

HYDROMETALLURGICAL RECOVERY OF LITHIUM AND COBALT FROM SPENT LITHIUM-ION BATTERIES

A thesis submitted to the Department of Materials Science and Engineering

African University of Science and Technology, Abuja

In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

By

Obetta, Emmanuel Chinonso

Supervisor:

Dr. Abdulhakeem Bello

African University of Science and Technology (AUST)

www.aust.edu.ng



P.M.B 681, Garki, Abuja F.C.T Nigeria

July, 2019

APPROVAL PAGE

**HYDROMETALLURGICAL RECOVERY OF LITHIUM AND
CARBONATE FROM SPENT LITHIUM ION BATTERY**

By

Obetta, Emmanuel Chinonso

**A THESIS APPROVED BY THE DEPARTMENT MATERIALS
SCIENCE AND ENGINEERING**

RECOMMENDED:

Dr. Abdulhakeem Bello
(Supervisor)

Head of Department
Materials Science and Engineering

APPROVED:

Chief Academic Officer

Dates

Certification

This is to certify that the thesis titled “*Hydrometallurgical recovery of lithium and cobalt from spent lithium-ion battery*” submitted to the Department of Materials Science and Engineering in the African University of Science and Technology (AUST), Abuja, Nigeria for the award of the Master's degree is a record of original research carried out by *Obetta, Emmanuel Chinonso*.

Abstract

The demand for lithium-ion batteries is high because of their high energy and power density, which most time is influenced by the lithium-ion cathode chemistry. However, the need for expensive and scarce metals, such as lithium and cobalt, in the cathode of these batteries will limit the supply of these batteries in the future. Thus, the need for a better way to retrieve the valuable metals in spent lithium-ion batteries. This study compares the morphology and chemical content of cathode active materials detached from the current collector (Aluminium foil) using DMSO, NMP and scratching. In addition, we investigated the viability of extracting cobalt and lithium by leaching using citric acid and precipitating using potassium hydroxide and sodium carbonate for cobalt and lithium, respectively. The results show that the morphologies of the cathode materials detached using the aforementioned methods are the same. Furthermore, the final result showed that cobalt and lithium can be recovered by leaching using citric acid (Leaching condition: solid/Liquid ratio (S/L) = 8 g/200 mL, 90 °C, 1 vol% H₂O₂) and precipitation [Precipitation condition: 4 M NaOH, pH = 12 (for cobalt)].

Acknowledgments

In all sincerity, I wish to acknowledge all those that contributed in one way or the other in ensuring the success of my masters' journey. I want to start by thanking the almighty God for making it possible for me to get to this level of my life and studies and for blessing me with all the people that served as my ladder rung. Special thanks to my supervisor, Dr. Abdulhakeem Bello, for making me understand what it takes for one to be a researcher. To my lovely family members, mum and dad, Nonye, Chekwus. Cherem, Ify and Amy, I want to say thank you for your support, financially and otherwise, and for not giving up on me. I appreciate the fatherly advice of our dear head of department, Prof. Onwualu. I cannot forget the assistance I received from Prof. Soboyejor and his battery energy group; thank you for giving me the privilege to be part of the group. Thanks to Dr. Vitalis Anye and AUST Faculties and technologist. And to my ever-loving classmate. I want to say thank you for your love and the assistance you render to me both inside and outside AUST. May God bless us all.

Dedication

I dedicate this work to my family all my family, for their sacrifices and prayers

Table of contents

Certification	i
Abstract.....	ii
Acknowledgments.....	iii
Dedication.....	iv
Table of contents.....	v
List of Tables	vii
List of Tables	ix
CHAPTER ONE	1
Introduction.....	1
1.1 Background of The Study	1
1.2 Motivation and Statement Of Problems.....	3
1.3 The Objective of The Study	5
CHAPTER TWO	6
Energy, Electricity, And Batteries.....	6
2.1 Energy	6
2.2 Electricity.....	7
2.3 Batteries	7
2.3.1 Brief History of Battery Development.....	7
2.3.2 Categories Of Batteries	9
2.3.3 Application of Secondary Batteries	10
2.4 The Lithium-Ion Battery	11
2.4.1 Component of Lithium-Ion Battery	12
2.4.2 Working Principle of Lithium-Ion Batteries	15
2.4.3 Important of Recycling Lithium-Ion Batteries.....	17
2.4.4 Demand For Lithium-Ion Batteries.....	17
2.4.5 Advantages of Lithium-Ion Battery	20
2.4.6 Disadvantages of Lithium-Ion batteries	20
2.4.7 Application of Lithium-Ion Battery	20
2.4.8 Current Challenges Associated with Lithium-ion Battery Growth.....	21
2.4.8 Danger and Environmental Threat of Lithium-ion Battery.....	21
CHAPTER THREE	30
Materials and Methodology	30
3.1 Materials description.....	30
3.2 Equipment.....	30

3.3	Experimental procedure	30
3.4	Material characterization.....	32
CHAPTER FOUR.....		33
RESULTS AND DISCUSSIONS		33
4.1	Battery Discharge.....	33
4.2	FTIR (Fourier transform infrared) spectroscopy.....	33
4.3	Scanning Electron Microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) Analyses.....	34
CHAPTER FIVE		37
CONCLUSION AND RECOMMENDATIONS		37
5.1	Conclusion	37
5.2	Recommendations.....	38
REFERENCE.....		1

List of Tables

Figure 1.1: Energy consumption by economic sector in ktoe [source: IEA].....	1
Figure 1.2: Graph of the demographic studies by WHO [4].....	2
Figure 1.3: New Policies Scenario Vs. EV30 @30 Scenario [Source: IEA].....	4
Figure 1.4: Projected annual sale Vs. Cumulative sale of Electric Vehicles [26]	5
Figure 1.5: Annual lithium-ion battery demand [source: BloombergNEF].....	5
Figure 2.1: Comparison of energy densities and specific energy of different secondary batteries [48]	11
Figure 2.2: Schematics of lithium-ion working principle [52]	16
Figure 2.3: Major market for recycled Lithium-ion batteries [54]	17
Figure 2.4: Global Lithium battery market, by chemistry, 2019, USD millions [56]	18
Figure 2.5: Global Lithium Battery market, by component, 2019, USD millions [56].....	19
Figure 2.6: Global lithium-ion battery market, by application, 2019 (%) [56]	19
Figure 2.7: The U.S. lithium-ion battery market size, by product, 2016–2027 (USD Billion) [57].....	19
Figure 2.8: Failure from cell, string, and module [59].....	22
Figure 2.9: General battery reactions [60]	23
Figure 2.10: Cell self-heating rate during forced thermal ramp test of Li-ion Gen 2 chemistry: anode = MCMB electrolyte = 1.2 M LiPF ₆ in EC:PC:DMC cathode = LiNi _{0.8} Co _{0.05} Al _{0.05} O ₂ separator = Celgard 2325 trilayer [59].....	24
Figure 3.1: Flow chart of the lithium and cobalt recovery from the spent lithium-ion.	32
Figure 4.1: FTIR spectra of the as-detached and uncalcined cathode material [B: as-detached cathode material; D: calcine cathode materials]	34
Figure 4.2: Morphology of cathode active material detached by (a) DMOS, (b) NMP (c) Scratching	35

Figure 4.3: Particle size distribution of the cathode materials detached by (a) DMOS, (b)NMP and (c) Scratching35

Figure 4.4: Morphology of leached residue for different solid to liquid (S/L) ratio the scratched off cathode materials: (a) 4 g/200 mL (b) 6 g/200 mL and (c) 8 g/200 mL35

Figure 4.5: EDS of spectra of different leaching filtrate with their corresponding elemental weight and atomic percent: (a) 6 g/ 200 mL and (b) 8 g/200 mL36

Figure 4.6: EDS spectra of the precipitate formed by the addition of KOH (left) and the corresponding elemental weight and atomic percent (right).....36

List of Tables

Table 2.1: Difference energy conversion and their roles [29]	6
Table 2.2: Overview of chemistry, energy and price indication of different lithium-ion cathodes [43].....	13
Table 3.1: Different leaching conditions of active cathode materials	31
Table 4.1: Voltage of lithium-ion batteries before and after discharge in a 3 wt.% NaCl solution.....	33

CHAPTER ONE

Introduction

1.1 Background of The Study

Energy is a fundamental need of every human being and has been described as a universal currency of technology without which society will not operate. The beginning of civilization is traced to when energy and its different forms were harnessed to assist humans in extending their capabilities and ingenuity[1,2]. Energy finds its relevance in places such as residential homes, industries, transportation, commercial and public services, agriculture and forestry, and fishing (Figure 1.1) [3]. Studies by the World Health Organization (WHO) highlighted vital roles played by household energy: preparing food and boiling water, preparing hot compresses, and the sterilization of utensils for patients [4]. Considering the transportation sectors, energy sources, such as petroleum, biofuels, natural gas, compressed and liquefied natural gas, and electricity account for 28% of global energy consumption [5].

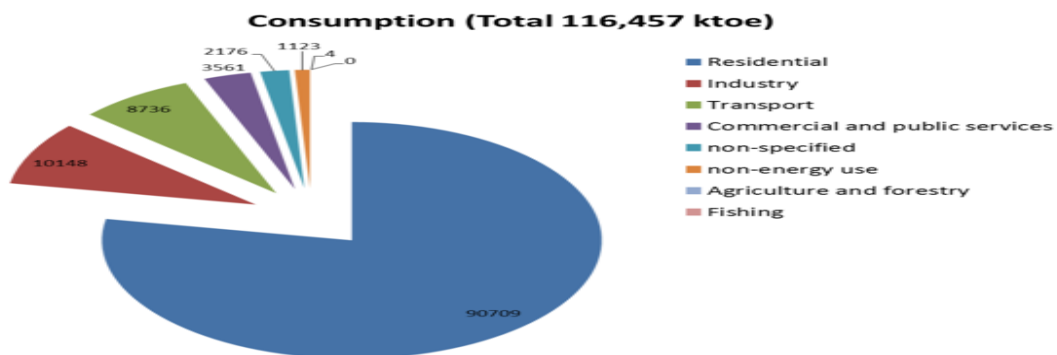
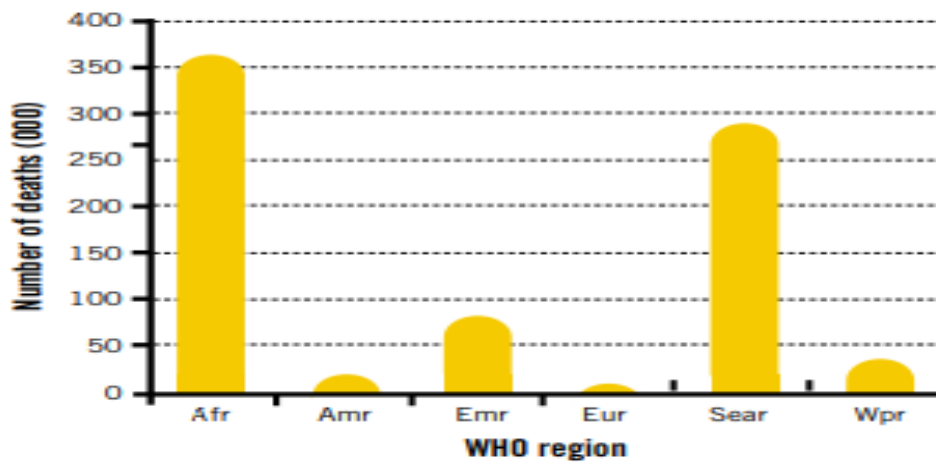


Figure 1.1: Energy consumption by economic sector in ktoe [source: IEA]

Energy has its pros and cons depending on the mode of generation and management. Fossil-based energy has played a great role in our homes and industries, but with tons of negative impacts on our environment. Demographic studies by the world health organization (WHO) shows that about 1.5 million people (with a greater percentage being children and women) have been killed by energy from wood burning, dung, coal, and other traditional energy sources, and most occurrence of the death is in Africa (Figure 1.2). They went further to state that air

pollution which comes from these sources is a major hindrance to millennium development goals (MDG) [4].



WHO distinguishes between the following geographical regions: African Region (Afr); Region of the Americans (Amr); Easter Mediterranean Region (Emr); European Region (Eur);South-East Asia region (Sear); Western Pacific Region (Wpr).

Figure 1.2: Graph of the demographic studies by WHO [4]

According to Midilli et al. [6], the development of Green Energy with no negative environmental and societal impact on our environment is the best way to secure a sustainable future as it has the capability of reducing greenhouse gases, maintaining a clean environment, and ensuring that we meet up with energy demands of the society. For sustainability, the development of renewable energy is considered a vital strategy. Green energy sources, like hydro, biomass, geothermal and wind energy, wave and tidal energy are numerous and inexhaustible in electricity production and contribute greatly to reducing carbon dioxide (CO₂), sulfur dioxide (SO₂), and Nitrogen dioxide (NO₂) emission [2, 8]. The reduction of these gases is very important because they contribute to the formation of acid rains.

Green energy has lots of benefits but its capability is limited by the fact that its generation is seasonal. To overcome this challenge, there is a need for the application of load or resource management that can ensure reconciliation of the state of art energy generation and energy storage technologies that will match the energy requirement of all time [8]. Ibrahim et al [9] buttress the fact that the development of storage systems is relevant to sustainable energy. This

shows that besides energy generation, energy storage has a fundamental role it plays in making energy available to the people who need it and at the time they need it. Varieties of energy storage systems abound on earth. And they include the following; Thermal energy storage (TES); chemical energy storage (CES); electrical energy storage system (EESS); electrochemical energy storage system and mechanical energy storage system (MESS) [8], [10]. Yang et al. [11] in their review presented lithium-ion battery as one of the electrochemical energy storage systems for Green Grid. The high volumetric and gravimetric energy density of the lithium-ion battery has earned it a place as the power source for portable electronics [12]. Studies have also shown that most of the metals used in Lithium-ion battery cathode materials are either expensive or scarce. The high cost of cobalt has been recorded as a limitation development of commercial lithium-ion that used LiCoO_2 [1]. Three decades ago lithium battery was commercialized [13], this implies that many Lithium-ion batteries are available in the market and our ability to find the best means of recovery all these expensive and scarce valuable metals will go a long way in ensuring continuity in this system of energy storage.

1.2 Motivation and Statement Of Problems

United nation (UN) agency working in the area of Energy in their report titled “The Energy Challenge for Achieving the Millennium Development Goals” outlines the roles play by the energy in ensuring that the Millennium development goal is achieved. They went further to direct people’s attention to the need to ensure sustainability in energy by replacing our conventional energy (fossil energy) source with renewable energy source[14], burning of fossil fuel accounts for 49% of the greenhouse gas (GHG) emission[15] and reducing it will ensure a reduction in global warming. Globally, transportation sectors contributes to 14% GHG emission [15, 16]. Ninety-five percent of the energy used in transportation comes from fossil sources such as gasoline and diesel [17]. Downsizing this energy source will reduce its negative impact on our environs. Strong efforts are being made to achieve this. Over 500 million cars vehicles and commercial cars abound in the world today, a number that is expected to double

within the next 20 years with an annual percentage increase of 3% [18], and the Public awareness of the greenhouse gas effect and a high price of fuel has called for the replacement of all these cars with Electrical vehicles (EVs), hybrid electrical vehicles (HEVs), and Plug-in hybrid electric vehicles (PHEVs). The international energy agency (IEA) predicted the number of electric vehicles that will be in the market by 2030 under two scenarios: With the current government policy, 125 million EV; with improved government policy, 228 million EV (Figure 1.3) [19].

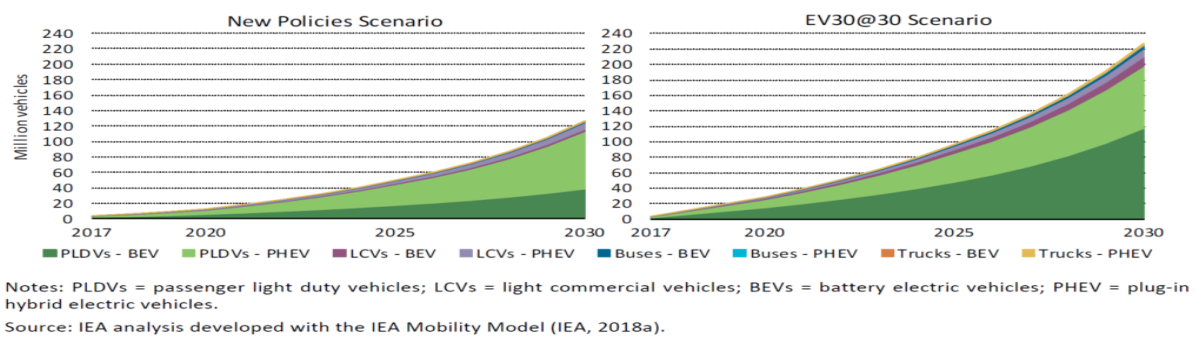


Figure 1.3: New Policies Scenario Vs. EV30 @30 Scenario [Source: IEA]

However, advancement in EV technology will be difficult if advanced energy storage systems with a high energy storage capacity and low emission potential are not made available[20]. Studies have shown that lithium-ion batteries are currently the best battery for EVs due to their relatively high power and energy density[21–23]. Among the lithium-ion battery, the cathode plays a greater role in determining the energy density of the cell and dominates the battery cost[24]. Based on the studies conducted by Argonne National Laboratory Battery Performance and Cost Model (BatPac), [20] inferred that the cost of the cathode material is nearly double of the cost of anode material, attributed to the fact that cathode contributes greatly in determining the working voltage, energy density, and rate capability of the LIB. By 2030, the light-duty vehicle fleet (cars and light commercial vehicles) represents the largest part of the fleet of electric four-wheelers, regardless of the scenario[25]. Electric vehicle sales are on the increase (Figure 1.4), while demand for lithium-ion batteries increases (Figure 1.5), hence the need for

a better way of recovering the valuable metals (lithium, cobalt, etc.) in lithium-ion battery cathode, so as to meet up with this future demand for lithium-ion batteries.

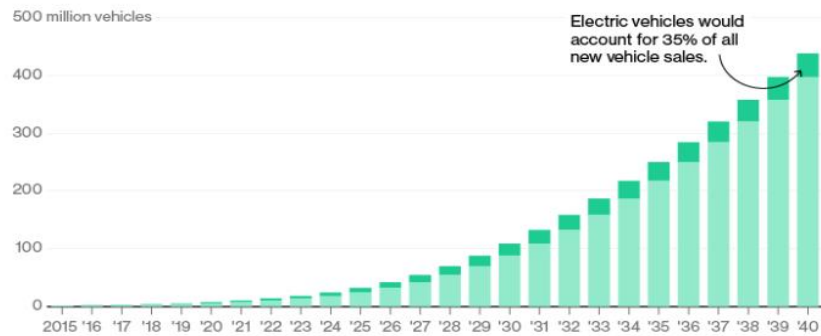


Figure 1.4: Projected annual sale Vs. Cumulative sale of Electric Vehicles[26]

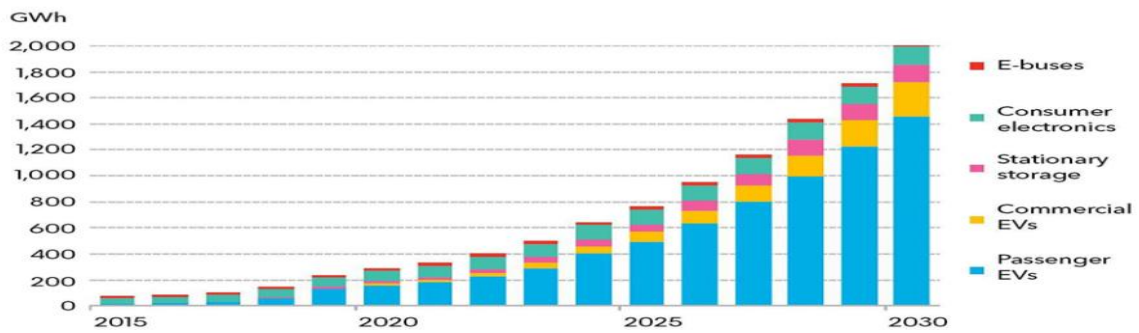


Figure 1.5: Annual lithium-ion battery demand [source: BloombergNEF]

1.3 The Objective of The Study

This study aims at recovering lithium (in its carbonate form) and cobalt (in its oxide form) from a spent Lithium-ion battery using hydrometallurgy.

CHAPTER TWO

Energy, Electricity, And Batteries

2.1 Energy

Energy is a term with no acceptable definition due to its ever-changing concept. It is a convertible quantity that defines the capacity for doing work [27]. Different energy types exist: kinetic energy is seen in the motion of particles (e.g., wind or moving water); Potential energy is the energy due to the position matter, for example, water stored in a dam, the energy in a coiled spring, and energy stored in molecules (gasoline). Several energy sources abound in our universe: mechanical, electrical, thermal (heat), chemical, magnetic, nuclear, biological, tidal, geothermal, and so on [28]. Energy and its conversions play a very important role in most of the activities that occur around (Table 2.1) [29]. The development and quality of our life, as well as the social and economic development of nations, depends on energy [30].

Table 2.1: Difference energy conversion and their roles [29]

from to	electro- magnetic	chemical	thermal	kinetic	electrical	nuclear	gravitational
electro- magnetic		chemilumines- cence	thermal radiation	accelerating charge phosphor	electro- magnetic radiation electro- luminescence	gamma reactions nuclear bombs	
chemical	photo- synthesis photo- chemistry	chemical processing	boiling dissociation	dissociation by radiolysis	electrolysis	radiation catalysis ionization	
thermal	solar absorption	combustion	heat exchange	friction	resistance heating	fission fusion	
kinetic	radiometers	metabolism muscles	thermal expansion internal combustion	gears	motor electro- strictions	radioactivity nuclear bombs	falling objects
electrical	solar cells photo- electricity	fuel cell batteries	thermo- electricity thermionics	conventional generator		nuclear batteries	
nuclear	gamma- neutron reactions						
gravitational				rising objects			

Energy is crucial for economic growth, therefore, the growth of a nation is a function of available energy. The process of economic development requires the use of higher levels of energy consumption since energy is essential for production, [31].

2.2 Electricity

Electricity is a phenomenon that involves static or moving electric charges. Electric charge is a fundamental property of matter borne by elementary particles. The particle involved in electricity is the electron, which carries a negative charge. Therefore, electricity is the result of the accumulation or motion of many electrons [32]. The first stage of electricity production is generation. Here, generators convert thermal, chemical, mechanical or nuclear energy to electrical energy, which is transmitted to points of use. In transmitting this electricity, an alternating current is used because it can be transmitted over a long distance with low energy loss. In the United State of America, this current is transmitted at a frequency of 60 Hz [33], whereas in Nigeria the transmission frequency is approximately 50 Hz (ie. Between 49.75–50.35 Hz) [34]. Finally, the voltage is stepped down to distribution levels and routed to distribution feeders. These supply primary voltage to customer transformers [33].

2.3 Batteries

A battery can be defined as the combination of one or more electrochemical cells that are capable of converting stored chemical energy into electrical energy [35]. Unlike liquid gasoline and diesel, compressed natural gas, liquid propane gas, compressed hydro, compressed air, and other any source that generate their energy in one system and store it in another system, Energy generation and storage in batteries are done in one system [36].

2.3.1 Brief History of Battery Development

Battery technology started in the 1780s when an Italian polymath Luigi Galvani observed a contraction in the muscles of a dead frog when it comes in contact with two dissimilar metals. He attributed the contraction to frog tissue characteristics. Therefore, he was not considered the first inventor of the battery since explain what he observed. Volta presumed that the frog's leg impulses were caused by different metals soaked in a liquid. He repeated the experiment using a cloth soaked in brine instead of a frog corpse and observed a similar voltage. In 1791, Volta published his observation. He went further to create the first battery called Voltaic pile

in 1800. Volta's pile had two problems: Electrolyte leakage due to the weight of the stack and short life span due to the chemistry of the components. William Cruickshank of Scotland resolved the leakage problem by laying the voltaic pile on its side to form the "trough battery." In 1835, William Sturgeon discovered that the short life span of the voltaic battery was caused by zinc degradation due to the buildup of hydrogen and impurities on its surface. However, he resolved the problem by treating zinc with mercury. The British chemist John Frederic Daniell used a second electrolyte that reacted with hydrogen to prevent buildup on the copper cathode. Daniell's two-electrolyte is known as the "Daniell cell".

The First Rechargeable Battery

In 1859, the French physicist Gaston Planté used sheet rolls of lead in sulfuric acid to create a battery. He observed that the battery returns to its original state when electricity is passed through it (due to the battery chemistry). Therefore, the battery marks the beginning of a rechargeable battery. In 1881, Camille Alphonse Faure improved on Planté's battery by replacing the sheet lead with plate lead. This new design made the batteries manufacture easy, hence the beginning of the widespread use of lead-acid batteries in automobiles

The Dry Cell

The difficulty in transporting liquid electrolyte batteries led to the design of dry cells in the late 1800s. The first dry batteries called Leclanché cell was produced by George Leclanché in 1866. Carl Gassner created an electrolyte from ammonium chloride and Plaster of Paris. He patented the new dry-cell battery in 1886 in Germany. Carl's new dry cells commonly known as "zinc-carbon batteries," became popular in the late 1950s.

20th Century Rechargeable Batteries

In the 1970s, COMSAT developed the nickel-hydrogen battery for use in communication satellites. These batteries store hydrogen in a pressurized gaseous form. Artificial satellites,

such as the International Space Station rely on these batteries. Several studies in the 1960s resulted in the creation of the nickel-metal hydride (NiMH) battery. NiMH batteries were commercialized in 1989 and were a cheaper alternative to the rechargeable nickel-hydrogen cells. Asahi Chemical of Japan built the first lithium-ion battery in 1985, however, Sony commercialized the battery in 1991. In the late 1990s, a soft, flexible casing was created for lithium-ion batteries and gave rise to the "lithium polymer" or "LiPo" battery[37]–[40].

2.3.2 Categories Of Batteries

Batteries are classified into two major categories, namely;

1. Primary batteries
2. Secondary batteries

Primary Batteries

Primary batteries are batteries that cannot be recharged once the power goes down because their active material cannot take its original form after the first usage [35]. The assembling of the components of this battery type is done in a charged state. Primary batteries use direct current to power our household items, such as flashlights and transistor radios [41]. In addition, these lightweight and cheap power sources are used in powering portable electric devices, such as lighting, photographic equipment, toys, memory backup. The benefit of this energy source is the shelf life, high energy density, moderate discharge rate, little or no maintenance requirement and ease of usage. The majority of primary cells come as single cylindrical cells and flat button or multi cells of these single-cell components. Some examples of primary cells include Zinc Manganese dioxide, Zinc/mercuric oxide battery, Zinc/silver oxide battery, Cadmium/ mercuric oxide battery, Zinc/air battery, Magnesium batteries, Aluminium batteries, Lithium batteries, Solid electrolyte batteries [42].

Secondary Batteries

In a Secondary battery, the charge and discharge are reversible and this implies the active materials can regain their form after the first usage. This type of battery is made up of many chemical and elemental components. The battery can be recharge after discharge by allowing the current to flow back in the direction contrary to the initial direction of the current, hence causing the electrode material to return to its initial state [1,2]. Secondary batteries are also referred to as electrochemical accumulators because they can be recharged [43]. This type of battery commonly referred to as rechargeable batteries are assembled in the discharged state [35]. Secondary batteries are used as the main source of battery in electrical vehicles, mine locomotives, submarines, or standby power required such as telephone exchange and emergency because they can endure many charging and discharging. They are also used to curb intermittency in electricity [41]. Some of the secondary batteries chemistry discussed by Burheim et al. [43] include lead-acid, nickel-cadmium (NiCd), nickel-metal hydride (NiMeH), Zebra (Zeolith Battery Research Africa), flow-cell batteries and lithium-ion batteries.

2.3.3 Application of Secondary Batteries

Secondary battery application is classified into two categories;

- 1.** In the first category, secondary batteries serve as an energy storage device that is connected to the primary energy source and supplying its energy to the load when needed. This is used in automotive and aircraft systems, emergency no-fail and standby (UPS) power sources, hybrid electric vehicles, and stationary energy storage (SES) systems for electric utility load levelling.
- 2.** In the second category, the secondary batteries are the primary source of energy that gets recharged after the energy has been used instead of being thrown away. These categories of secondary battery applications are used in portable consumer electronics, power tools, electric vehicles, etc., for reducing cost. They are also used in applications that need draining of power beyond that obtainable in primary batteries [42].

Secondary batteries are characterized by their high power density, high discharge rate, flat discharge curves, and good low-temperature performance. However, their energy densities are lower than those of primary batteries.

2.4 The Lithium-Ion Battery

In a lithium-ion battery, energy is generated by the transfer of lithium-ion from the cathode to anode of the battery cell (Charging) or the transfer of lithium-ion from the cathode to the anode of the battery cell (Discharging) [36]. The electrodes of the lithium-ion battery are intercalation compounds and this allows for de-intercalation and intercalation of lithium-ion from the cathode into the lattice lithium-ion battery anode during charging, or the other way round during discharging. During discharging, the anode is rich in lithium-ion with low potential while the cathode is poor in lithium-ion with high potentials, and this causes the movement of lithium from the anode to the cathode [8, 9]. This to and from the movement of Lithium-ion between the electrodes of lithium-ion battery earns it the name “rock chair battery” [45]. By the work of Dr. John Goodenough, Lithium-battery was commercialized in 1990 [2, 9]. Li-ion batteries since their commercialization have been the power of the house of personal digital electronics revolution [47]. Lithium metal is attractive as a battery anode material because of its lightweight, high voltage, high electrochemical equivalence, and good conductivity. Figure 2.1 compares energy densities and specific energy of different rechargeable/secondary lithium batteries.

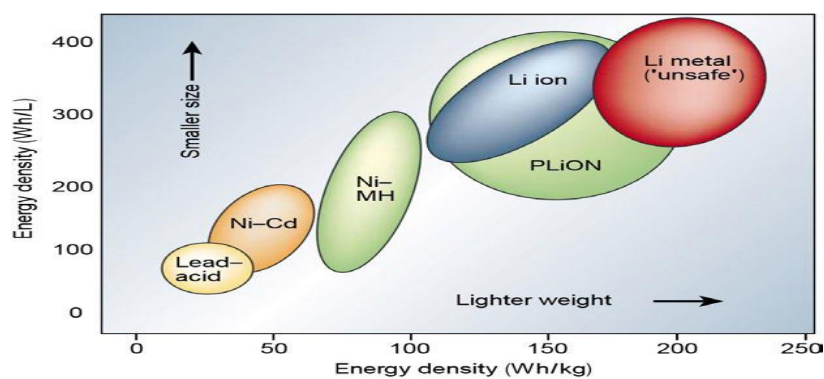


Figure 2.1: Comparison of energy densities and specific energy of different secondary batteries [48]

2.4.1 Component of Lithium-Ion Battery

There are five main components of lithium-ion batteries with the inclusion of the metallic or plastic casing of the Li-ion batteries [36]. However, lithium-ion batteries have four major components: cathode, anode, electrolyte and separator, without which the battery will function. [49]. This section describes the different components of the lithium-ion battery.

Cathode: this is the positive electrode material of the cell that consists of intercalation compounds of lithium-ion, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiFePO_4 and $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ [44]. The commercially available lithium-ion battery makes use of positive electrode active materials that come in the form of lithiated metal oxide placed on a substrate [36]. In a lithium-ion battery, the substrate is usually a thin film aluminium foil current collector, while the cathode active materials are usually a layer structure or tunnelled structure [45]. Difference chemistry used in lithium-ion battery technology includes the following: LFP, NMC, LCO, NCA, and LMO, and most manufacturers make use of these combinations to achieve a specific result [36]. The first oxide cathode material studied is the layered LiCoO_2 that has monovalent Li^+ and trivalent Co^{3+} ions are ordered on the alternate (111) planes of the rock salt structure with a cubic close-packed array of oxide ion [24]. Table 2.2 compares the different cathode chemistry of the lithium-ion battery.

Table 2.2: Overview of chemistry, energy and price indication of different lithium-ion cathodes [43]

Acronym Chemistry	LCO (LiCoO ₂)	LMO LiMn ₂ O ₄	NMC LiNi _{1/3} Mn _{1/3} CoO ₄	LFP LiFePO ₄
Voltage/V	3.8–4.4	3.8–4.1	3.8–4.0	3.2–3.5
(Theor.) Sp. Energy /Wh kg ⁻¹	(530) 190	(440) 150	(550) 160	(590) 160
Vol. Energy /Wh L ⁻¹	560	418	260	260
Cost, 2015/16 /US\$ (NOK) Wh ⁻¹	0.2 (1.5)	0.17 (1.3)	0.25 (1.9)	0.16 (1.2)
Corresp. Cycle Cost ^a /cent\$ (øre) kWh ⁻¹	2–18 (13–134)	2–15 (11–114)	2–22 (17–167)	1–14 (11–107)

^a Single cycle cost is based on 20–90 % SoC window, 80% SoH lifetime, and 2 000–20 000 cycles

The following are attributes of good cathodes materials used in lithium-ion batteries [45];

1. High free energy of reaction with lithium
2. Potential to accept large quantities of lithium
3. Reversibly accept lithium without structural deviations
4. High lithium-ion diffusivity
5. Excellent electronic conductivity
6. Insoluble in the electrolyte
7. Synthesized using cheap reagents
8. Low production cost

Anode: the anode is the negative electrode that consists of graphite carbon with a layered structure coated on a copper current collector. The first generation of commercialized lithium-ion batteries made use of coke as the anode material. However, graphitic carbon is currently in use because of its higher specific capacity, enhanced cycle life and rate capability. Mid-1990s electrodes were mostly graphite spheres, and a greater percentage of the graphite utilized were Mesocarbon Microbead (MCMB) with a good specific capacity of about 300 mAh/g, and low surface area, thus, providing low irreversible capacity and good safety properties. Recently, a wider variety of carbon types has been used in negative electrodes. Some cells use natural graphite, available at a very low cost, while others use hard carbons that offer capacities higher than graphitic materials. The structure of carbon affects its electrochemical properties and the intercalation capacity of lithium. The stacking of the basic unit of the carbon with a constitute

of a planar sheet of carbon atom arranged in a hexagonal array determines the structure of the graphite. The stacking in Bernite graphite is mostly ABABAB and this leads to the formation of 2H graphite whereas the stacking in the 3R graphite is ABCABC. The best way to identify graphite is using the percentage of 2H and 3R since most real graphite combines the two stacking patterns [45].

Electrolyte: Four types of electrolytes have been used in Li-ion batteries: liquid electrolytes, gel electrolytes, polymer electrolytes and ceramic electrolytes[8,10]. A polymer electrolyte is formed by dissolving an ionic conducting substance in a high molecular weight polymer. A gel electrolyte is made by dissolving salt and solvent in a high molecular weight polymer. A common example of Li-ion batteries gel electrolyte are films of PVDF-HFP, LiPF₆ or LiBF₄ salt dissolved in carbonate solvent. The absence of flammable, low volatility and high viscosity component make polymer electrolytes suitable for lithium-ion battery development. The advantage of gel electrolytes is that the polymer absorbs the solvent, therefore, making it difficult for leakage to occur in a battery produced using this type of electrolyte. A typical lithium-ion battery employs a liquid electrolyte that is absorbed by the electrodes of the cell. Ceramic electrolytes refer to inorganic solid-state materials that are ionically conductive. Propylene carbonate (PC) can degrade graphite electrodes during co-intercalation of lithium, thus, making lithium-ion battery industries work on other solvents for electrolyte solution solvents. These solvents include ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). Most cells utilize LiPF₆ with high conductivity and good safety properties. The LiPF₆ is cost-effective, hygroscopic and yields hydrofluoric acid (HF) upon reaction with water, Therefore, it must be handled in a dry environment. Organic salt with better stability in water has also been produced. An example of this organic salt is BETI (lithium bisperfluoroethanesulfonimide) [45]

Separators: This is a microporous polymer membrane that is designed to allow the exchange of lithium ions between the two electrodes but not electrons [47]. The positive and negative

electrodes are electrically isolated by this microporous polyethylene or polypropylene separator film in batteries that employ a liquid electrolyte [45]. This is used to avoid short-circuiting that can lead to the discharge of the battery [50].

Requirements for Li-ion separators:

- High machine direction strength to permit automated winding
- Low dimension shrinkage
- Ability to resist being punched by electrode materials
- Pore size that is less than 1 μm
- Get moist easily by the electrolyte
- Compatible and stable in contact with electrolyte and electrode materials [45].

2.4.2 Working Principle of Lithium-Ion Batteries

The active materials in Li-ion cells operate by reversibly incorporating lithium in an intercalation process, a topotactic reaction where lithium ions are reversibly removed or inserted into a host without a significant structural change to the host. When a Li-ion cell is charged, the positive material is oxidized and the negative material is reduced. In this process, lithium ions are de-intercalated from the positive material and intercalated into the negative material [45]. Charging of lithium-ion batteries involves the movement of lithium-ion from the cathode of the battery cell to the anode cell through the electrolyte/separator while discharging involves the return of the lithium-ion from the anode to the cathode. There is a simultaneous flow of electrons out of the external circuit to provide electricity, as shown in figure 2.2 [20]. The equation below represents the half redox charging and discharging of a lithium-ion battery as the lithium ions move between the anode and cathode [51]

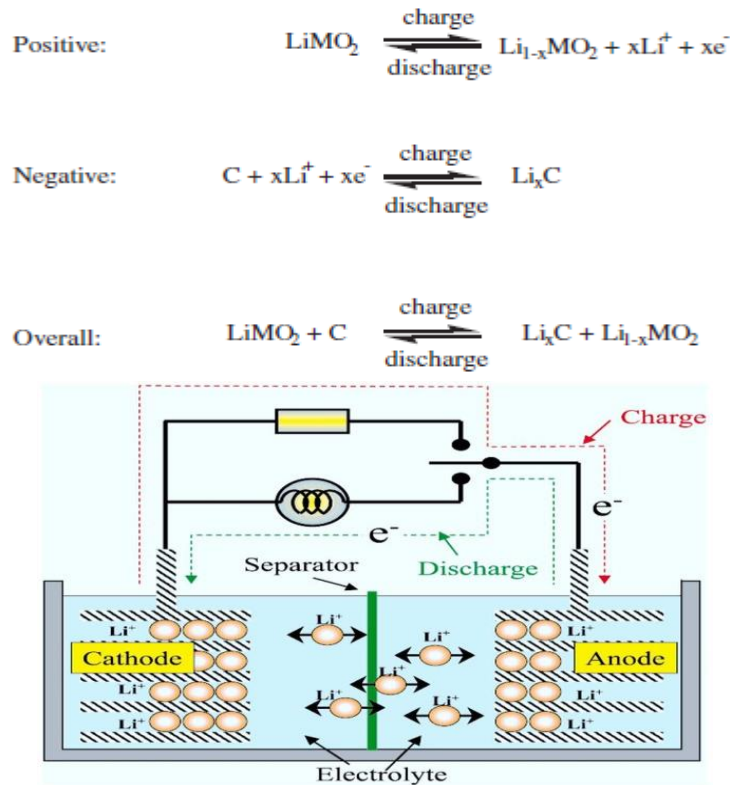


Figure 2.2: Schematics of lithium-ion working principle [52]

The basic design of Li-ion cells today is still the same as those cells Sony commercialized two decades ago, although various kinds of electrode materials, electrolytes, and separators have been explored. The commercial cells are typically assembled in a discharged state. During the charging process, the two electrodes are connected externally to an external electrical supply. The electrons are forced to be released at the cathode and move externally to the anode. Simultaneously the lithium ions move in the same direction, but internally, from cathode to anode via the electrolyte. In this way, the external energy is electrochemically stored in the battery in the form of chemical energy in the anode and cathode materials with different chemical potentials. During discharging, the reverse of what happened in charging occurs. This is also known as “the shuttle chair” mechanism, where the Lithium ions travel between the anode and cathodes during charge and discharge cycles. A Li-ion battery is constructed by connected basic Li-ion cells in parallel (to increase current), in series (to increase voltage) or combined configurations. The combination of different battery cells forms a module, and the combination of different battery modules forms a complete battery pack [47].

2.4.3 Important of Recycling Lithium-Ion Batteries

In the transportation sector, the need to shift from the use of Greenhouse gas (GHG) gas emitting vehicle has resulted in the fastest growth in the lithium-ion battery recycling market to support the limited lithium metal used in the lithium-ion battery of EVs, with the major recycling market taken place in China and USA (Figure 2.3). With the present market projection, the use of lithium cobalt oxide (LCO) battery is expected to continue generating the highest revenue in the lithium-ion battery recycling market up till 2030 [53]. This is because such energy storage is widely used in portable consumer electronics, including mobile phones, laptops, and tablets [53], [54]. Recycling lithium-ion batteries secures the supply of raw materials, such as lithium and cobalt used in such batteries, thereby reducing reliance on mineral resources extraction and refining. In addition, Lithium-ion battery recycling bridges the demand-supply gap [22, 24].

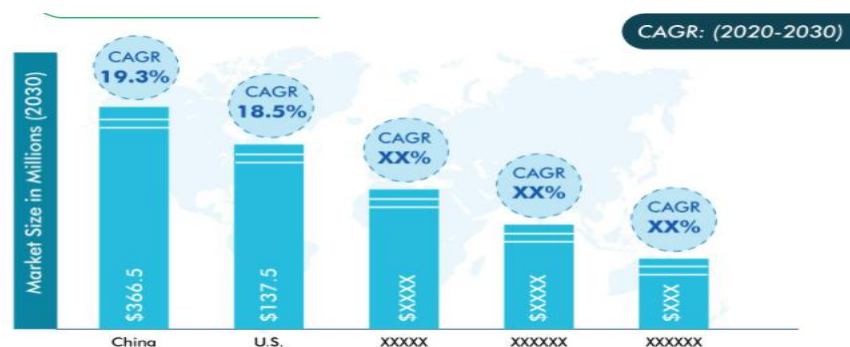


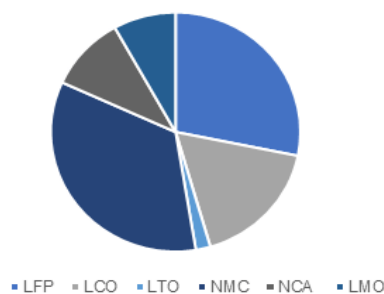
Figure 2.3: Major market for recycled Lithium-ion batteries [54]

2.4.4 Demand For Lithium-Ion Batteries

Increasing demand for consumer electronics, plug-in vehicles, automation and battery-operated materials handling equipment in industries, and the growing need for research and development drives the growth of lithium-ion batteries and has led to the rapid expansion of battery production capacity. The global lithium-ion battery market was valued at USD 36.7 billion in 2019 and is expected to hit USD 129.3 billion by 2027, at a compound annual growth rate (CAGR) of 18% from 2020 to 2027 [53]. The interest to solve the problems associated with an upsurge in environmental pollution increased the demand for electric vehicles and a

corresponding increase in the lithium-ion battery industry. Globally, about USD 40 billion worth of lithium-ion batteries penetrated the market in 2019 and is anticipated to grow by 15% through 2026. The demand for electric vehicles will make a positive impact on the lithium-ion battery industry. The automotive segment accounted for the majority of the market share in 2019 [56]. According to [55], the market for lithium-ion batteries is expected to register a compound annual growth rate (CAGR) of 22.58% between 2020 and 2025. The major factors driving the market studied are the emergence of new and exciting markets, via electric vehicle and energy storage systems (ESS)(for both commercial and residential applications), declining lithium-ion battery prices, and the increasing sale of consumer electronics [55]. The growth of the market is attributed to the growing demand for lithium-ion battery in electric vehicles (EVs) and grid storage as it offers high-energy density solutions and lightweight.

The lithium-ion battery market is segmented by chemistry (LFP, LCO, LTO, NMC, NCA, and LMO) (Figure 2.4); component (cathode, anode, electrolytic solution, and Others) (Figure 2.5); end-use Industry [electrical and electronics (smartphones and tablet/PC, UPS, and Others) and automotive (cars, buses, and trucks; scooters and bikes; and trains and aircraft), and industrial (cranes and forklift, mining equipment, and smart grid and renewable energy storage)] (Figure 2.6). It also covers global opportunity analysis and industry forecast to 2027. This report is published on valuate report in the chemical industries Category [56]. Figure 2.7 shows the market for the lithium-ion product from 2016 – 2017.



Source: www.gminsights.com

Figure 2.4: Global Lithium battery market, by chemistry, 2019, USD millions [56]

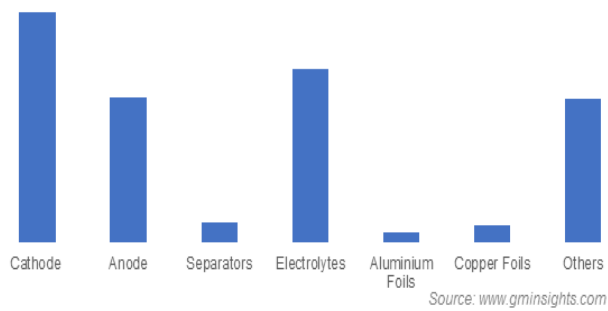


Figure 2.5: Global Lithium Battery market, by component, 2019, USD millions [56]

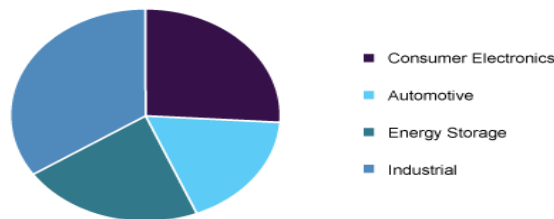


Figure 2.6: Global lithium-ion battery market, by application, 2019 (%) [56]

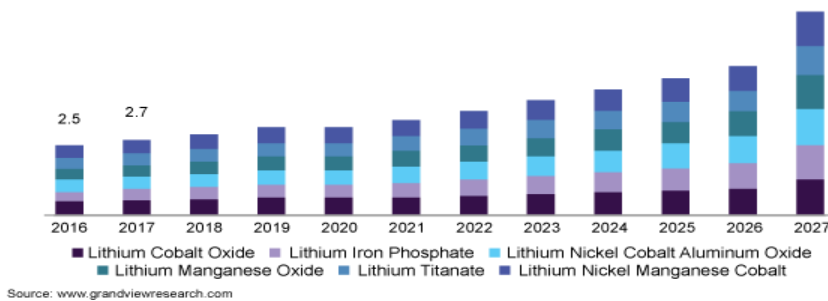


Figure 2.7: The U.S. lithium-ion battery market size, by product, 2016–2027 (USD Billion) [57]

An increase in sales of electric vehicles in China is projected to drive the market for lithium-ion batteries because of government subsidies and purchase shares on non-electric vehicles in big cities. In addition, electric vehicle companies, such as Nissan, BMW, Tesla, Chevrolet, Ford, Toyota, and Fiat mainly in the United States, United Kingdom, Germany, and China is anticipated to propel market growth. Moreover, electric vehicles (EV) and hybrid electric vehicles (HEVs) will continue to observe growth as we shift from fossil fuels to electric batteries. In addition, the government's strict regulations on emission standards to protect the

environment and decrease the degradation-based possibilities are likely to play a critical role in influencing the market for lithium-ion batteries [57].

2.4.5 Advantages of Lithium-Ion Battery

1. Lithium-ion batteries are relatively lightweight batteries.
2. The energy density of Lithium-ion batteries is relatively high, therefore more energy can be stored in them due to the presence of lightweight and highly reactive lithium and carbon electrode.
3. The discharge rate of lithium-ion batteries is low compare to other battery technology. For instance, lithium-ion batteries lose 5% of charge in a month while NIMH batteries looses 20% of their charges
4. The memory effect observed in other batteries does not occur in a lithium-ion batteries, hence lithium-ion batteries do not need to be discharge completely.
5. Lithium-ion batteries can be cycled a hundred times.

2.4.6 Disadvantages of Lithium-Ion batteries

1. The cost of lithium-ion batteries is relatively high.
2. Lithium-ion batteries are sensitive to high temperatures and can be easily degraded by heat.
3. Complete discharge of a lithium-ion battery means the end of life for the battery.
4. Lithium-ion has a low life span [58].

2.4.7 Application of Lithium-Ion Battery

Lithium-ion batteries are used in consumer electronics, such as cell phones, laptop computers, personal data assistants, as well as military electronics, including radios, mine detectors, and thermal weapons sights. Potential applications of Lithium-ion include aircraft, spacecraft, satellites, and electric or hybrid electric vehicles [45].

These battery units have high penetration across consumer electronics products that require high energy density. The ongoing growth of the e-commerce industry fueled the demand for

consumer electronics on a global scale, thereby complementing market demand for lithium-ion battery units [56].

The lithium-ion battery is used in electronic devices such as smartphones, power tools, and digital cameras, and this will probably increase the demand for the battery, as storage or power backup devices, in the railways, manufacturing sectors, and solar power, etc. Long life span, reduction in battery prices, and high density will drive the market for lithium-ion batteries over the forecast period [57].

2.4.8 Current Challenges Associated with Lithium-ion Battery Growth

Currently, the lithium-ion battery deployment is anticipated to witness subdued growth on account of the ongoing COVID-19 pandemic. Governments across the globe have implemented social distancing measures of varying degrees to control the spread of disease. Large-scale lockdown of manufacturing units and shortage of manpower is a few of the factors that will decrease lithium-ion battery installation of lithium-ion battery units [56]. In addition, the growing demand for other batteries, such as lithium-air, flow batteries, sodium nickel chloride, and lead-acid batteries in energy storage, consumer electronics, and electric vehicles are projected to restrain the lithium-ion battery market [57].

2.4.8 Danger and Environmental Threat of Lithium-ion Battery

The fire on two Boeing 787 Dreamliner associated with Li-ion batteries highlights the importance of battery safety, which is set to trigger extensive research and development to enhance the safety of Li-ion batteries, beyond pursuing high-energy-density [47]

Safety is critical in any energy storage device, including batteries. Batteries contain an oxidizer (cathode) and fuel (anode) in a sealed container, which under normal operation, converts chemical energy to electrical energy with minimal heat and negligible gas. If allowed to react chemically in an electrochemical cell, the fuel and oxidizer convert the chemical energy

directly into heat and gas. This reaction is a chain reaction because of the intimate contact of fuel and oxidizer. Therefore, safety needs to be addressed at the cell, string, module, pack, and ultimately vehicle levels because failure at any of the levels will cause a severe failure at a higher level. Figure 2.8 shows failures at each of these levels that can destroy all components of the full battery system.

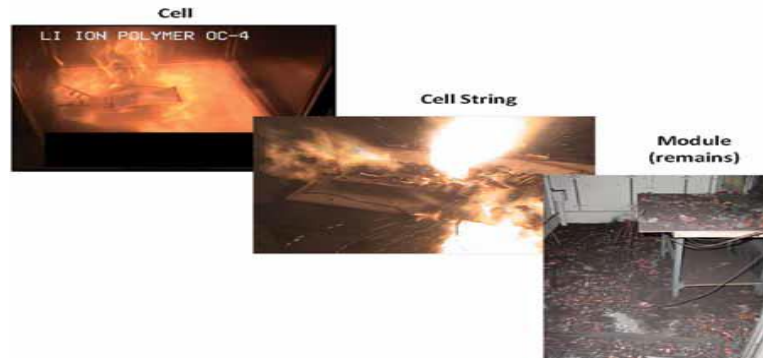


Figure 2.8: Failure from cell, string, and module [59]

Failure at these levels can lead to the loss of a complete vehicle. Safety is not a function of one criterion or parameter, rather, it is determined by approaches that work together to enhance safety. These approaches include (a) reducing the probability of an event and (b) lessening the severity of the outcome when an event occurs. Thermal stability is the most important of several parameters that determine the safety of Li-ion cells, modules and packs [59].

The goal of many battery development programs is to increase the run time of electronic devices or extend the driving range of EVs, which is achieved by increasing the energy content. Thus, new electrode materials with increased capacity and voltage are being developed and new cell and battery pack designs appear in the marketplace. This energy increase necessitates the design of safe battery packs and cells. Therefore, safety at every step of battery design (materials selection, cell design, electronic controls, and module/pack design) is important [59]. High energy density and the presence of flammable organic electrolyte causes fire hazards in lithium-ion batteries, hence, the need for a better way of using, storing, and handling batteries. Manufacturing defects, such as imperfections or contaminants in the manufacturing process can cause thermal runaway. The reaction vaporizes the organic electrolyte, leading to casing

pressurization. The failure of the casing will result in the release of flammable and toxic gases. The severity of a runaway is related to the buildup and release of pressure from inside of the cell. Cells with a means of releasing this pressure (i.e., pressure relief vents or soft cases) produce less severe reactions than cells that contain the pressure and rupture due to high pressure (i.e., unvented cylindrical cells). Therefore, cell construction can be a major variable in determining the severity of a battery incident. The resulting reaction includes rapid venting of thick smoke (i.e., smoke bomb/smoker), to a road flare, to a steady burn, to a fireball to an explosion, as shown in Figure 2.9 [60].



Figure 2.9: General battery reactions [60]

Typical Battery Failure Modes

Thermal abuse: Heat generation caused by battery thermal abuse is hazardous. For example, short-circuiting will heat the cell because of Joule heating (I^2R) until the cell begins to produce heat by internal chemical reactions (i.e., above the temperature where the onset of self-heating reactions begins). Overcharge can generate heat within the cell due to other oxidative chemical reactions that can trigger thermal runaway. To characterize heat and gas generation that might occur in abnormal conditions, cells and packs are exposed to elevated temperature abusive conditions (that represent the field environment).

The cell response during this test falls into three regimes: onset, acceleration, and thermal runaway (figure 2.10).

The figure shows the temperature rise during the thermal ramp of a fully charged lithium-ion cell. Here, an external source of heat (that simulates an abuse event) is used to raise the temperature of the cell to the onset temperature [$T(\text{onset})$] i.e, self-rating drate of $0.2\text{ }^\circ\text{C}/\text{min}$.

This low heat generation can be allowed in the battery packs. Increased reactivity is the result of SEI decomposition, exposing the reactive anode to the self-heating reactions with the electrolyte. Non-dissipation of the heat will cause a continuous rise in temperature due to sustained exothermic reaction, which can lead to the second regime known as the acceleration regime [T(acceleration)]. This stage is characterized by rapid and accelerating heat release. This stage results from increased electrolyte reduction at the anode due to continuing loss of the SEI and to the onset of electrolyte oxidation at the active cathode surface. This reaction is a function of active material chemistries and state of charge. Venting and release of smoke may occur during the second regime. Additional heating causes the cell to enter the regime (runaway), which is the regime of self-heating rate of ≥ 10 °C/min caused by the high-rate cathode and anode reactions. Intervention in this regime is always very difficult.

Runaway temperature [T(runaway)] depends on cell size, design, and materials. T(runaway) varies from 130 °C to well over 200 °C in lithium-ion cells. Cathode materials that release oxygen at high temperatures have especially high reaction rates and reaction enthalpies. Thermal runaway time can be delayed by minutes, hours, or days, depending on the design of the battery pack and the operating environment. Studies have shown that physical damage, electrical abuse such as short circuits and overcharging, and exposures to elevated temperature can cause a thermal runaway. This refers to rapid self-heating from an exothermic chemical reaction that can result in a chain reaction thermal runaway of adjacent cells.

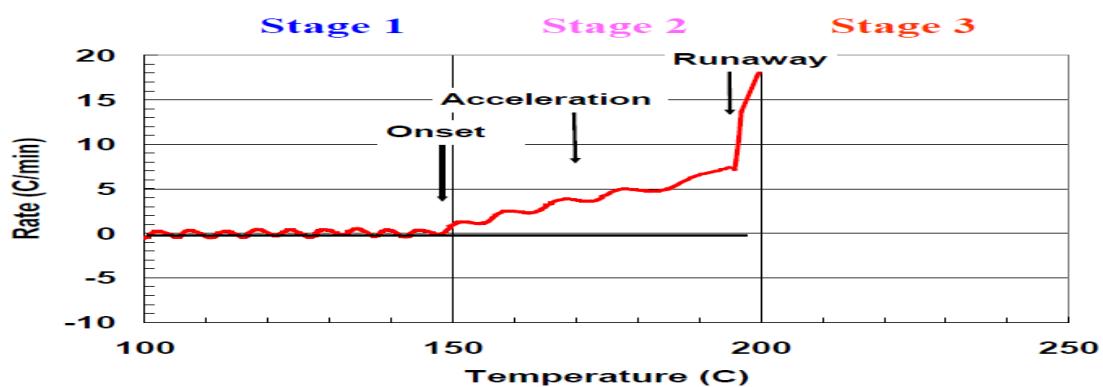


Figure 2.10: Cell self-heating rate during forced thermal ramp test of Li-ion Gen 2 chemistry: anode = MCMB | electrolyte = 1.2 M LiPF6 in EC:PC:DMC | cathode = LiNi0.8Co0.05Al0.05O2 | separator = Celgard 2325 trilayer [59]

Physical damage: Physical damage, such as puncture, crush, vibration, or shock can create an internal short circuit within the cell or battery pack, causing current flow in an unintended and unanticipated manner. Cells and batteries with higher specific energy (Wh/ kg) and energy density (Wh/L) will respond more to abuse by puncture, crush, or shock. In addition, cells with flammable electrolytes or materials have the potential to produce secondary fires.

Charge and discharge failures: Failure in the battery management system (BMS), such as pack control electronic can lead to the battery over or over-discharge. The ability to withstand overcharge depends on the current level (low charging current is more likely to result in benign failure), as well as the chemistry of the battery. The response of cells and battery packs during overcharge depends on overcharge parameters (current, maximum voltage), thermal environment, and cell materials and is a complex function of several failure mechanisms. Cathode chemistry determines the thermal response of lithium-ion batteries. During the charge cycle, lithium is removed from the cathode oxide material. Different cathode oxide chemistries have different levels of lithium when fully charged; varying from $\text{Li}_{0.5}\text{CoO}_2$ to LiFePO_4 at 100% SOC. Overcharging continues to remove lithium from the structure, resulting in permanent crystallographic changes and increased oxidation potentials. Measurements of heat flow from the cells and cell skin temperature during overcharging show that there is a rapid increase in heat generation when all of the lithium has been removed from the cathode.

Short Circuit: External short circuit is the most common type of battery abusive condition. All safety test protocols (for shipping approval, as well as use environments) include short circuit tests. A cell is connected to a test circuit in which the external resistance is either matched to the unit impedance or is set as low as 1 m.ohm The current and cell temperature is monitored, as well as cell response, such as venting and possible self-ignition. Cells typically can withstand an external short circuit, since the thermal output is small and the cell is in contact with the test fixture. Thermal management will dictate if the response of cells will be benign or exhibit thermal runaway. Large cells (i.e., over 10 Ah), cells that can sustain very large short

circuit currents, cells that have higher internal resistance, and cells with low inherent thermal stability are more prone to exhibit thermal runaway [59].

Safety Devices

Safety devices are incorporated into cells, modules and battery packs to protect against odd conditions and to manage heat and gas generation. Some of these safety devices include;

- Shutdown separators between anode and cathode prevents ionic conduction if cell internal temperature exceeds a certain limit, thus preventing further cell charge/discharge.
- Cell vent or Tear-away tab allows the safe release of gas if excessive pressure builds up within cells.
- Current interrupt device (CID) protect against over-current that breaks the internal electrical connection when the internal pressure reaches a set value.
- Positive temperature coefficient of expansion (PTC) disks is often placed in the cell header to limit high current.
- Current limiting fuses may be used in place of PTC devices when a sustained discharge is not preferred.
- Diodes may be used to prevent inadvertent charging (blocking diode) or to steer the discharge current around a weak cell as in a discharge (bypass diode).
- Battery Management System (BMS) that controls electrical distribution with a battery pack and protects against over- or under-voltage conditions.

Current Researches on Recycling Lithium-ion Battery

Techniques for recycling portable batteries can be broken into three general categories: mechanical, pyrometallurgical and hydrometallurgical processes. Often, a combination of these techniques is used in succession for the recovery of different materials [61].

Pre-treatment separation processes

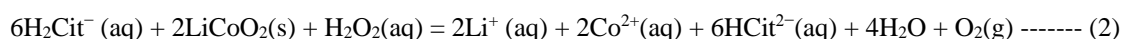
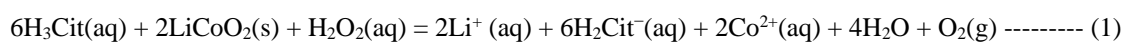
The first stages of LIB recycling involve a pretreatment step to separate the cathode active materials from the battery casing, separator, current collector, electrolyte, carbonaceous additives, and connections. The approaches utilized in the literature should be divided into lab- scale and large/industrial- scale methods. Lab- scale approaches result in excellent cathode active material separation and efficiency and are often used in experiments that focus on leaching and/or subsequent metal recovery. On the other hand, industrial- scale approaches have high process capacity and throughput, but metal separation is less refined.

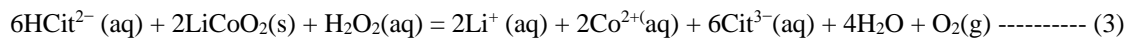
In a typical lab- scale approach, the LIB cell is first discharged by soaking the cell in a saturated brine solution for approximately 24 [62]. To avoid short-circuiting and self-ignition, the spent LIB samples were first fully discharged for 24 h by submersion in a 5 wt.% NaCl solution, and then manually dismantled using sharp-nosed pliers in a fume hood. After the removal of both the plastic and metal cases, the cathode, anode, and separator of each LIB were uncurled and separated. The cathodes were dried for 24 h at 60 °C and cut into small parts (10 mm x 20 mm) with scissors [63]. Jelena et al.[64] separated cathode material from aluminum current collector using three methods: the first separation method was achieved using 5 M NaOH for 30 mins; the second method involves the use of NMP in an ultrasonic bath for 60 mins; the last method entails annealing the whole cathode materials in the air at 600 °C, thus making it possible for the cathode materials to be stripped up from the current collector. The result recorded higher separation inefficiency in cathode material separated using method 1 (NaOH). Li-Po et al.[63] confirmed that with organic liquid (Solid/Liquid ratio: 1:10 gmL^{-1}) cathode materials can be removed from the aluminum current collector at a temperature between 40 °C and 80°C, ultrasonic power between 160–400 W (frequency: 40Hz), and ultrasonic time between 30–120 min. The cathode materials separated from Al foil were then filtered, washed with deionized water and dried. The objective of this study was to develop an effective process for separating and recovering Al and cathode material from spent LiBs. Zeng et al. [65] used theoretical analysis

and experimental study to verify the feasibility of using heated ionic liquid (IL) to separate cathode material from an aluminum current collector; the result shows that with proper control of the major process parameters that the cathode material-peeling rate of 99% efficiency can be achieved.

Leaching of Cathode Materials

Zheng et.al [66] studied the effects of molar ratio, solid-liquid ratio, reaction time and temperature on cobalt leaching efficiency, taken into consideration the leaching kinetics and the apparent activation energy of the leaching reaction. The results of their experiment reveal that leaching of efficiency of 99.07% was achieved using citric acid to lithium cobalt oxides molar ratio, 4:1, solid-to-liquid ratio, 15 g/L, reaction temperature, 90 °C, the reaction time, 5 h and the concentration of H₂O₂, 1.0 vol. Around 55%, 80% and 95% of aluminum, cobalt and lithium, respectively were leached out from the cathode using H₂SO₄ solution and some percentage of H₂O₂, according to an experiment by Dorella et. al. [67]. Shuva et.al. [68] leached lithium and cobalt from LiCoO₂ by increasing temperature, the concentration of HCL and solid-to-liquid ratio. They discovered that with hydrochloric acid concentration = 3 M, solid-liquid ratio = 1:20 (gm/ml), Temperature = 80°, time = 60 min, hydrogen peroxide = 3.5% and stirring speed = 400 rpm, that 89% lithium and cobalt can be recovered. In addition, Li et al.[69] conducted leaching experiment on LiCoO₂ using 1.25 M citric acid, 1.0 vol.% hydrogen peroxide and a solid-to-liquid ratio of 20 g L⁻¹, leaching time of 30 min and temperature at 90 °C, with agitation at 300 rpm, in a batch extractor. The result of their experiment shows that approximately 100 % Li and more than 90% cobalt were recovered. According to them, leching equation according to them may be any of equations (1), (2) and (3).





Metal Precipitation

In the precipitation experiment by Dorella et al. [67] NH_4OH was added to a leach liquor to increase the pH. At a pH of 5, aluminium was separated from cobalt and lithium. After filtration, the aqueous solution was taken to the next stage where Cyanex 272 was used to recover around 85% of cobalt via liquid-to-liquid extraction. Based on the experiment by Shuva et al. [68] more than 95% of cobalt was precipitated from leach liquor at pH value between 11 and 12, leaving 93% lithium and sodium hydroxide (NaOH) in the leached liquor. In the same experiment, lithium was precipitated out of the liquor using Lithium carbonate at 100 °C [68]

CHAPTER THREE

Materials and Methodology

3.1 Materials description

Spent lithium-ion laptop batteries from AUST ICT office; hydrogen peroxide (H_2O_2); sodium chloride (NaCl); sodium carbonate Anhydrous (Na_2CO_3)(about 99.5% purity) and potassium hydroxide pellet (KOH) (about 85% purity) were obtained from Loba Chemie Pvt Ltd, 107 Woodhouse Road, Jehangir Villa Mumbai India; citric acid ($C_6 H_8 O_7$) (was purchased from BDH Laboratory Supplies Poole, BH15 1TD England; n-methyl-2-pyrrolidone (NMP); Dimethyl sulfoxide (DMSO).

3.2 Equipment

Scanning electron microscope (SEM/EDX) [zeiss model, EVO/LS10)]; Fourier transform infrared (FTIR) spectrometer [thermo scientific Nicolet Is5 spectrometer); vacuum desiccator; Muffle furnace; pH and conductivity meter; ball Milling machine; vacuum desiccator; bottom flask; magnetic stirrer, vapor condenser.

3.3 Experimental procedure

Battery discharge: The batteries were discharged by immersing in a 3 wt% NaCl solution for a period of 24 h. The PH and conductivity of the solution before the discharging process were 7.782 and 48.1 mS/cm, respectively. The PH and conductivity of the discharging solution after the battery discharge were 7.213 and 50 mS/cm respectively.

Dismantling of the batteries: First, the batteries were dismantled by mechanically removing the steel casing using a plier and high cutter scissors, and then, the electrodes (cathodes and anodes) were unrolled from each other.

Cathode active materials detachment from the aluminum current collector: In separating the cathode active material from the aluminum current collector, two techniques were employed;

Chemical dissolution: two chemical dissolution methods were used in detaching the cathode active materials from the current collector (Aluminum foil), and they include dissolution by NMP and DMSO at 70 °C for 90 min under mechanical agitation.

Mechanical scratching: active materials detachment from the current collector by mechanically scratching it off using a cutter knife

Calcining and grinding of the cathode active materials: Calcining was conducted at 750 °C for 3 h using a muffle furnace to remove PVDF and carbon (organic materials) from the active materials. In addition, the calcined active material was ground using a ball mill for 10 min and at a speed of about 260 rpm to enhance leaching efficiency.

Leaching of the calcined cathode materials: Leaching was conducted on the calcined active materials using a citric acid solution and hydrogen peroxide under the three conditions shown in Table 3.1.

Table 3.1: Different leaching conditions of active cathode materials

LEACHING PROCESS	CONDITIONS
1	1.25 M citric acid, 90 °C; S/L: 4 g/200 ml; 1vol % H ₂ O ₂
2	1.25 M citric acid, 90 °C; S/L: 6 g/200 ml; 1vol % H ₂ O ₂
3	1.25 M citric acid, 90 °C; S/L: 8 g/200 ml; 1vol % H ₂ O ₂

3.3.6 Precipitation of the cobalt and lithium: First, to precipitate cobalt in the form of its hydroxide [Co(OH)₂], 4 M KOH was added to the filtrate from the leached solution at a PH of 12. This process leads to the formation of a pink precipitate, which was later filtered, washed, and dried. Second, a saturated solution of sodium carbonate was added to the filtrate from the cobalt precipitation step. The setup was stirred for 4 h at 80 °C to precipitate lithium in the form of its carbonate.

The Flow chart for the entire recycling process is as shown in Figure 3.1.

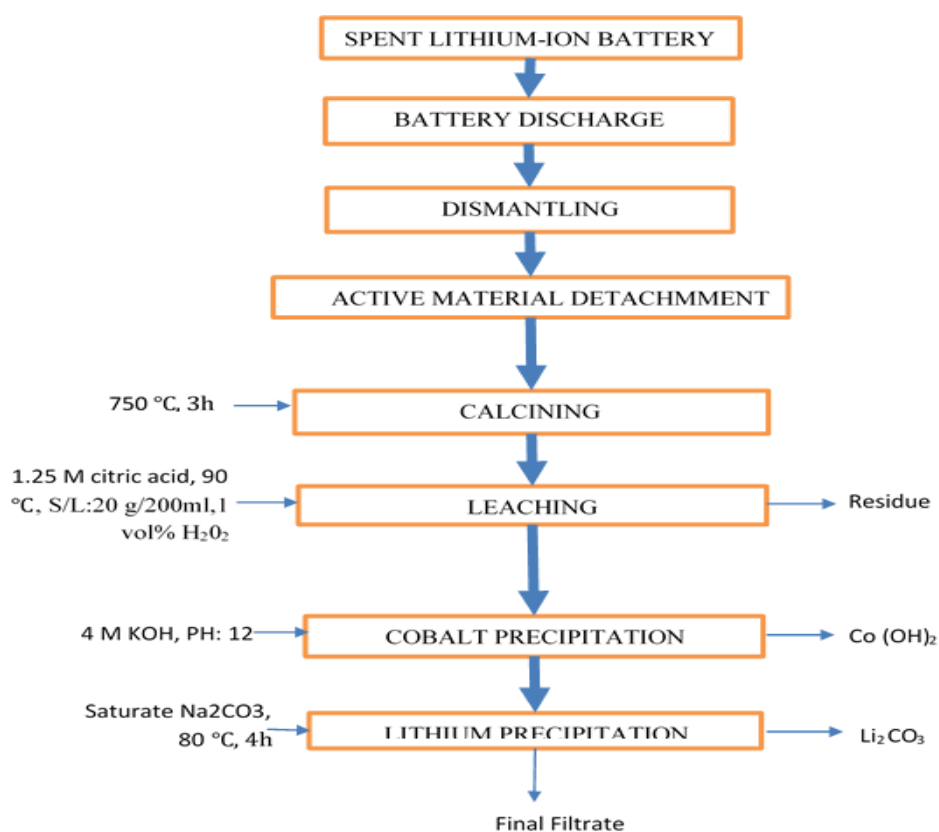


Figure 3.1: Flow chart of the lithium and cobalt recovery from the spent lithium-ion.

3.4 Material characterization

Fourier transform infrared (FTIR) spectroscopy was conducted on the cathode active material using Thermo scientific Nicolet is5 spectrometer in the range of 400–4000 cm⁻¹, before and after calcining. In addition, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were conducted on the cathode material before and after leaching of the active cathode materials. Moreover, EDS was also conducted on the Precipitate formed from the addition of KOH to the leaching filtrate to determine the elements present in it.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Battery Discharge

The battery was discharged before the dismantling to avoid thermal runaway. The discharging of the batteries was carried out using a 3 wt.% NaCl solution. The electrical conductivity and pH of the discharge solution before the discharging process are 48.5 mS/cm and 7.782 and the electrical conductivity and pH of the discharge solution after the discharging process is 50.2 mS/cm and 7.123. The increase in conductivity and decrease in pH of the discharge solution is probably because of the increase in the metal content of the solution after discharge. The result of the discharge process is presented in Table 4.1.

Table 4.1: Voltage of lithium-ion batteries before and after discharge in a 3 wt.% NaCl solution

Battery	Initial Battery Voltage (V)	Final Battery voltage (V)
1	3.500	0.333
2	3.771	0.403
3	3.707	0.971
4	3.755	0.428
5	3.571	0.063

The lithium-ion batteries were discharged using sodium chloride salt solution. The ability of the salt solution to discharge the batteries is due to the synergic effect of short-circuiting and electrolysis of salt solution [70].

4.2 FTIR (Fourier transform infrared) spectroscopy

The cathode materials detached from the aluminum current collector were calcined to burn off some organic matters, such as Polyvinylidene fluoride (PVDF). To confirm the success of the calcining process, FTIR was used, and the FTIR spectra are shown in figure 4.1.

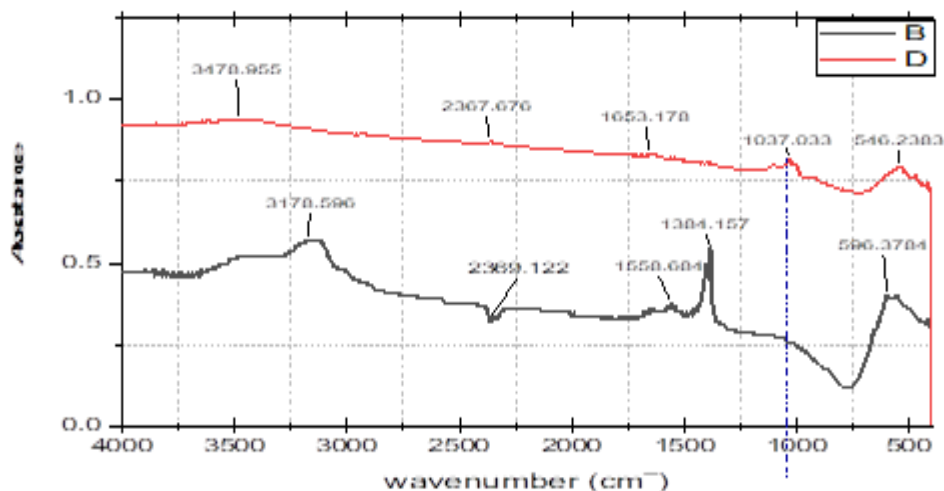


Figure 4.1: FTIR spectra of the as-detached and uncalcined cathode material [B: as-detached cathode material; D: calcine cathode materials]

PVDF is a fluorocarbon with a C-F functional group and the wavenumber of aliphatic organic fluoro compound, C-F stretched, lies between $1150\text{--}1000\text{ cm}^{-1}$. From the FTIR spectra, the as-detached cathode materials spectrum (with red colour) has a weak stretched peak corresponding to a wavenumber, 1037 cm^{-1} , which lies between $1150\text{--}1000\text{ cm}^{-1}$. This peak shows that PVDF is present in the as-detached cathode material. The disappearance of this peak in the calcined cathode materials spectrum (with black colour), as traced by the blue dotted line, confirms the effectiveness of the calcining process in removing the PVDF from the cathode material.

4.3 Scanning Electron Microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) Analyses

The micrographs shown in figures 4.2 (a, b, and c) are SEM images of the cathode materials detached from the aluminum current collector using DMOS, NMP, and scratching, respectively. The images show that the particles of the cathode materials remove using the above-mentioned methods have the same morphology: smooth surface, irregular shape and non-porous surface. In addition, their particle sizes range from $10\text{--}20\text{ }\mu\text{m}$, as shown in figures 4.3 (a, b, and c).

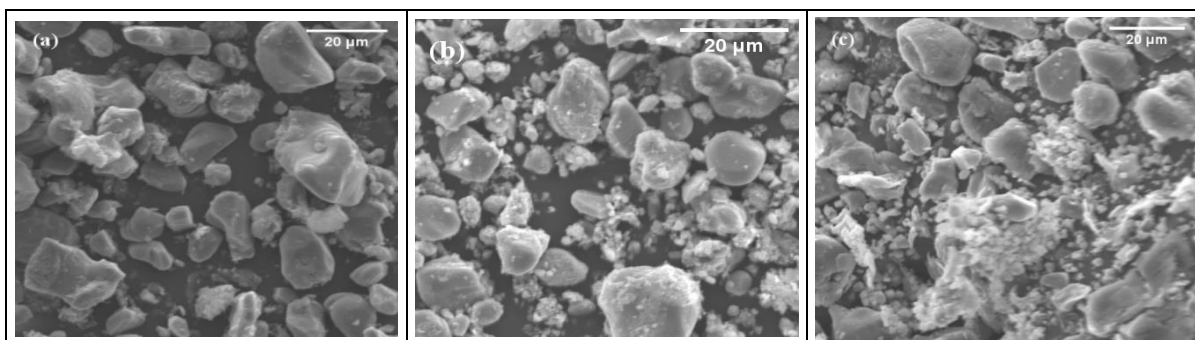


Figure 4.2: Morphology of cathode active material detached by (a) DMOS, (b) NMP (c) Scratching

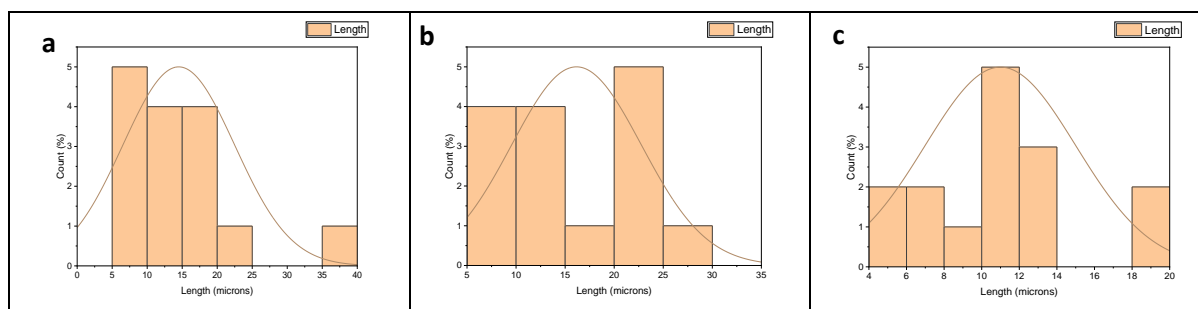


Figure 4.3: Particle size distribution of the cathode materials detached by (a) DMOS, (b)NMP and (c) Scratching

Figures 4.4 (a, b and c) shows the SEM images of cathode materials leached using different solid-to-liquid ratios: (a) 4 g/200 mL, (b) 6 g/200 mL, and (c) 8 g/200 mL, respectively. The micrographs reveal that some morphological changes have occurred. Pores have been introduced into the particles, as a result of the leaching process. These pores show that some elements have gone into the leached filtrate from the particles; thus, the cause of the rough surface of the cathode material.

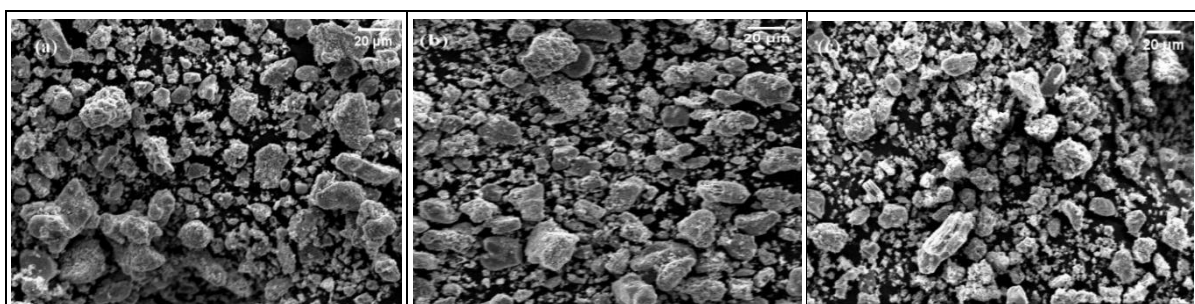


Figure 4.4: Morphology of leached residue for different solid to liquid (S/L) ratio the scratched off cathode materials: (a) 4 g/200 mL (b) 6 g/200 mL and (c) 8 g/200 mL

EDS analyses

The EDS spectrum of the leaching filtrate obtained using 6 g/200 mL (Figure 4.5a) and 8 g/200 mL solid-to-liquid (S/L) ratio (Figure 4.5b) indicates that the valuable metals (Co, Ni, Mn)

were successfully leached using the citric acid solution. EDS could not confirm the presence of lithium in the leached filtrate because of its inability to detect elements that are lighter than boron [71]. The tables under the EDS spectra correspond to the weight percent and atomic percent of the different elements present in the leaching filtrate.

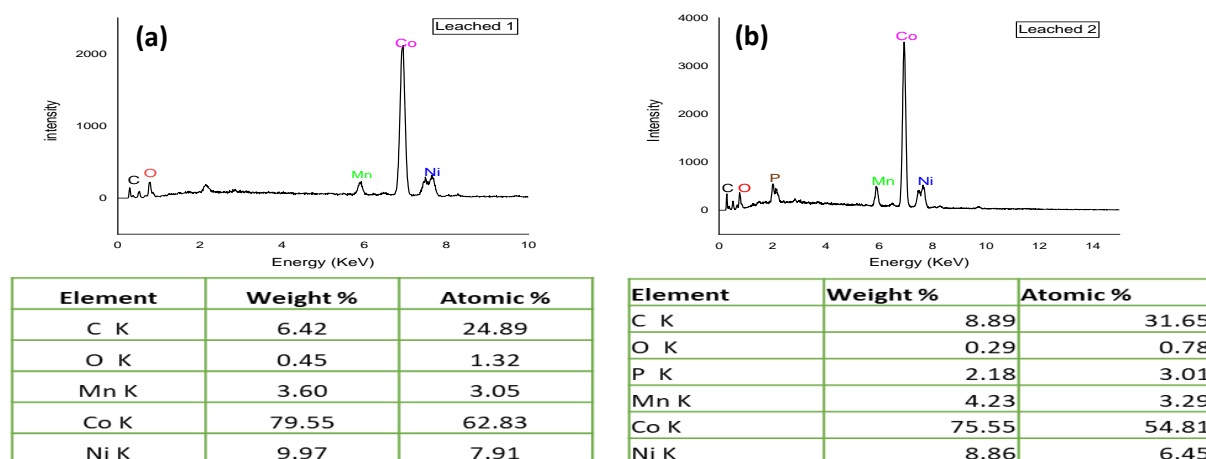


Figure 4.5: EDS of spectra of different leaching filtrate with their corresponding elemental weight and atomic percent: (a) 6 g/ 200 mL and (b) 8 g/200 mL

Figure 4.6 shows the EDS spectrum of the precipitate obtained by the addition of 4 M KOH and the corresponding elemental and weight percentage table. The result shows that a high percentage of cobalt can be precipitated by the addition of the KOH at a pH of approximately 12. The potassium in the spectra is from the KOH used in the precipitation process. In addition, KOH has the potential to Mn and Ni; thus, the reason for the small percentage of Mn and Ni present in the spectra. However, the spectra have shown that more cobalt can be precipitated at a pH of 12.

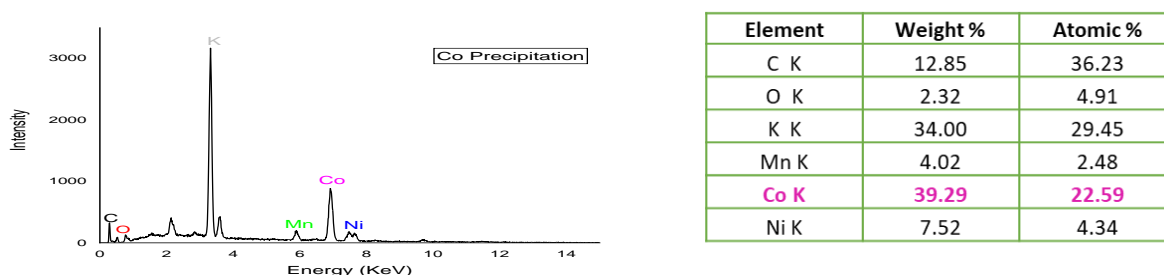


Figure 4.6: EDS spectra of the precipitate formed by the addition of KOH (left) and the corresponding elemental weight and atomic percent (right).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

For sustainable energy systems, a shift from our conventional energy system to the renewable energy system, such as geothermal-, solar-, hydro-energy system, is inevitable. To ensure perfect sustainability, where energy supply matches the demand, an energy storage system is needed, and lithium-ion batteries because of their high energy and power density are the best battery to achieve these objectives. However, the high cost of the valuable metals, such as cobalt, lithium, manganese and nickel, used in the lithium-ion batteries limits their production. Thus, the need for a better battery recycling method. In this study, we focused on the recovery of lithium and cobalt from lithium-ion batteries using the hydrometallurgical technique. This technique involves three stages: pre-treatment, leaching and precipitation stage. In the pre-treatment stage, the battery was discharged using 3 wt.% NaCl within a period of 24 h. In addition, the cathode active materials were detached from the aluminum current collector by dissolving them in DMSO, NMP and through the scratching method. The results show that any of the methods can be used to remove the cathode materials from the current collector (Aluminium foil). In the leaching stage, 1.25 M citric acid of different solid-to-liquid (S/L) ratios were used to leach the valuable metals into the solution: 4 g/200 mL, 6 g/200 mL, and 8 g/200 mL. However, leaching the best result was obtained using 8 g/200 mL. These cathode material leachings are carried out using 1 vol% hydrogen peroxide (H_2O_2), as the reducing agent, and a leaching temperature of 90 °C. The final stage for the recovery of lithium and cobalt from a spent lithium-ion battery involves the used of potassium hydroxide (KOH) and sodium carbonate (Na_2CO_3) to precipitate cobalt (with a few percentages of Manganese and Nickel) and lithium, respectively.

5.2 Recommendations

Further research in this area should focus on obtaining the optimal condition of the leaching and precipitation techniques used in this present study. In addition, having discovered that the scratching method can detach cathode materials from the current collector just like DMSO and NMP used in the previous studies, more effort and research should focus on the design and development of a simple machine for scratching off the cathode materials from the current collector.

REFERENCE

- [1] “Energy and Civilization | The MIT Press.” <https://mitpress.mit.edu/books/energy-and-civilization> (accessed Nov. 17, 2020).
- [2] M. Asif and T. Muneer, “Energy supply, its demand and security issues for developed and emerging economies,” *Renew. Sustain. Energy Rev.*, vol. 11, no. 7, pp. 1388–1413, 2007, doi: 10.1016/j.rser.2005.12.004.
- [3] “Nigeria Energy Situation - energypedia.info.” https://energypedia.info/wiki/Nigeria_Energy_Situation (accessed Nov. 22, 2020).
- [4] World Health Organization (WHO), *Household Energy and Health Household Energy and Health*. 2006.
- [5] “Use of energy for transportation - U.S. Energy Information Administration (EIA).” <https://www.eia.gov/energyexplained/use-of-energy/transportation.php> (accessed Nov. 23, 2020).
- [6] A. Midilli, I. Dincer, and M. Ay, “Green energy strategies for sustainable development,” *Energy Policy*, vol. 34, no. 18, pp. 3623–3633, Dec. 2006, doi: 10.1016/j.enpol.2005.08.003.
- [7] H. Balat, “Contribution of green energy sources to electrical power production of Turkey: A review,” *Renewable and Sustainable Energy Reviews*, vol. 12, no. 6, pp. 1652–1666, Aug. 2008, doi: 10.1016/j.rser.2007.03.001.
- [8] R. A. Huggins, *Energy storage*, vol. 9, no. 3. 2001.
- [9] H. Ibrahim, A. Ilinca, and J. Perron, “Energy storage systems-Characteristics and comparisons,” *Renew. Sustain. Energy Rev.*, vol. 12, no. 5, pp. 1221–1250, 2008, doi: 10.1016/j.rser.2007.01.023.
- [10] M. Sevket and Y. Tepe, “Classification and assessment of energy storage systems,”

- no. February, 2016, doi: 10.1016/j.rser.2016.11.102.
- [11] Z. Yang, J. Zhang, M. C. W. Kintner-meyer, X. Lu, D. Choi, and J. P. Lemmon, “Electrochemical Energy Storage for Green Grid: Status and Challenges,” *ECS Meet. Abstr.*, pp. 3577–3613, 2011, doi: 10.1149/ma2011-02/4/155.
- [12] A. Manthiram, “An Outlook on Lithium Ion Battery Technology,” *ACS Cent. Sci.*, vol. 3, no. 10, pp. 1063–1069, 2017, doi: 10.1021/acscentsci.7b00288.
- [13] X. Zeng *et al.*, “Commercialization of Lithium Battery Technologies for Electric Vehicles,” *Adv. Energy Mater.*, vol. 9, no. 27, 2019, doi: 10.1002/aenm.201900161.
- [14] United Nations, “The Energy Challenge for Achieving the Millennium Development Goals Energy and the MDGs,” *UN Energy*, 2006.
- [15] R. Panda and M. Maity, “Global Warming and Climate Change On Earth : Duties and Challenges of Human Beings,” vol. 4, no. 1, pp. 122–125, 2021.
- [16] B. Wiggins, “Cars Are a Major Source of Greenhouse Gas Emissions — Some Cities Are Finally Taking Action.” <https://www.globalcitizen.org/en/content/cities-car-bans-greenhouse-gas-emissions/> (accessed Mar. 07, 2021).
- [17] “Global Greenhouse Gas Emissions Data | Greenhouse Gas (GHG) Emissions | US EPA.” <https://www.epa.gov/ghgemissions/global-greenhouse-gas-emissions-data> (accessed Mar. 07, 2021).
- [18] “Transportation and Energy Issues.” <https://www.aps.org/policy/reports/popa-reports/energy/transportation.cfm> (accessed Nov. 12, 2020).
- [19] “Global EV Outlook 2018 – Analysis - IEA.” <https://www.iea.org/reports/global-ev-outlook-2018> (accessed Mar. 08, 2021).
- [20] J. Xu, S. Dou, H. Liu, and L. Dai, “Cathode materials for next generation lithium ion

- batteries,” *Nano Energy*, vol. 2, no. 4, pp. 439–442, 2013, doi:
10.1016/j.nanoen.2013.05.013.
- [21] Y. Hua *et al.*, “Sustainable value chain of retired lithium-ion batteries for electric vehicles,” *J. Power Sources*, vol. 478, no. June, p. 228753, 2020, doi:
10.1016/j.jpowsour.2020.228753.
- [22] M. K. Tran and M. Fowler, “Sensor fault detection and isolation for degrading lithium-ion batteries in electric vehicles using parameter estimation with recursive least squares,” *Batteries*, vol. 6, no. 1, 2020, doi: 10.3390/batteries6010001.
- [23] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, “Li-ion battery materials: Present and future,” *Mater. Today*, vol. 18, no. 5, pp. 252–264, 2015, doi:
10.1016/j.mattod.2014.10.040.
- [24] A. Manthiram, “A reflection on lithium-ion battery cathode chemistry,” *Nat. Commun.*, vol. 11, no. 1, pp. 1–9, 2020, doi: 10.1038/s41467-020-15355-0.
- [25] M. A. Hasan and R. B. Chapman, “The environmental footprint of electric versus fossil cars — Science Learning Hub,” 2019.
<https://www.sciencelearn.org.nz/resources/2833-the-environmental-footprint-of-electric-versus-fossil-cars> (accessed Mar. 07, 2021).
- [26] T. Randall, “Here’s How Electric Cars Will Cause the Next Oil Crisis,” 2016.
<https://www.bloomberg.com/features/2016-ev-oil-crisis/> (accessed Mar. 08, 2021).
- [27] “energy | Definition, Types, & Examples | Britannica.”
<https://www.britannica.com/science/energy> (accessed Mar. 11, 2021).
- [28] J. Abbess and J. Abbess, *Introduction to Renewable Energy*. 2015.
- [29] V. Smil, *Energy: a beginner’s guide*. Oneworld, 2006.

- [30] I. J. P. ´ Erez Arriaga, H. Rudnick, and M. Rivier, “Electric Energy Systems. An Overview 1.1 A first vision 1.1.1 The energy challenges in modern times.”
- [31] B. Hantal, “Essay on Energy: Importance and Sources.”
<https://www.yourarticlelibrary.com/essay/essay-on-energy-importance-and-sources/42595> (accessed Mar. 11, 2021).
- [32] S. B. McGrayne, E. E. Suckling, E. Kashy, and F. N. H. Robinson, “Electricity,” 2020.
<https://www.britannica.com/science/electricity> (accessed May 15, 2021).
- [33] B. Novakovic and A. Nasiri, “Introduction to electrical energy systems,” *Electr. Renew. Energy Syst.*, pp. 1–20, 2016, doi: 10.1016/B978-0-12-804448-3.00001-3.
- [34] “Transmission Company of Nigeria.” https://www.tcn.org.ng/blog_post_sidebar27.php (accessed May 15, 2021).
- [35] “Types of Batteries/ Power Source: Working Principles and Advantages.”
<https://www.elprocus.com/batteries-types-working/> (accessed Jan. 27, 2021).
- [36] J. Warner, *Handbook of lithium-ion battery pack design: chemistry, components, types and terminology*. Elsevier Inc., 2015.
- [37] “Battery Working Principle: How does a Battery Work? | Electrical4U.”
<https://www.electrical4u.com/battery-working-principle-of-batteries/> (accessed Jan. 16, 2021).
- [38] Bobby, “History Of Batteries: A Timeline - News about Energy Storage, Batteries, Climate Change and the Environment,” 2014.
<https://www.upsbatterycenter.com/blog/history-batteries-timeline/> (accessed May 10, 2021).
- [39] M. Bellis, “History and Timeline of the Battery,” 2019.
<https://www.thoughtco.com/battery-timeline-1991340> (accessed May 10, 2021).

- [40] BatteryIndustry.tech, “A brief history of the battery.” <https://batteryindustry.tech/a-brief-history-of-the-battery/> (accessed May 10, 2021).
- [41] M. Cultu, “M SC PL O E – C EO M SC PL O E – C EO,” vol. II.
- [42] F. Mezei, *Handbook of batteries*, Third Edit. McGraw-Hill, 2011.
- [43] O. S. Burheim, “Secondary Batteries,” in *Engineering Energy Storage*, Elsevier, 2017, pp. 111–145.
- [44] J. Jiang and C. Zhang, *fundamentals and Applications of lithium-ion Batteries in Electric Drive Vehicles*. 2015.
- [45] G. M. Ehrlich, *Handbook of batteries*, Third edit., vol. 33, no. 04. 1995.
- [46] M. Yoshio, A. Kozawa, and R. J. Brodd, *Lithium-ion Batteris*. 2009.
- [47] D. Deng, “Li-ion batteries: Basics, progress, and challenges,” *Energy Sci. Eng.*, vol. 3, no. 5, pp. 385–418, 2015, doi: 10.1002/ese3.95.
- [48] J. M. Tarascon and M. Armand, “Issues and challenges facing rechargeable lithium batteries,” *Nature*, vol. 414, no. 6861. Nature Publishing Group, pp. 359–367, Nov. 15, 2001, doi: 10.1038/35104644.
- [49] samsung SDI, “The Four Components of a Li-ion Battery.” <https://www.samsungsdi.com/column/technology/detail/55272.html?listType=gallery> (accessed Jan. 19, 2021).
- [50] H. . Kiehne, *Battery Technology Handbook, Second Edition, H.A. KIEHNE, eBook - Amazon.com*. 2007.
- [51] D. L. Thompson *et al.*, “important of design in lithium ion battery recycling,” *R. Soc. Chem.*, p. 19, 2020, doi: 10.1039/d0gc02745f.
- [52] Y. Nishi, “The development of lithium ion secondary batteries,” *Chem. Rec.*, vol. 1,

no. 5, pp. 406–413, 2001, doi: 10.1002/tcr.1024.

- [53] “Lithium-ion Battery Market Size USD 129.3 Billion By 2027 At A CAGR of 18.0% | Valuates Reports,” 2020. Accessed: Mar. 15, 2021. [Online]. Available: <https://www.prnewswire.com/news-releases/lithium-ion-battery-market-size-usd-129-3-billion-by-2027-at-a-cagr-of-18-0--valuates-reports-301181156.html>.
- [54] P&S intelligence, “Lithium-Ion Battery Recycling Market Report | Forecast, 2030,” 2020. Accessed: Mar. 12, 2021. [Online]. Available: <https://www.psmarketresearch.com/market-analysis/lithium-ion-battery-recycling-market>.
- [55] “Lithium-Ion Battery Market Size, Share, Growth, Analysis 2020-25.” <https://www.mordorintelligence.com/industry-reports/lithium-ion-battery-market> (accessed Mar. 15, 2021).
- [56] A. Gupta and N. Paranjape, “Lithium Ion Battery Market Outlook 2020-2026 | Share Analysis,” 2019. Accessed: Mar. 15, 2021. [Online]. Available: <https://www.gminsights.com/industry-analysis/lithium-ion-battery-market>.
- [57] “Lithium-ion Battery Market Size & Share Report, 2020-2027.” <https://www.grandviewresearch.com/industry-analysis/lithium-ion-battery-market> (accessed Mar. 16, 2021).
- [58] M. Oswal, J. Paul, and R. Zhao, “A comparative study of Lithium-ion Batteries,” 2015.
- [59] D. Doughty and E. P. Roth, “A general discussion of Li Ion battery safety,” *Electrochem. Soc. Interface*, vol. 21, no. 2, pp. 37–44, 2012, doi: 10.1149/2.F03122if.
- [60] R. Reif, M. Liffers, N. Forrester, and K. Peal, “Lithium Battery Safety,” *Prof. Saf.*, no. February, pp. 32–38, 2010.

- [61] A. Boyden, V. K. Soo, and M. Doolan, "The Environmental Impacts of Recycling Portable Lithium-Ion Batteries," *Procedia CIRP*, vol. 48, pp. 188–193, 2016, doi: 10.1016/j.procir.2016.03.100.
- [62] T. Or, S. W. D. Gourley, K. Kaliyappan, A. Yu, and Z. Chen, "Recycling of mixed cathode lithium-ion batteries for electric vehicles: Current status and future outlook," *Carbon Energy*, vol. 2, no. 1, pp. 6–43, 2020, doi: 10.1002/cey2.29.
- [63] L. P. He, S. Y. Sun, X. F. Song, and J. G. Yu, "Recovery of cathode materials and Al from spent lithium-ion batteries by ultrasonic cleaning," *Waste Manag.*, vol. 46, pp. 523–528, 2015, doi: 10.1016/j.wasman.2015.08.035.
- [64] J. Senćanski, D. Bajuk-Bogdanović, D. Majstorović, E. Tchernychova, J. Papan, and M. Vujković, "The synthesis of Li(Co[sbnd]Mn[sbnd]Ni)O₂ cathode material from spent-Li ion batteries and the proof of its functionality in aqueous lithium and sodium electrolytic solutions," *J. Power Sources*, vol. 342, pp. 690–703, 2017, doi: 10.1016/j.jpowsour.2016.12.115.
- [65] X. Zeng and J. Li, "Innovative application of ionic liquid to separate Al and cathode materials from spent high-power lithium-ion batteries," *J. Hazard. Mater.*, vol. 271, no. 2014, pp. 50–56, 2014, doi: 10.1016/j.jhazmat.2014.02.001.
- [66] Y. Zheng *et al.*, "Leaching procedure and kinetic studies of cobalt in cathode materials from spent lithium ion batteries using organic citric acid as leachant," *Int. J. Environ. Res.*, vol. 10, no. 1, pp. 159–168, 2016, doi: 10.22059/ijer.2016.56898.
- [67] G. Dorella and M. B. Mansur, "A study of the separation of cobalt from spent Li-ion battery residues," *J. Power Sources*, vol. 170, no. 1, pp. 210–215, 2007, doi: 10.1016/j.jpowsour.2007.04.025.
- [68] A. H. Shuva and A. S. W. Kurny, "Hydrometallurgical Recovery of Value Metals from

- Spent Lithium Ion Batteries,” vol. 1, no. 1, pp. 8–12, 2013, doi: 10.12691/materials-1-1-2.
- [69] L. Li, J. Ge, F. Wu, R. Chen, S. Chen, and B. Wu, “Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant,” *J. Hazard. Mater.*, vol. 176, no. 1–3, pp. 288–293, 2010, doi: 10.1016/j.jhazmat.2009.11.026.
- [70] M. Lu, H. Zhang, B. Wang, X. Zheng, and C. Dai, “The Re-Synthesis of LiCoO_2 from Spent Lithium Ion Batteries Separated by Vacuum-Assisted Heat-Treating Method,” vol. 8, pp. 8201–8209, 2013.
- [71] P. M. V. Raja and A. R. Barron, “An Introduction to Energy Dispersive X-ray Spectroscopy - Chemistry LibreTexts.”
[https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_\(Barron\)/01%3A_Elemental_Analysis/1.12%3A_An_Introduction_to_Energy_Dispersive_X-ray_Spectroscopy](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/01%3A_Elemental_Analysis/1.12%3A_An_Introduction_to_Energy_Dispersive_X-ray_Spectroscopy) (accessed May 22, 2021).