved quadrupling the GDP of the country and raising GDP per capita to $3,000. The authors point out that the development pathway is not feasible due to limited availability of natural resources and lack of eco-efficiency. Circular economy in this context is defined as “the circular (closed) flow of materials and the use of raw materials and energy through multiple phases” [175]. Yuan et al. demonstrated a three-tier approach to implementing circular economy which contributes to a more refined understanding of the concept. The first tier is at the micro-level and the onus falls on the industry to carry out cleaner production audits and adopt environmentally friendly processes. The second or meso level involves the creation of an eco-industrial network to lead coordinated efforts. At the macro level, eco-jurisdictional zones are established where both production and consumption activities are focused. This three-tiered implementation strategy by the Chinese central government which features resource recovery endeavors at all levels acutely demonstrates the core idea and purpose of circular economies [173], [175]. In the context of energy transitions and storage spurred by LIBs, this relates to the management framework of the LIB domain and modulating existing systems to prompt changes conducive to the creation of a circular economy.

4.3. Environmental and Ethical Aspects of Lithium and Cobalt Mining

Lithium is an integral part of lithium-ion batteries and green technology in general. As indicated in the previous sections, the demand for the metal will rise in conjunction with the demand for lithium. Despite being an abundant metal, economically exploitable reserves are concentrated in Australia, Chile, Argentina and China presently and these countries make up the majority, over 90%, of the supply of lithium for commercial applications [176]. A possible option to meet the increasing demand of lithium would be to increase the output from mining operations. However, this raises a few issues. Lithium reserves are distributed between brines and hard rock with a large percentage of the metal being stored in brines. Brines are located under saline expanses such as salt lakes and are characterized by having a total dissolved mineral salts value in the range of 170 - 330 g/l [31], [177]. The typical process for lithium extraction from brines involves pumping the brine from beneath salt lakes and transferring them to open air evaporation ponds. Following this, evaporitic technology which involves successive evaporation steps to concentrate lithium salts is employed. The lithium salts are subsequently sent to a treatment plant for further recovery [177].

The evaporatic technology, schematic shown in figure 23, employed is not a sustainable method owing to the significant water usage. Up to 95% of the brine water undergoes evaporation to concentrate lithium salts for further extraction. The next aspect is the usage of fresh water for purification processes which could total 50 m3 per ton of battery grade Li2CO3 [177]. In addition to the water requirement and loss, the evaporation causes an imbalance in the hydrodynamic systems of brine and fresh water whose ecological impacts are not fully understood. Another issue is the amount of waste generated over the course of the extraction process. Apart from lithium, the other salts such as magnesium, calcium, sodium and potassium tend to aggregate in the evaporation ponds as they are not usually extracted. The typical composition of brine in the Salar de Atacama is shown in figure 24 [178]. Since these ions form a major part of the brine composition, it is estimated that one tonne of Li_2CO_3 can produce up to 115,041 kg of waste [32], [177]. Buildup of this waste can severely disrupt local ecosystems and take up significant amounts of space or land area if not disposed of properly. Moreover, over the course of the operation of the evaporation pond, lithium can accumulate in the ponds and pile tailings [179]. These deposits can make their way into local ecological systems and cause negative biophysical effects in living organisms. Conversely, the chemical agents utilized during the extraction of lithium from hard rock deposits may leach into the effluent stream and potentially contaminate natural water reserves. All lithium extraction activities can have marked influence on local flora and fauna due to forced changes in ecological systems such as pH or TDS [32], [177], [180], [181]. The Salar de Atacama, one of the world's largest active sources of lithium, is a relevant case study that acutely depicts the impact of lithium mining on the environment and local communities [182].

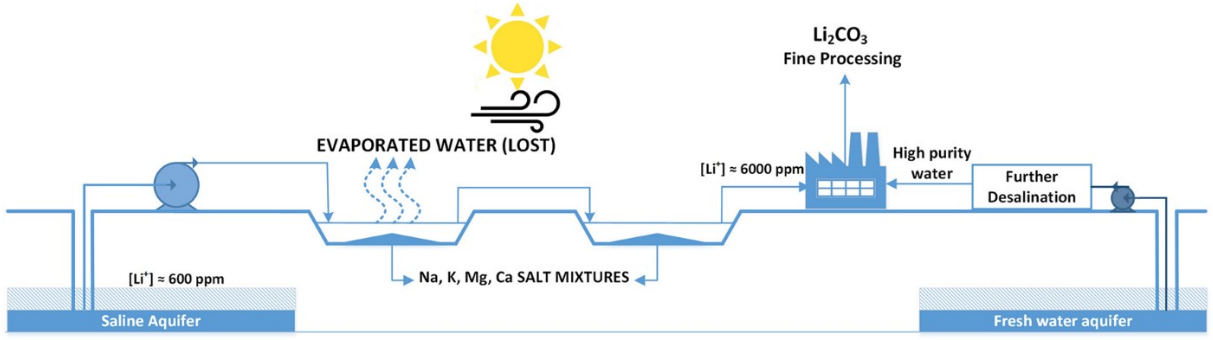

Figure 23: Schematic representation of Evaporitic Technology. Reprinted from ref [183], *copyright 2020 Elsevier*

In addition to being environmentally unsustainable, evaporitic technology is also similarly handicapped from an economic perspective. The primary challenge is the duration of the process. A period of 18 to 24 months is usually required to achieve lithium concentrations in the brine suitable for further treatment. The residence time is also highly dependent on weather conditions which further add uncertainties to the extraction process. With demand for lithium increasing at a breakneck pace, evaporitic technology becomes highly unreliable in a scenario where solar irradiation, wind and rain levels fall below the optimal thresholds. Another factor holding back lithium extraction from brines is the composition of the brines themselves. Subsequent recovery techniques following evaporation need to be modified according to the metal ion makeup of the brine. Therefore, a treatment process at one brine reserve will not yield comparable results at a different site and need to be modified accordingly thereby adding on to the tediousness of lithium extraction from brine. As a result of the limitations discussed above, it can be surmised that lithium mining will be unable to adapt to the changing lithium market in addition to posing a host of negative environmental effects [177]–[180], [182]–[184].

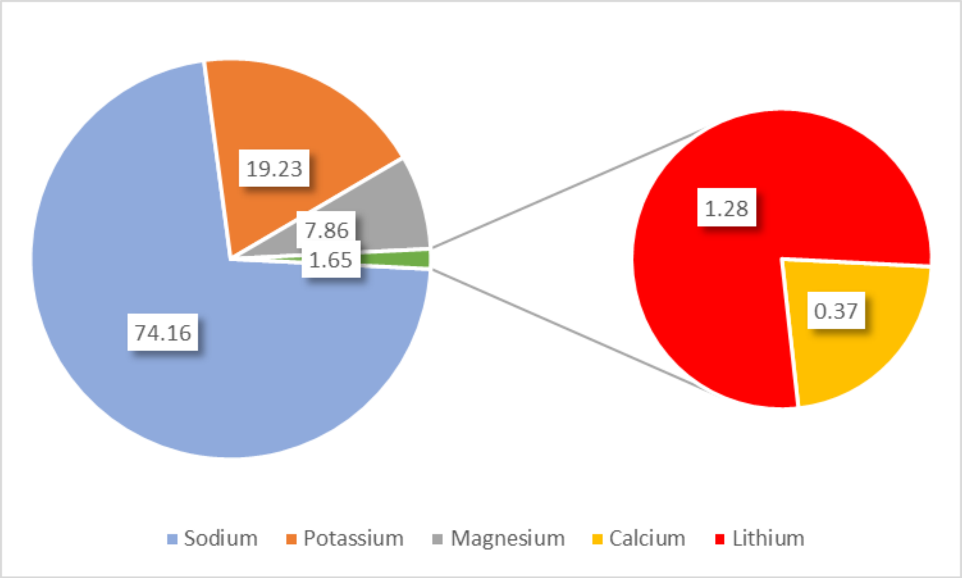

Figure 24: Typical mineral composition of Salar de Atacama brines in g/kg of brine [42]

Cobalt is another important constituent of LIBs and the largest producer and exporter of cobalt by volume is the Democratic Republic of Congo (DRC). Artisanal and Small-scale Mining (ASM) of cobalt is still prevalent in Congo where the mining operations are handled by subsistence miners who utilize rudimentary tools to extract cobalt ore. DRC accounts for 64.3% of global cobalt production and 20% of the metal's national supply is sourced from ASM operations [185]. Being an impoverished nation that is constantly punctuated by political unrest and internal conflicts, artisanal miners receive little to no form of social security or workplace protection from local governments [186]. Due to the lack of support infrastructure, ASM workers are subject to human rights exploitation that extends to child labor and hierarchal harassment. Furthermore, the absence of legal framework for workers protection and workplace safety standards exacerbates the risk of injuries and even fatalities. Efforts such as the 2011 OECD guidelines have been formulated of late to formalize and regulate the ASM sector, however, corporate actors tend to outsource the risk by subcontracting leading to the pervasiveness of inhumane working conditions for artisanal miners [187].

Metal mining in general has come under the scanner recently due to the unethical practices followed in and around extraction sites [188]–[191]. The main issues in the limelight currently are trivializing loss of life, improper safety training, non-adherence to health and safety regulations and distrust between management and workers. These issues lead to worker exploitation with the primary reason being the lower rate of literacy amongst the labor force [191]. Moreover, the remote setting of the reserves makes it difficult to conduct frequent regulatory checks. Workers are often exposed to adverse working conditions and are seldom provided with proper protective gear [185], [186], [192]. Another ethical concern raised is the right of the local community to the water used for refining operations. Taking the Salar de Atacama as an example, 1800 tons of water is required for refining one ton of lithium, however, the annual rainfall in the Atacama Desert is less than 4 inches. To make matters worse, the area is prone to drought. Local pastoralists bear the brunt of the arid conditions triggered by lithium mining as the industry consumes a large portion of the locality's fresh water supply. The non-monetary aspect of lithium mining includes the terrain themselves as certain mining locations encroach on land held sacred by indigenous communities [180], [182], [193]–[195].

4.4. Supply Risk of Raw Materials for Lithium-ion Batteries

As the demand for lithium-ion batteries continuously increases, it gives rise to certain risks associated with the supply of raw materials indispensable for its manufacture. Helbig et al. performed a supply risk assessment of the 10 key elements involved in the fabrication of LIBs [25]. The risk categories used for evaluation are 'risk of supply increase', 'risk of supply reduction', ‘political risk’ and ‘concentration risk’. The researchers identified that the most risk is associated with lithium and cobalt while aluminum and titanium showed the lowest supply risk. The other elements, copper, iron, nickel, graphite, manganese and phosphorus demonstrated a mid-level supply risk. A similar assessment was done on the six types of LIB - Lithium Cobalt Oxide (LCO), Lithium Manganese Oxide (LMO), Lithium Nickel Manganese Cobalt (NMC), Lithium Nickel Cobalt Aluminum Oxide (NCA), Lithium Iron Phosphate / Graphite (LFP-C) and Lithium Iron Phosphate / Lithium Titanate (LFP-LTO). Among them, the highest supply risk corresponded to LCO-C batteries and lowest to LFP-LTO batteries. In order to mitigate these risks, the authors suggest focusing future research on decreasing the material intensity of lithium and reducing dependency on cobalt-based battery technologies. However, these strategies could result in a decrease in the energy density of the batteries. The assessments also included government policy and legislation as well as the ethical aspects of extraction from conflict regions to arrive at the conclusions described earlier [25].

In another study conducted by Watari et al., it was concluded that, in the absence of secondary supply, supply constraints will affect lithium by 2030 due to the substantial rise in EVs [196]. In the scenario analyzed by the researchers, it was projected that global demand for lithium would reach an estimated 370 kilotonnes by 2050, while optimistic projections for global supply of lithium are projected to peak at 243 kilotonnes. A summary of the projections is depicted in figure 25 [196]. The study further accounted for the addition of secondary supply of lithium sourced through the recycling of End-of-Life (EOL) batteries. The findings indicate that through the implementation of an 80% recycling rate in conjunction with primary supply, the global availability of lithium can be augmented to 362 kilotonnes, thereby significantly reducing the disparity between supply and demand. This research further highlights the significance of recycling operations in mitigating supply risks [196].

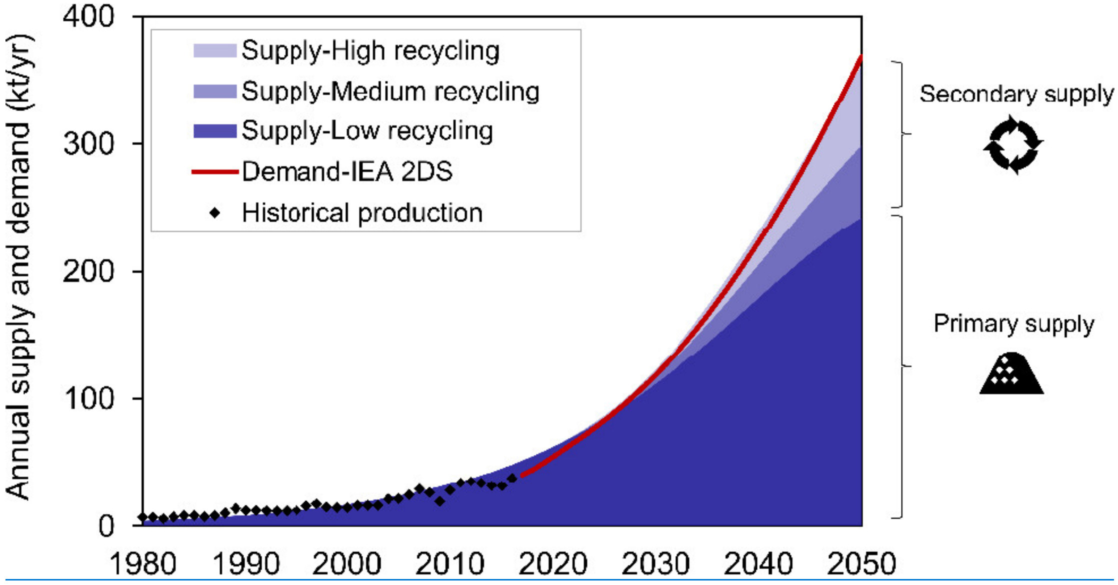

Figure 25: Demand-Supply predictions of lithium by 2050 including secondary supply by Watari et al. Reprinted from ref. [196], *copyright 2019 ACS Publications*

4.5. Challenges to the Implementation of a Circular Economy

A circular economy for lithium-ion batteries is crucial to bring the purported energy transitions involved in sustainable development to fruition. However, there are significant challenges hindering an exhaustive shift to a circular economy. This work identifies 5 key hurdles that need to be overcome in order to expedite the shift to a circular economy. The primary challenge is the design of the batteries themselves. The battery casings, holders and lids are not designed for facile or automated dismantling which hinders the extraction of active material. Destructive techniques, size reduction, separation activities and other pretreatment steps need to be done in order to extract the active material prior to the recycling or regeneration process. This leads to a large amount of waste and energy expenditure. In order to instigate a paradigm shift in this regard, battery manufacturers need to re-model the outer casing of battery packs to a design that is appropriate for machine assisted dismantling. However, this raises further complexities such as modifying the design of the equipment or appliance the battery was intended for in order to accommodate the change. Such modifications would require associated changes across the manufacturing line [37], [101], [197], [198].

Another challenge holding back a global shift to a LIBs circular economy is the lack of sourcing infrastructure for spent LIBs. Barring the European Union directives and legislation in countries such as Japan, China and certain provinces/states in the USA and Canada, there is no cohesive framework for the collection and handling of spent LIBs. The existing legislation encourages battery manufacturers to recycle a certain percentage of the batteries manufactured by the brand or other brands operating in the region [6]. However, this approach is not optimal as the procurement of lithium-ion batteries (LIBs) remains a significant challenge due to the lack of a comprehensive collection and transportation infrastructure. As a result, a significant proportion of LIBs are ultimately disposed of in landfills, which is an unsustainable solution from both an environmental and economic perspective. A recent addition to the equation is the introduction of companies such as Li-Cycle, Redwood Materials and Global Material Alliance which specialize in battery recycling with their business model being designed to profit from the sale of the recovered materials from the spent LIBs [199]. The challenge of spent battery sourcing has been partially overcome as battery manufacturers and recyclers have begun to enter into agreements of late that enable the supply of raw materials from spent LIBs back to manufacturers thereby complementing their supply chain for battery production [200]–[202]. Despite the acknowledged importance of collaborative agreements between battery manufacturers and recyclers as a means of promoting sustainable development, the establishment of a comprehensive and coordinated global initiative in this regard has yet to be fully realized

Fully or partially charged batteries possess the risk of explosion when improperly handled such as puncturing the battery due to short circuiting. Breaching the temperature threshold can lead to explosions as well because the solid electrolyte interface that usually protects the graphite anode decomposes at temperatures above 90 °C and at 120 °C leads to the release of combustible gasses. Also, oxygen gas is released once the metal oxide layer starts to degrade. Violent reactions are initiated owing to the interaction between the oxygen and combustible gasses leading to the thermal runaway effect. Due to the risk of explosion, recyclers need to stabilize the battery before further processing [6], [100]. The potential for explosion in LIBs poses significant safety concerns, which could impede the growth of the LIBs recycling industry and delay the development of alternative supply chains for meeting the demand for lithium through the implementation of closed-loop systems. Another significant constraint for circular economy lies with the end user. Consumer acceptance of recycled products tends to be negative due to the perception that their quality is inferior to the original product. This leads to a lack of confidence in the usage of LIBs whose raw materials are derived from recycled sources [203], [204]. In order to establish a truly circular economy for lithium-ion batteries, it is imperative that consumer confidence be enhanced through highlighting the performance of recycled batteries and providing evidence of comparable results to those sourced through mining [204]. Upcycling is a strategy that can potentially be adopted to inspire consumer confidence once there is sufficient awareness of the concept as the very nature of the process implies an increment in quality or utility from the original application.

The final, and probably the most immediately relevant, challenge standing in the way of establishing a circular economy for LIBs is the cost of transportation of EOL batteries. The primary reason behind the cost constraint is the hazards associated with EOL LIB such as that of explosions discussed earlier. This compounds the cost of transportation as certain regulations needs to be stringently followed [205]. Taking the USA for instance, EOL LIBs are considered as Class 9 Hazardous materials and have distinct packaging specifications to deter the occurrence of unfortunate incidents such as accidental activation or short circuits [206]. A study conducted by

Foster et al. revealed that transportation cost for spent LIB can amount to as much as $2.5/lb. and accounts for about 46% of the overall recycling costs [207]. Safety compliance is a contributing factor to the transportation costs accounting for nearly half of the recycling cost. Thus, resolving the logistical challenge can significantly further the advancement towards a bona fide circular economy for LIBs.

Table 10: Summary of challenges for the implementation of lithium-ion battery circular economy

	Challenge	**Description**
1.	Battery Design	Battery casing designs are not conducive to mass dismantling
2.	Spent Battery Sourcing	Lack of global infrastructure for sourcing of spent LIBs
3.	Safety Risk	LIBs handling introduces risk of explosion which hampers industrial interest
4.	Consumer Acceptance	Consumer perception of recycled products tend to be negative and cast doubts on its quality
5.	Transportation Costs	EOL LIBs are considered as hazardous goods and their transportation costs are drastically high due to the need for complex safety compliance measures

4.6. Countermeasure for Challenges

Research and innovation to counter the challenges preventing the establishment of a circular economy for lithium-ion batteries is currently underway with the underlining trend being a transition from established, albeit energy intensive, pyro- and hydro-metallurgical techniques. As discussed in section 4, direct regeneration or direct recycling of spent batteries is receiving increased research attention where relithiation to replenish the lost lithium and restore capacity of spent cathodes is achieved by chemical, electrochemical, physiochemical and hydrothermal methods [92], [155], [208]. The non-destructive nature of direct recycling techniques eliminates multiple pretreatment and intermediary steps of traditional metallurgical recycling processes. However, this strategy introduces a set of complications which hinders its commercial adoption.

The first impediment is the inability to control and repeat the degree of direct relithiation as the amount of lithium loss leading to capacity decay is not consistent in spent batteries leading to non-uniform feed material. Additionally, coin cells were used to test the capacity restoration of the electrodes in most laboratory studies which possesses a typical active material composition ranging from 80 to 90% by weight with a corresponding electrode load of approximately 3 mAh cm-2. In comparison, industry requirements call for multilayered pouch cell with around 95 wt. % active material composition and an electrode load of 3 mAh cm−2 [209]. Therefore, translating the laboratory gains to industrial standards requires stringent testing using pouch cells to establish the veracity of the technique.

As discussed in earlier sections, the manual disassembly of spent battery casings and shells requires tedious manual labor and research is currently underway to jump this hurdle. Li et al. designed an automated disassembly system for EOL LIB pouch cells which features pouch trimming, housing removal and electrode sorting modules [44]. Their patented disassembly system was capable of automatically separating the electrode sheets, housing films and separators while maintaining the structural integrity of the cathode sheets. Additionally, configuration to non-destructively recover lithium following disassembly from spent electrodes have also been explored by Xu et al. [210]. The researchers utilized a roll-to-roll system involving a solid ceramic lithium-ion electrolyte tube around which the electrodes are wound. The working principle is the movement of lithium ions from electrode surface to the interior of the tube compartment to form LiOH and the ionic movement is instigated by charging the system. Additionally, hydrogen gas is released which is collected for use in green applications in keeping with the principles of a circular economy. These two works is part of a large body of research seeking to bridge the gap between lab-scale success and industrial adoption. Further innovations in the niche of continuous non-destructive spent LIB recycling would help relieve a prominent impediment to establishing a circular economy.

Technical implementation needs to be backed by policy and legislation in order to establish an efficient recycling mechanism for LIB recycling [211]. A policy framework that has shown promise in Europe and Japan and is currently being adopted in other parts of the world is Extended Producer Responsibility (EPR) [212]. The core principle here in the context of batteries is that the responsibility for sourcing and recycling of spent batteries is passed on to battery producers and producers whose products feature these batteries from tax payers and government authorities. In recent years, certain provinces and states in Canada and USA have either already adopted or is mulling the incorporation of EPR to ensure a cohesive waste management framework which extends to spent batteries amongst other products such as plastics and paper [212], [213]. The implementation of Extended Producer Responsibility (EPR) strategies could not only enhance current recycling efforts, but also address the challenge of sourcing spent batteries. By implementing deposit return systems akin to those utilized for plastic recycling, EPR would facilitate the centralization of spent battery collection and disposal [214].

4.7. Conclusion

A growing number of industries and governments have placed a high priority on the implementation of sustainable business practices, and have demonstrated a strong commitment to adopting methods that align with these goals. Powering the rapid development of the industrialized world without disrupting natural systems is a top priority and lithium-ion batteries are ideally poised to disrupt existing fossil fuel reliant systems. Recycling, regeneration and reuse of the lithium-ion batteries takes a front seat as they are indispensable in the upcoming energy transition as these processes enable manufacturers to keep up with the skyrocketing demand of LIBs. A considerable body of research is focused on optimizing the processes previously mentioned, with notable progress being made in the field. The current trend is to move away from established metallurgical recycling treatments for spent LIB and gravitate towards non-destructive direct regeneration methods capable of creating a second generation of batteries that can be immediately reused for commercial applications. Direct regeneration also offers an eco-friendlier route towards LIB circular economy as it minimizes greenhouse gas emissions and requires a lower energy input as compared to metallurgical processes owing to the lower temperature requirement of the processes used. The trend has been taken one step further in recent years where recycling is being slowly phased away by upcycling endeavors which has the capacity to stay abreast of the pace of advancements in the electronic and battery industry while simultaneously enhancing the existing value chain.

The establishment of a circular economy is critical to ensure a self-sustaining lithium-powered future. The five major challenges hindering the creation of a circular economy for LIBs is outlined in section 6 and finding solutions to those will be the major objective for researchers and policy makers alike in the foreseeable future. Among these challenges, the logistical hurdle posed by the colossal costs associated with the transportation of spent LIBs is a matter of immediate concern. Curtailing these costs, which makes up a major chunk of total recycling costs, can expedite the creation of a circular economy by facilitating mass adoption of recycling, upcycling and regeneration operations.

The recycling of spent LIBs has a significant positive impact on the environment and the increasing demand for LIBs raw materials presents a plethora of economic opportunities, thereby fostering commercial interest in this field. As more battery recyclers enter the market, the pace of innovation in terms of metal recovery processes will increase due to higher competitiveness in the market and lead to the development of more high efficiency techniques capable of handling large feeds with maximum efficiency and minimal environmental cost. Furthermore, collaborative agreements between battery recyclers and manufacturers as well as a mature spent battery sourcing infrastructure on a global scale holds the key to accelerating towards the circular economy goal. Another facet of a LIB circular economy that further adds to its appeal is that the alternative avenues currently explored for a sustainable future offers considerable resistance for commercial adoption. For instance, technology such as fuel cells are currently plagued by a lack of infrastructure and regulatory framework, thereby, reducing the feasibility of their widespread use in the foreseeable future. LIB dominant technologies, on the other hand, possess a more consolidated infrastructure and policy framework, albeit a fledgling and fragmented one, that can be leveraged for massive commercialization. The integration of this extant network into a more advanced circular economy model is, thus, a relatively viable objective that can ensure a long-term resolution for issues related to sustainability.

Chapter 5. Summary and Future Work

Since the popularity of LIBs are bound to witness a surge in the coming years, the importance of recycling to support a lithium-powered future is more critical than ever. Transforming LIB markets in keeping with the principles of a circular economy holds the key to sustainable energy transitions in this regard. This thesis offers a holistic overview of LIB recycling and waste management in the circular economy context. A systematical analysis of LIB recycling is performed in this thesis with the ambitious objective to participate in global research endeavors seeking to aid the transition towards alternative sources of energy. Initially pretreatment methodology was optimized to obtain the suitable conditions that facilitate economic as well as safe disassembly of batteries with overarching objective to incorporate all laboratory activities to industrial scale. Subsequently, recovery and regeneration of spent active materials in the cathode and anode were successfully achieved using environment friendly process flows. This was followed by a discussion on attempts at direct regeneration of spent cathodes, the non-destructive mode of recycling, which included conclusions on why the methodology employed did not achieve expected results. Finally, an investigation into circular economies and the challenges hindering the establishment of a global LIB circular economy was performed. The purpose of this endeavor was to emphasize that achieving a sustainable lithium-powered future is contingent not only upon technical feasibility, but also upon the implementation of supportive policies and infrastructure.

Over the course of the research conducted to formulate the thesis, attempts were made to directly regenerate the spent cathode active material by utilizing molten salts and hydrothermal treatment to replenish the lithium lost during battery operation. However, the attempts were only partially successful and, consequently, were not fully incorporated in the work. The difficulty in direct relithiation could be attributed to the complexity of the NCM622 cathode material chemistry as described in chapter 3. As discussed, direct regeneration is the most environmentally and economically suitable research methodology that is being developed. Nonetheless, it should be acknowledged that direct regeneration is yet to be established on an industrial scale and faces various hurdles that require resolution. A primary challenge is the need to devise proficient techniques for the separation of the various battery components as the cathode and anode materials are typically interconnected in intricate structures. Moreover, to guarantee that the regenerated materials are fit for utilization in new batteries, their functionality must be assessed to ensure they meet the quality criteria.

Future efforts will be focused on improving direct regeneration methodologies to achieve high levels of capacity restoration while developing techniques conducive for industrial implementation. The primary objective is to establish a mechanism capable of directly regenerating non-uniform feedstock to achieve uniform regeneration and produce standardized results. This is essential for implementing a continuous process and ensuring efficient and effective regeneration of LIB cathode materials. Furthermore, an in-depth life cycle analysis of current recycling methodologies will be conducted to identify redundancies and inefficiencies. This analysis will serve as a basis for optimizing the recycling processes and ensuring long-term sustainability of the lithium-ion battery industry. Efficient LIB recycling is crucial for a sustainable future. Direct regeneration and optimization of existing recycling processes can facilitate a circular economy for LIBs, reducing waste and preserving natural resources. Industry and policymakers must collaborate to develop and implement sustainable policies and infrastructure to support this transition.

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Appendix A: Cycling Performance Results for Direct Regeneration Attempts

The direct regeneration methodology followed in Chapter 3 was part of a series of trials to directly regenerate spent NCM622 cathode materials using a combination of molten salt relithiation and hydrothermal treatment. Variations of the experimental methodology discussed in Chapter 3 along with the corresponding cycling performance indicative of partial capacity restoration is shown in the figures below.

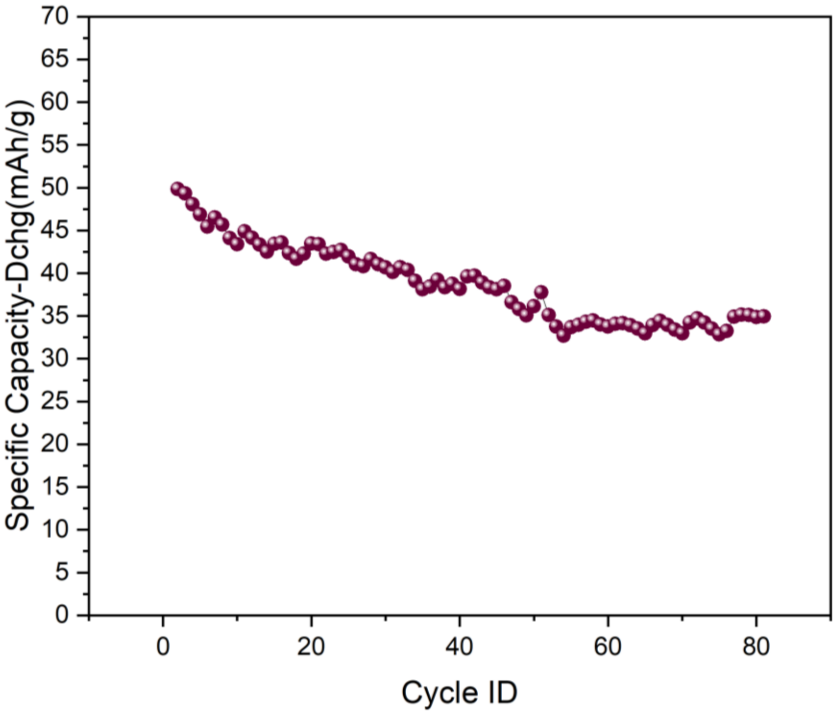

Figure A-1: Direct regeneration attempt using Li2CO3 as the molten salt

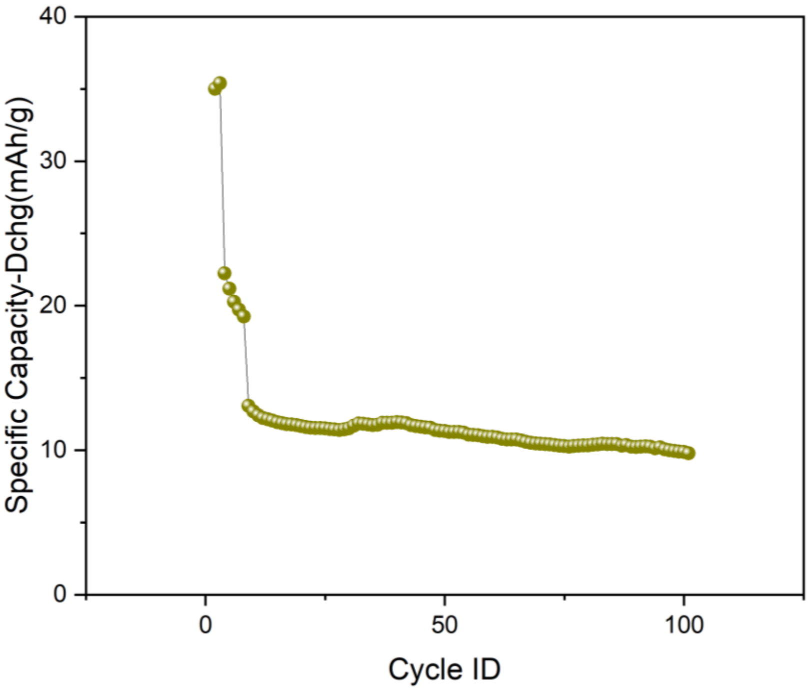

Figure A-2: Direct regeneration attempt using eutectic mixture of LiOH and Li2CO3 as the molten salt

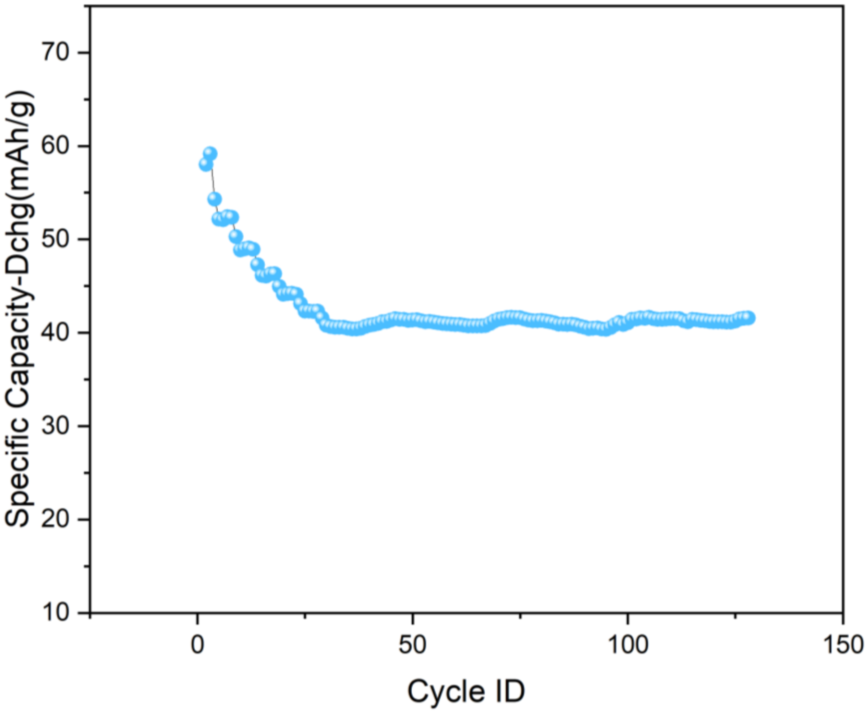

Figure A-3: Direct regeneration attempt with hydrothermal treatment performed first followed by molten salt treatment

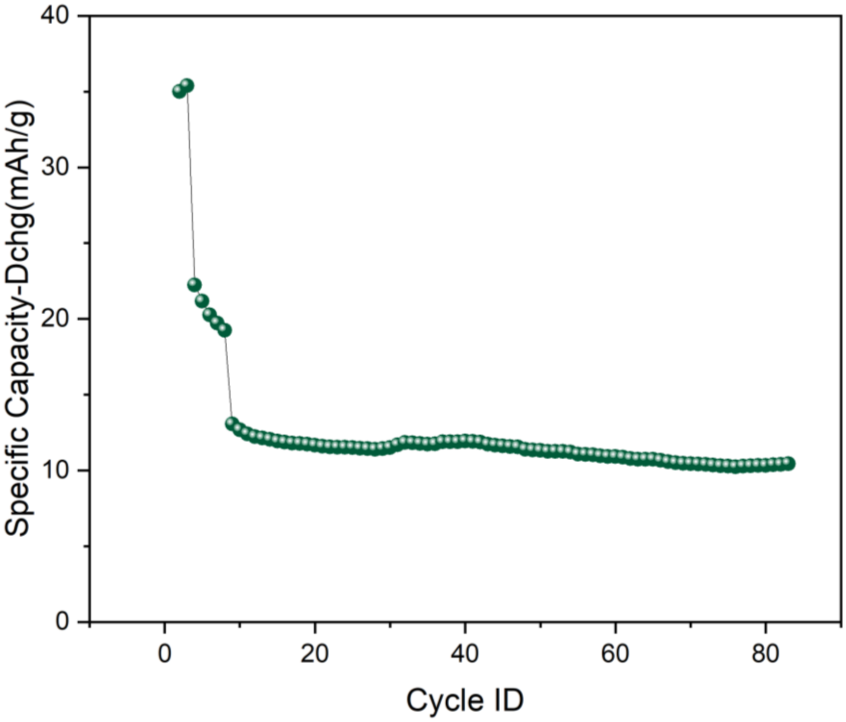

Figure A-4: Direct regeneration attempt utilizing two iterations of molten salt + hydrothermal treatment