RECYCLING AND REGENERATING COPPER AND ALUMINUM CURRENT COLLECTORS OF SPENT LITHIUM–ION BATTERIES

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirement for the Degree

of Master of Science

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December 2023

RECYCLING AND REGENERATING COPPER AND

ALUMINUM CURRENT COLLECTORS OF

SPENT LITHIUM–ION BATTERIES

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Thesis

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ABSTRACT

The global shift towards electric vehicles and renewable energy sources has prompted an increase in demand for energy storage systems, specifically lithium-ion batteries (LIBs). As the production of LIBs continues to grow, it becomes increasingly important to consider end-of-life strategies for these batteries. A strong focus on transitioning from landfilling to an efficient recycling system is necessary to ensure the reduction of total global emissions, especially those from LIBs. Furthermore, LIBs contain many resources that can be reused after recycling; however, the compositional and component complexity of LIBs poses many challenges. One of the challenges in recycling LIBs is the difficulty of separating and purifying the individual components, which include the cathode, anode, electrolyte, and current collectors (CCs). This study focuses specifically on the recycling and reusing of copper (Cu) and aluminum (Al) foils, which serve as the anode and cathode current collectors of LIBs, respectively. The CCs are an important component of LIBs, as they provide electrical conductivity and collect and distribute the current generated during battery operation. Reusing CCs can reduce the overall environmental impact of LIB production and disposal, as well as conserve valuable resources. However, the recycling and reuse of CCs requires an efficient purification method to remove impurities and restore the material's quality. The recycling process for LIBs involves dismantling and separating the various components of the battery, including the CCs. The CCs are then processed through a purification step to remove any impurities such as electrolyte residues and other

contaminants. The current method for purifying recycled CCs involves a combination of mechanical and chemical processes, including crushing, sieving, and leaching. This study explores the effectiveness of the purification method and tests the performance of the purified CCs in the manufacturing of new LIBs. To test the effectiveness of the purification method, the study compares the performance of new LIBs made with recycled CCs and virgin CCs. The process of manufacturing new LIBs involves coating the CCs with active materials to create the anode and cathode. The coated CCs are then assembled with a separator and electrolyte to form a complete LIB. The performance of the new LIBs is evaluated by measuring their capacity and cycling stability. Capacity refers to the amount of energy that the battery can store, while cycling stability refers to the battery's ability to maintain its capacity over multiple charge and discharge cycles. The results of the study indicate that the purification process effectively removes impurities from the recycled CCs, allowing them to be reused in the manufacturing of new LIBs. The performance of the new LIBs made with recycled CCs is comparable to that of new LIBs made with virgin CCs. However, the cycling stability of the recycled CCs is lower than that of virgin CCs. This suggests that further improvements in the purification method are necessary to increase the cycling stability of the recycled CCs.

The use of recycled CCs in the manufacturing of new LIBs has several advantages. First, it reduces the environmental impact of LIB production and disposal, as it conserves valuable resources and reduces the need for mining and refining new materials. Second, it lowers the cost of LIB production, as recycled materials are often cheaper than new materials. Finally, it contributes to the development of a more sustainable energy system, as it supports the circular economy and reduces dependence on non-renewable resources.

DEDICATION

This thesis is dedicated to my family and friends, especially my mother and my father, who have always stood by my side and supported me and my kids Arian and my Antoshka. All my teachers for molding and shaping my career and helping me reach this point in my life.

ACKNOWLEDGEMENTS

The contents of this thesis would not have been possible without the contributions of many individuals and organizations. First, I would like to thank my advisor, Dr. Siamak Farhad and Dr. Rashid Farahati, who showed me the way to do this research and was with me during my thesis project. Also special thanks to Schaeffler Transmission USA to sponsor my education and give me the opportunity to enhance my technical knowledge on Mechanical engineering as well as for allowing us to observe the manual disassembly process. And special thanks to Dr. Ranna Tolouei, Dr. Mahdi Amiriyan, and Joshua Dunham, whose guidance and support were imperative to this project.

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CHAPTER I

INTRODUCTION

1.1. WHY LI-ION BATTERIES AND WHY RECYCLING THEM.

Always the recycle the metal is more economic and safer for environment than to extraction them from their ore.

- Environmental problems:
- Air pollution.
- Greenhouse gas.
- Noise.
- Acid rain.

Are involved in this process.

Since 1850, when the pre-industrial era began, humans, in their pursuit of energy for various activities, increasingly turned to fossil fuels. However, the excessive use of fossil fuels has led to the accumulation of heat-trapping greenhouse gases in Earth's atmosphere. If we examine the temperature graph of the Earth from 1880 to 2020, as published by NASA, we can observe that the Earth's surface temperature has risen by more than 1 degree Celsius (1.8 degrees Fahrenheit).

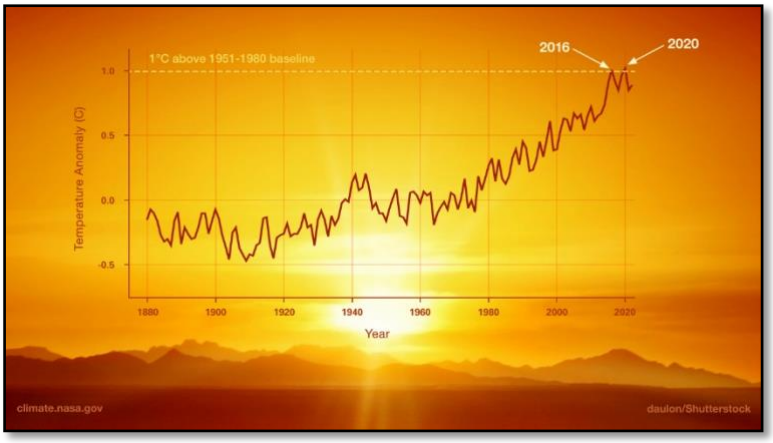


Figure 1: Average global temperature. NASA's Goddard Institute for Space Studies.

As a result, we can see that a 1-degree Celsius increase could have an impact on the global climate, leading to more wildfires, longer periods of drought, and an increase in the intensity of winds and tropical storms."

So, one of the important reasons why we have to transfer from fossil fuels is to protect the environment and electrical cars that get energy from rechargeable batteries is an intelligent idea.

Figure 2: Mellimage/Shutterstock.com, center - Montree Hanlue/Shutterstock.com - NASA.

In the graph below, we can see the growth of the production of electric cars in the world.

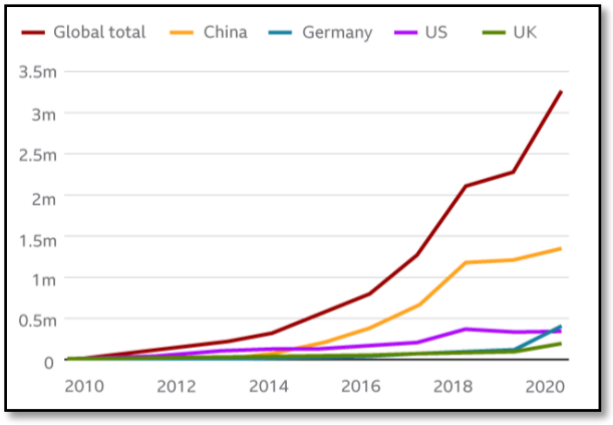


Figure 3: Global sales of electric cars accelerate– Source www.ev-volumes.com

But the reserves of minerals on the Earth are not unlimited and in the not so-distant future, their stock will end. Therefore, the recovery of worn-out batteries seems to be inviable.

$$Al^{3} + 3e^{-} \longrightarrow Al$$

Economic considerations: For example, bauxite (Al2O3) is the ore which we use to extract aluminum. To convert the aluminum oxide into aluminum with high purity, we need to utilize an electrolysis technique. In this process we need huge amounts of electricity because for every mole aluminum that weighs only 27g we need 3 moles of electrons.

The automotive industry is poised for a significant transformation due to the Electric Vehicle (EV) revolution, which is spurred by the urgent need to reduce greenhouse gas emissions and enhance air quality in urban areas while aligning with global decarbonization goals. Notably, in 2017, global EV sales reached a milestone, surpassing one million cars sold annually for the first time [1].

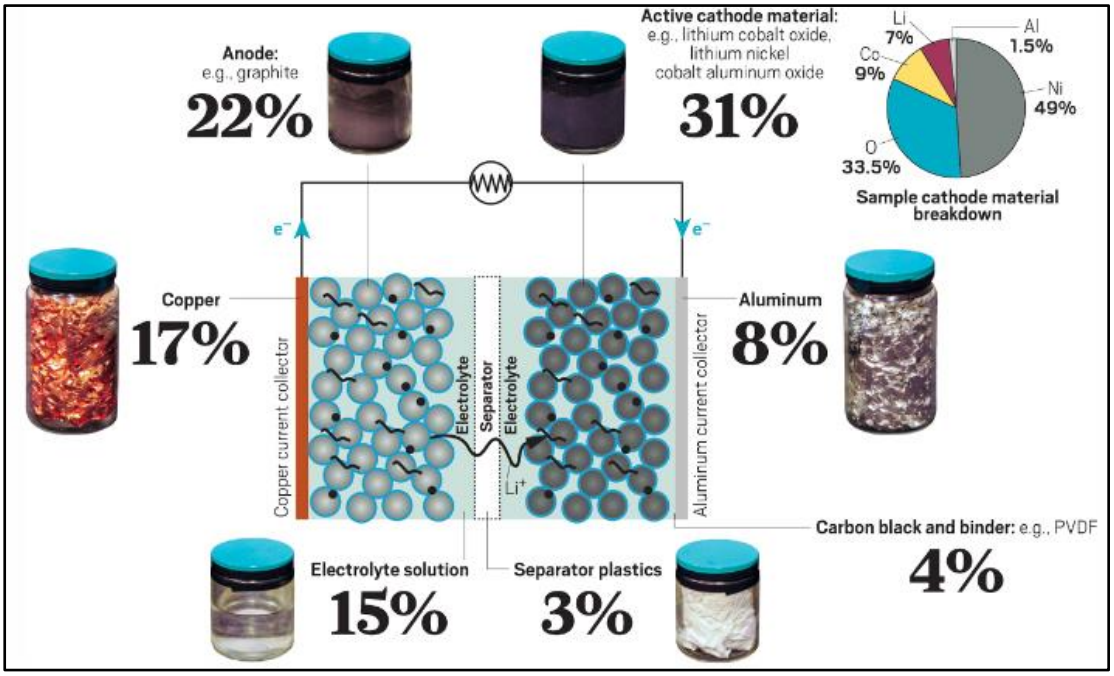


Figure 4: The percentage of material composition inside of the lithium-ion battery [8].

With the ever-growing need for lithium-ion batteries (LIBs), particularly from the electric transportation industry, many LIBs are bound to retire soon, thereby leading to serious disposal problems and detrimental impacts on environment and energy conservation. Currently, commercial LIBs are composed of transition metal oxides or phosphates, aluminum, copper, graphite, organic electrolytes with harmful lithium salts, polymer separators, and plastic or metallic cases. The lack of proper disposal of spent LIBs most likely results in grave consequences, such as environmental pollution and waste of resources. Thus, the recycling of spent LIBs has started to receive attention in recent years. However, owing to the pursuit of LIBs with higher energy density, higher safety and a more affordable price, the materials used in LIBs are of a wide diversity and ever-evolving, consequently bringing difficulties to the recycling of spent LIBs. [2].

To sustain the future of the automotive industry, especially if it aims to produce tens of millions of EVs each year, it is crucial to adopt responsible resource management during EV battery manufacturing. This includes the implementation of a

material and energy-efficient 3R system, which stands for reduce, re-use, and recycle. This approach is imperative to ensure the long-term sustainability of the industry, given the increasing demand for EVs. Owing to the high energy density, long lifespan and low self-discharge, LIBs are more portable than other commercial energy storage devices.

There is a widespread consensus that, for both environmental and safety considerations, storing end-of-life EV batteries in stockpiles or, worse yet, disposing of them in landfills are not viable options. Instead, effective management of end-of-life EV waste will necessitate regional solutions [3].

Following the waste management hierarchy, reusing these batteries is generally preferred over recycling as it allows for the extraction of maximum economic value and minimizes environmental impacts. Many companies across the globe are already experimenting with repurposing EV Lithium-Ion Batteries (LIBs) for various energy storage applications. Enhanced sensor technology and improved monitoring methods for batteries, both during their operational lifespan and at the end of it, can better match the characteristics of individual end-of-life batteries to potential second-use applications. This approach offers advantages in terms of longevity, safety, and market value.

Under conservative assumptions regarding an average battery pack's weight (250 kg) and volume (half a cubic meter), the accumulated waste from these packs is estimated to reach approximately 250,000 metric tons and half a million cubic meters when electric vehicles reach the end of their lifespan. While re-use and existing recycling methods can divert some of this waste from landfills, the sheer volume of EV waste is significant, especially considering the rapid growth of the EV market [1].

Dealing with this waste poses several substantial challenges in terms of storage, manual testing, dismantling, and the chemical separation processes involved in recycling [4].

It's worth noting that the environmental impact of manufacturing EVs is heavily influenced by raw material extraction and lithium-ion battery production, which in turn affects the demands on end-of-life dismantling and recycling systems [4].

In the waste management industry, re-use is considered more favorable than recycling [MT]. Energy storage markets are emerging as energy regulators worldwide shift towards cleaner energy sources. Energy storage is especially in demand in areas with weak power grids that require reinforcement, in regions where a high percentage of renewables necessitates balancing supply and demand, where opportunities for energy trading with the grid exist, and in off-grid applications. Second-use battery projects are beginning to develop in areas where regulatory and market conditions align [6]. However, managing large concentrations of waste, whether for refurbishment, re-manufacturing, dismantling, or final disposal, can create significant logistical and environmental challenges. [5].

1.2. INTERNAL COMPONENTS OF THE LI-ION BATTERY

Current collectors (CCs) play a crucial and essential role in the composition of lithium-ion batteries (LIBs) and other battery types. These CCs serve as a vital bridge, providing support to the active materials, including cathodes, anodes, binders, and conductive additives. Additionally, they facilitate the electrochemical connection of the entire structure of anodes and cathodes with an external circuit.

Recent advancements have seen various aspects of CCs being modified, including their thickness, hardness, compositions, coating layers, and structures. These modifications aim to enhance different facets of battery performance, such as

improving the cycle life of charge and discharge, increasing energy density, and enhancing the rate at which a cell can perform.

1.3. RECYCLING METHOD OF LI-ION BATTERY

Extractive metallurgy is the science and art of extracting and refining ores. Extractive metallurgy is divided into three main branches: pyrometallurgy, hydrometallurgy, and electro-metallurgy. Pyrometallurgy is the process of producing metals at high temperatures. The method of hydrometallurgy involves dissolving ore in aqueous solutions and producing metal ions to dissolve ions. Finally, in electrometallurgy, as the name implies, electricity is used to produce metals. Generally, pretreatment processes are designed to segregate the components and materials within spent Lithium-Ion Batteries (LIBs) based on various physical characteristics, including shape, density, conductivity, and magnetic properties, among others, as described by Xu et al. in 2008. These pretreatment steps enable the separation and concentration of components, materials, and metallic scraps that share similar physical properties. This, in turn, enhances the recovery rate while simultaneously reducing the energy consumption during subsequent pyrometallurgical or hydrometallurgical processes. (Huang et al. 2018).

1.3.1. PYROMETALLURGICAL METHOD

Pyrometallurgy is characterized using high temperature to extract metals from ores or concentrates of used materials. Pyrometallurgy, as one of the methods of production of copper, iron, and nickel is very important in many countries; and metal extraction based on thermal methods (pyrometallurgy) is a major volume of metal production in industry. About 90% of the copper produced in the world is obtained from sulfur ores by pyrometallurgy. Currently, both hydrometallurgy and pyrometallurgy

methods are used to produce copper. Usually, hydrometallurgy method is used in ores that are lower quality grade, but pyrometallurgy method is used for higher quality ores. Today, the orientation and approach of the copper industry is towards the hydrometallurgical method.

Examples of applications of pyrometallurgy can be seen in the iron and steel industries. This is the reaction for iron production:

$$Fe2O3\ (s) + 3C\ (s) \rightarrow 2Fe\ (l) + 3CO\ (g)$$

1.3.2. HYDROMETALLURGICAL METHOD

Hydrometallurgy is a method used to extract metals from minerals using aqueous solutions. It plays a significant role in the extraction of metals, particularly rare ones like copper. Typically, hydrometallurgical processes encompass several key steps, including mineral beneficiation, leaching, solid-liquid separation, concentration, purification, and the retrieval of the metal's intrinsic value.

1.3.3. PHYSICAL OR DIRECT METHOD

Of all non-ferrous metals, aluminum and Copper have the most widespread use. Aluminum and copper are almost easy to find everywhere, all cans, parts of automobiles, household appliances, aluminum foils, and electricity transmission wires all contain copper. After steel, aluminum is the second-largest metal that has the highest recycling in the world. The remaining inclusions from the environment, which are difficult or expensive to be removed completely, damage the performance of the recycled metals. Silicon and Iron are the most harmful impurities in aluminum, and they could decrease the mechanical properties of aluminum rapidly.

In this thesis, an attempt has been made to use a pyrometallurgical method to recycle current collectors made of copper and aluminum.

1.3.4. PURIFICATION METHOD OF ALUMINUM AND COPPER

Gases such as oxygen and nitrogen, when dissolved in molten metals during the melting process, can lead to defects like porosity and inclusions in the final casting parts. To mitigate this issue, one of the purification methods involves passing a stream of purifying gas, such as argon, through the molten metal. In the aluminum industry, there are primarily two methods used for molten aluminum purification: flux purification and gas purification. Some also employ filtration methods like tube filters, ceramic foam filters, and deep bed filters for molten aluminum purification.

Flux used in molten aluminum purification typically consists of salts with characteristics such as a low melting point, low density, low surface tension, high activity, and a strong adsorption capacity for oxidation slag. In flux purification, the flux is added to the aluminum melt, forming numerous fine droplets that wet and absorb oxides present in the aluminum melt. These absorbed oxides dissolve and coalesce into new droplets that rise to the surface. After cooling, the formed scum can be easily removed.

Gas purification is the primary method for purifying primary aluminum, and gases like chlorine, nitrogen, or a mixture of chlorine and nitrogen are employed. The mixture of chlorine and nitrogen serves to remove hydrogen, separate oxides, and eliminate certain metal impurities in the aluminum, such as magnesium. Commonly used compositions include 90% nitrogen + 10% chlorine and 10% chlorine + 10% carbon dioxide + 80% nitrogen. The latter is preferred for its effectiveness, as carbon dioxide helps diffuse chlorine and nitrogen efficiently, reducing the operation time.

Aluminum castings are typically produced from remelted aluminum ingots or molten aluminum generated by electrolytic aluminum plants. One of the advantages of aluminum casting is its ability to produce near-net-shape products, maximizing productivity and minimizing the need for extensive post-processing.

During the charging and preparation of the holding furnace, a layer of aluminum slag, either in liquid or solid form, accumulates on the surface of the molten aluminum. This slag contains a substantial amount of aluminum oxide, which can be re-melted to recover the aluminum, preventing its loss [6].

CHAPTER II

METHOD

2.1. DIRECTION METHOD

The below algorithm shows (Figure 5) all the steps for recycling and preparing used batteries.

One of the techniques to recycle the batteries is the direct method. In this method before anything the batteries must be discharged. Not discharging batteries could be the case of firing and explosion. After discharging the batteries, they are crushed by a crusher and hummer mill.

The crushed batteries go into a separation tank to separate electrolytes from solid components.

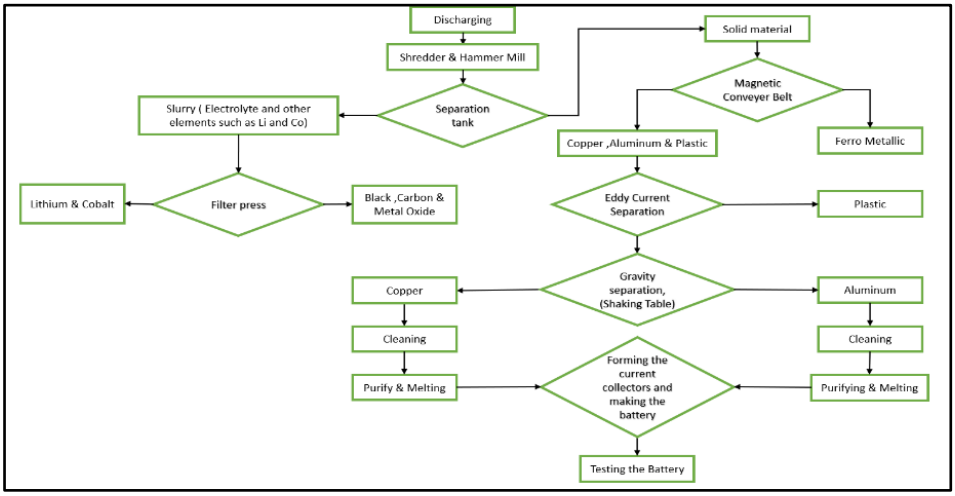


Figure 5: Algorithm of recycling method and preparing the battery.

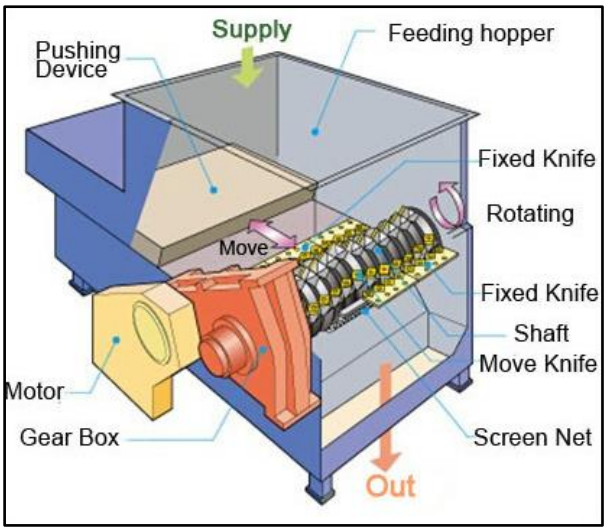


Figure 6: Shredder machine. www.Industrysearch.com [10].

Ferro metallic components are separated by a magnetic conveyer belt.

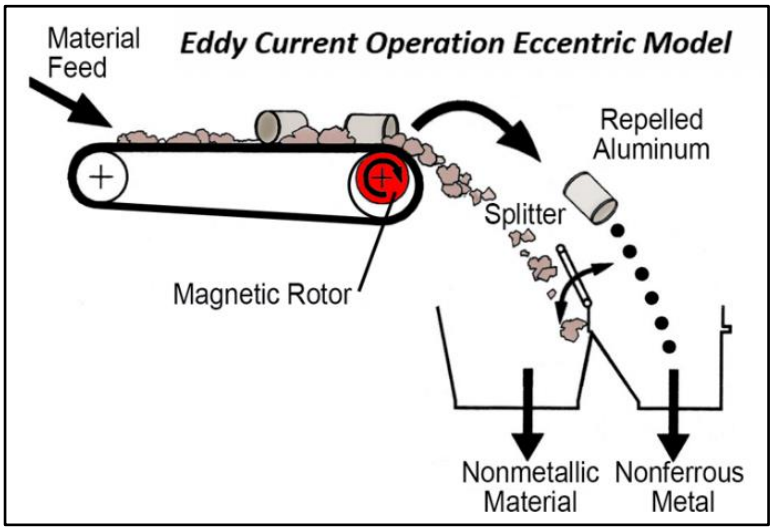


Figure 7: Magnetic conveyer belt [10].

To separate aluminum and copper from the plastic separators, an effective method is to employ an eddy current separator. These devices are designed for the purpose of segregating non-ferrous conductive metals from non-conductive recycled materials.

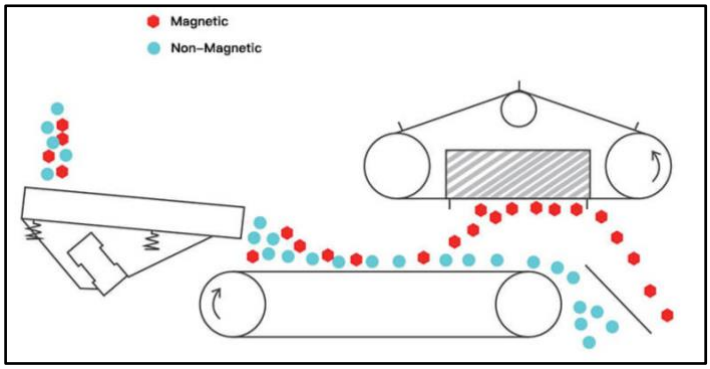


Figure 8: Eddy current separation for separate nonmetallic materials [11].

After separating the plastics from the aluminum and copper by the eddy current method, we should separate the aluminum from copper by a gravity separation table. Gravity separation is a method used in the industry by use of which we separate components. These components are either in the form of a suspension or a dry granular mixture. Here the force of gravity plays an important role: that is the components of the mixture have different specific weights, so the gravity separation table is commonly used to separate particles by weight and density. Several variables influence the optimum concentration result: Variables such as the rotation speed, shaking, particle size, and the deck slope. This way, light and heavy components can be separated from one another.

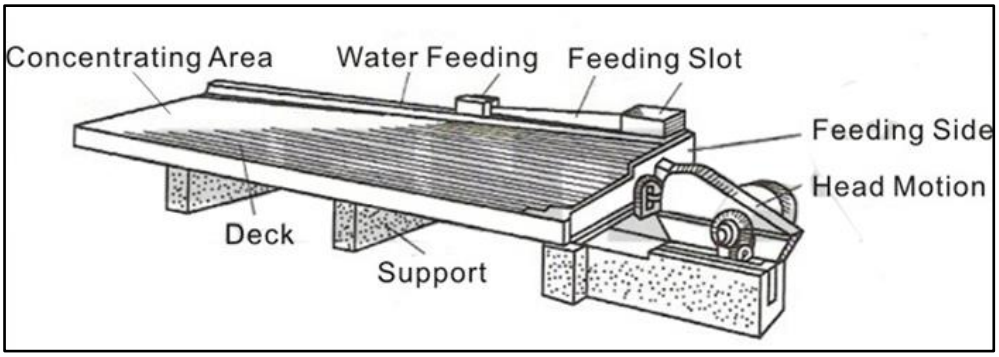


Figure 9: Gravity separation table [12].

Then we melt the aluminum and copper in an electrical or gas fire furnace and during the melting, the melt could be purified by degassers.

On the other hand, ultrasonic washing containers are employed to separate electrode materials from their supporting substrates. These containers are also useful for separating cathodic active materials from aluminum foils. Li et al. [22, 23] used ultrasonic energy together with N-methyl pyrrolidone (NMP).

After being sorted and discharged, lithium-ion batteries are shredded and broken down into small pieces using a shredder. The ground batteries are transferred to the separation tank. The separation tank will separate mixed plastics and metals from the slurry which contains granular solids: Carbon, Metal Oxide, and Lithium Carbonate. The slurry is then transferred and collected in the filter tank where it will eventually be processed by a filter press.

The filter press uses pressure filtration to separate the carbon and metal oxide from the lithium brine solution. Here, the slurry is pumped into a filter press. Then the filtered water/lithium mixture is transferred and then pumped to the evaporation system.

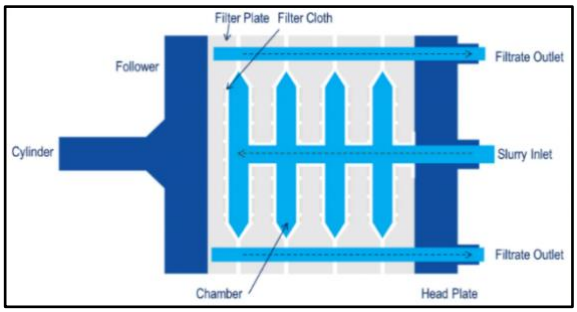


Figure 10: Filter press separator [13].

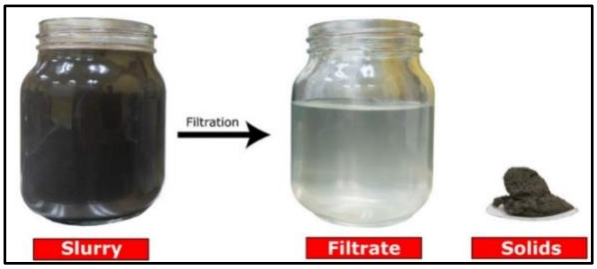


Figure 11 the result of process [13].

Once the slurry has undergone filtration in the filter press, the remaining liquid or lithium brine is then moved to a temperature-controlled evaporation system. Within this system, an evaporator is utilized to remove excess water, concentrating the brine to a specified level. The concentrated lithium brine is subsequently pumped into a mixing tank.

Once the lithium brine solution is concentrated to meet the desired specifications, it is transferred to a mixing tank. At this stage, soda ash is introduced into the lithium brine to facilitate the precipitation of lithium carbonate (Li_2CO_3). The solution undergoes further processing in a filter press, where the lithium carbonate is retained between the plates, and the remaining liquid is discharged.

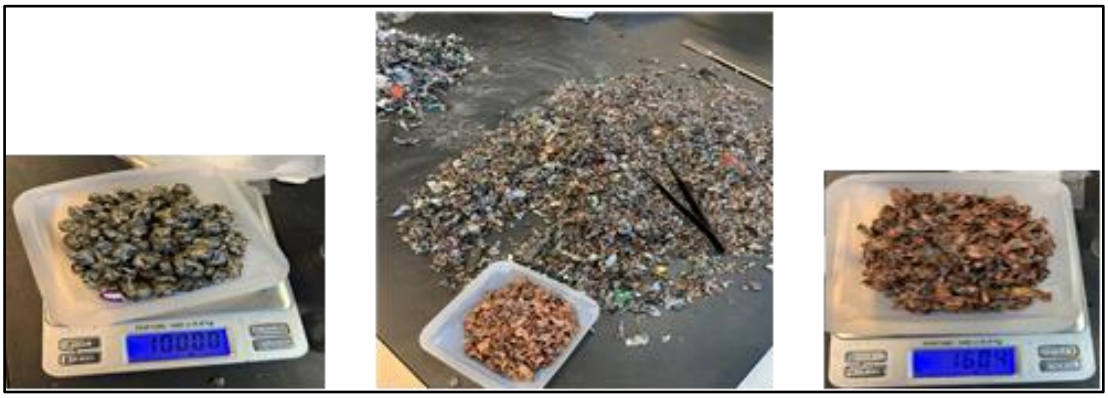
Depending on the specific chemistry involved, the filtrate can potentially be returned to the heated tank system for further evaporation. This process can create a closed-loop zero liquid discharge system, which aids in the separation and recycling of batteries.

3.1. 2.2 PREPARATION OF CURRENT COLLECTORS FROM RECYCLING MATERIAL

After separating the aluminum and copper's current collector from the other components of the battery, their surfaces are cleaned after being recovered from the worn-out batteries.

Next, they have then melted them with a small resistance oven to use again to make the current collectors for new batteries. One of the most important parameters to be aware of is the melting efficiency.

Efficiency is determined by the ratio of the weight of output material to the total of input material in the furnace. In other words, all the metal that enters the furnace is not converted into a product some of it is oxidized by combining with oxygen. Therefore, the shape of current collectors that we have prepared for melting are very effective in melting efficiency. For this purpose, by compressing the current collectors, it reduced their contact surface to prevent further contact with oxygen, thus preventing oxidation.



(b) (a) (c)

Figure 12: Material obtained (a) Fluff; (b) separated Al; (c) separated Cu.

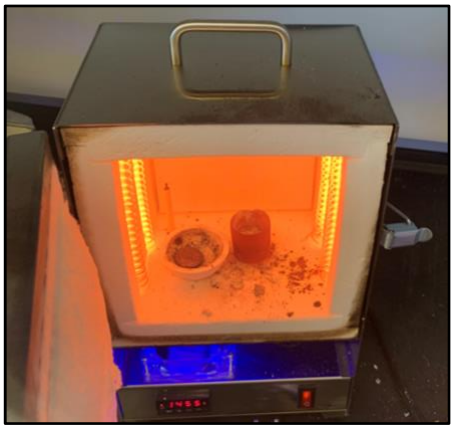


Figure 13: The resistance furnace for preparing melt.

This issue occurred in the case of aluminum during the crushing process. As you can see in figure 12, the aluminum current collector during crushing is in the form

of bullets and apparently have a surface melt at high temperatures. But this has made their cleaning of the surfaces from the cathode difficult and therefore has led to an increase in impurities at the grain boundaries. The cathodes are generally composed of lithium cobalt oxide or lithium nickel cobalt aluminum oxide. But copper as you see in the figure 12, after crushing didn't join and it's good because we have opportunely to clean the coating of the current collectors and then to increase the melting efficiency, compacted by a press. The material of the smelting crucible used for melting was made from graphite and could have an effect on our samples during the melting process.

Samples are melted by an electric furnace and mechanically shaped into discs 10 mm in diameter and 1 mm thick. The molten material made of aluminum and copper current collectors is poured into a graphite mold in the form of a disk.

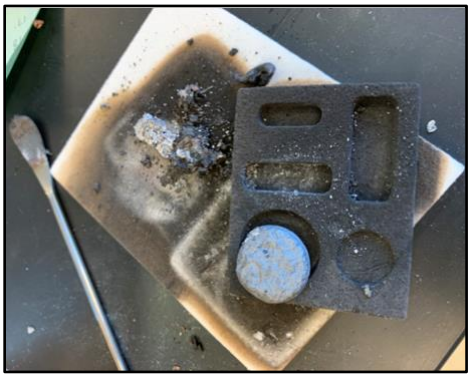


Figure 14: Copper melt.

The surface of the aluminum current collectors shows that there is porosity that is about 200 microns in size. This is gas porosity that usually forms because they were imprisoned during solidification.

Solubility of the gas in aluminum and copper at solid stat is extremely lower than liquid state. So, the gas that dissolved in the melt during the solidification was the cause of this porosity.

To eliminate this gas, the metal was first dried by heating before melting and finally degasser material like chlorine or fluorine is included during the melting process or a rotary degasser by Argon was used.

After solidification, a press was used to form new current collector. Then samples were polished into discs that are 20 mm in diameter and 1 mm thick to be used in new batteries.

Figure 15: press for forming the samples (DAKE -50 Tone).

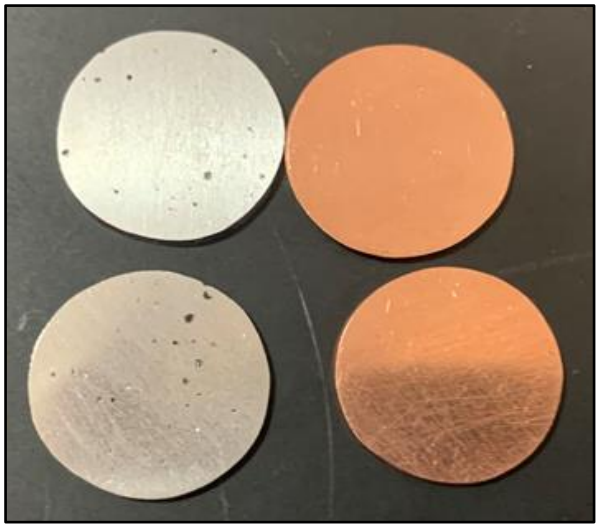


Figure 16: Current collectors made from used batteries.

To understand how the melting could affect the purification of current collectors, the chemical components of the copper and aluminum we checked before melting by Scanning Electron Microscope (FEI Explorer-Aspex).

Figure 17: Scanning Electron Microscope, Aspex Explorer.

3.2. 2.3 MAKING HALF-CELL BATTERIES FROM RECYCLING AL AND CU CCS

Using the Al and Cu CCs from the second phase of this study, cathodes and anodes were fabricated and tested in four half-cells. Cathodes were made by mixing LiNi1/3Mn1/3Co1/3O2 (NMC111) with polyvinylidene fluoride (PVDF) binder and acetylene black as the conductive material in a ratio of 90/5/5 weight percent, respectively. The NMC was mixed with NMP in a Thinky centrifugal mixer (Thinky

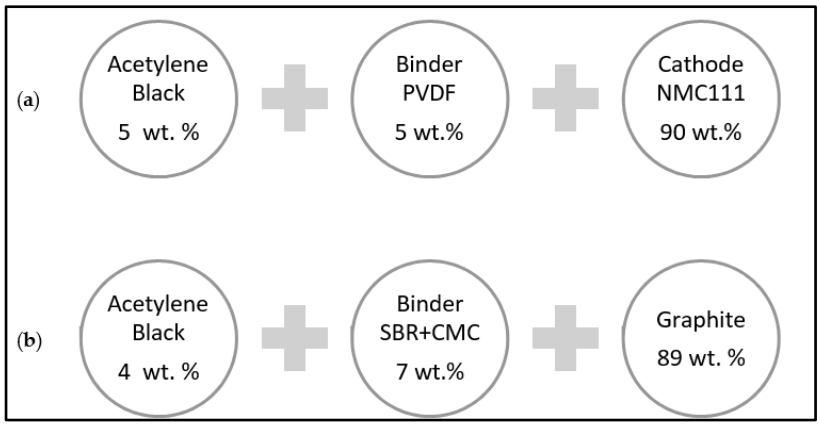


Figure 18:Schematic representation of materials mixed in (a) Cathode and (b) Anode.

U.S.A., Inc., Laguna Hills, CA) at 1000 rpm for 2 min. The binder and conductive material were added gradually using the same mixing program. Using a similar procedure, anodes were made by mixing graphite with carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) binders and acetylene black as the conductive material in a ratio of 89/7/4 weight percent, respectively, as shown in Figure 18.

Four coin-cell type half-cells were assembled using the anodes and cathodes made from recycled materials along with half-cells made from new electrode material. Half-cell components and coin-cell assembly can be seen in Figure19. Coin-cells were assembled by placing punched cathodes or anodes, polypropylene (PP)/polyethylene (PE)/polypropylene (PP) tri-layer separator, then Li metal chip in coin-cell casings along with a wave spring. Each half-cell was tested at two C-rates of C/5 and C/10.

Aluminum Current-Collector	Copper Current-Collector
Cathode (Ni-Mn-Co)	Anode (Graphite)
Separator PP/PE/PP	Separator PP/PE/PP
Li Metal	Li Metal
Stainless Steel Spacer	Stainless Steel Spacer
Wave Spring	Wave Spring

Figure 19: The assembly of half-cell LIBs, (**a**) cathode and (**b**) anode.

To analyze the effect of chemical reactions during battery cycling on the CCs' chemical compositions, the half-cells were opened after cycling to observe the reappearance of surface impurities on the CCs after testing using SEM and EDX.

CHAPTER III

RESULTS AND DISCUSSION

3.1. SURFACE IMPURITIES OF CLEANED CCS BY ULTRASONIC TECHNIQUE

For the first phase of this study, the impurity reduction of washed CCs was analyzed. The EDX results by elemental weight percentages of the anode can be found in Figure 20. Two measurements on and below the surface were taken from

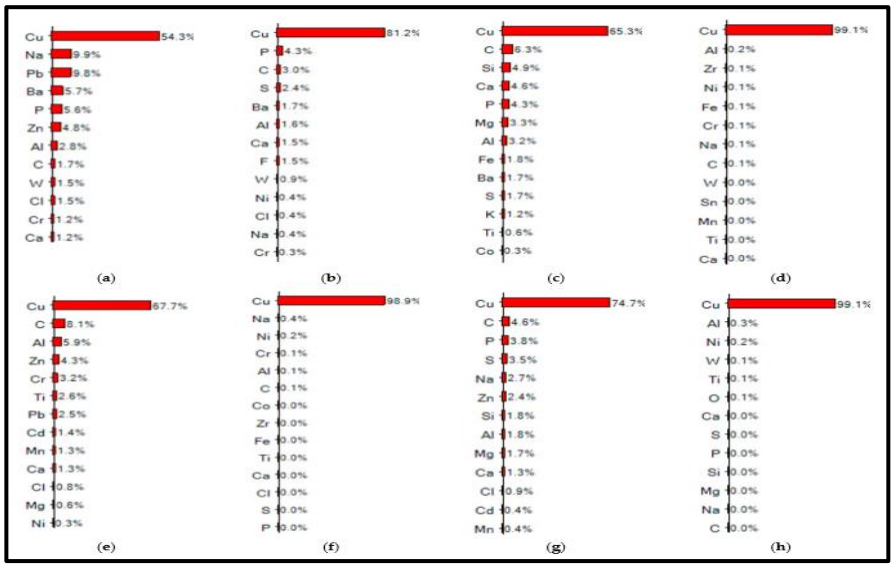


Figure 20: The EDS results for recycled Cu CCs show the composition (**a**) on the surface as-received without cleaning, (**b**) below the surface as-received without cleaning, (**c**) on the surface after cleaning by NMP, (**d**) below the surface after cleaning by NMP, (**e**) on the surface after cleaning by RO, (**f**) below the surface after cleaning by RO, (**g**) on the surface after cleaning by ethanol, and (**h**) below the surface after cleaning by ethanol.

four anode CC samples after NMP, RO, and ethanol cleaning, and one as-received sample as a control. A summary of the result can be seen in Figure 21.

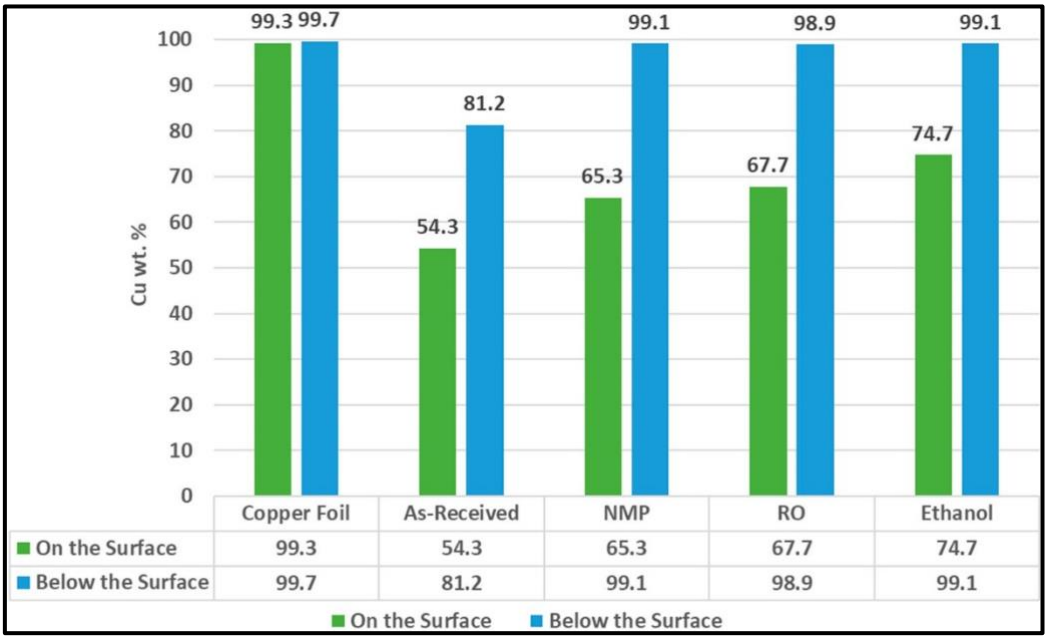


Figure 21: The weight percentage of Cu on and below the surface of a LIB-graded fresh Cu foil, recycled Cu as-received from spent batteries, and recycled Cu after washing with NMP, RO, and ethanol.

The as-received Cu foils showed 45.7 wt.% of impurities on the surface. For reference, new Cu foil supplied to manufacturing facilities contains only 0.7 wt.% of surface impurities. The most effective solution for washing the electrode surface was ethanol (77.4%), followed by RO (67.7%), with NMP being the least effective (65.3%). As expected, impurities below the surface were much less than those above the surface with 18.8 wt.% for as received and ~1 wt.% for washed samples. Ethanol and NMP were most effective at washing impurities below the surface. In contrast to impurities on the surface, CCs washed with NMP showed fewer impurities than those washed with RO.

The data strongly indicates many impurities are present on and below the surface of used CCs. The impurities are due to the aggressive electrochemical environment inside a battery with potential contribution coming from shredding after retirement. These impurities must be washed before proceeding to the melting phase of the recycling process. As shown previously, the best solution for cleaning the surface of recycled Cu is ethanol, which removes up to 25.3% of surface impurities. Similar results were found for reducing impurities in Al CCs. Thus, all CCs subjected to melting were first cleaned with ethanol for 4 min at 24 ◦C (75 ◦F) in an ultrasonic cleaner before melting.

Figure 22: The ultrasonic device for clean the current collectors (Branson 2510).

3.2. SURFACE IMPURITIES OF CCS AFTER MELTING AND BATTERY TESTING.

Results from the EDX and elemental assessment of impurities on the surface of Al collectors are shown in Figures 23. SEM images of Al CCs at three relevant stages for assessment: as received, after melting, and after battery testing. For these Al CCs, three impurities were found comprising of Cu, Mn, and Ni. Overall, Al purity increased by 2.2 wt.% after recycling and decreased only by 1.1 wt.% after battery testing.

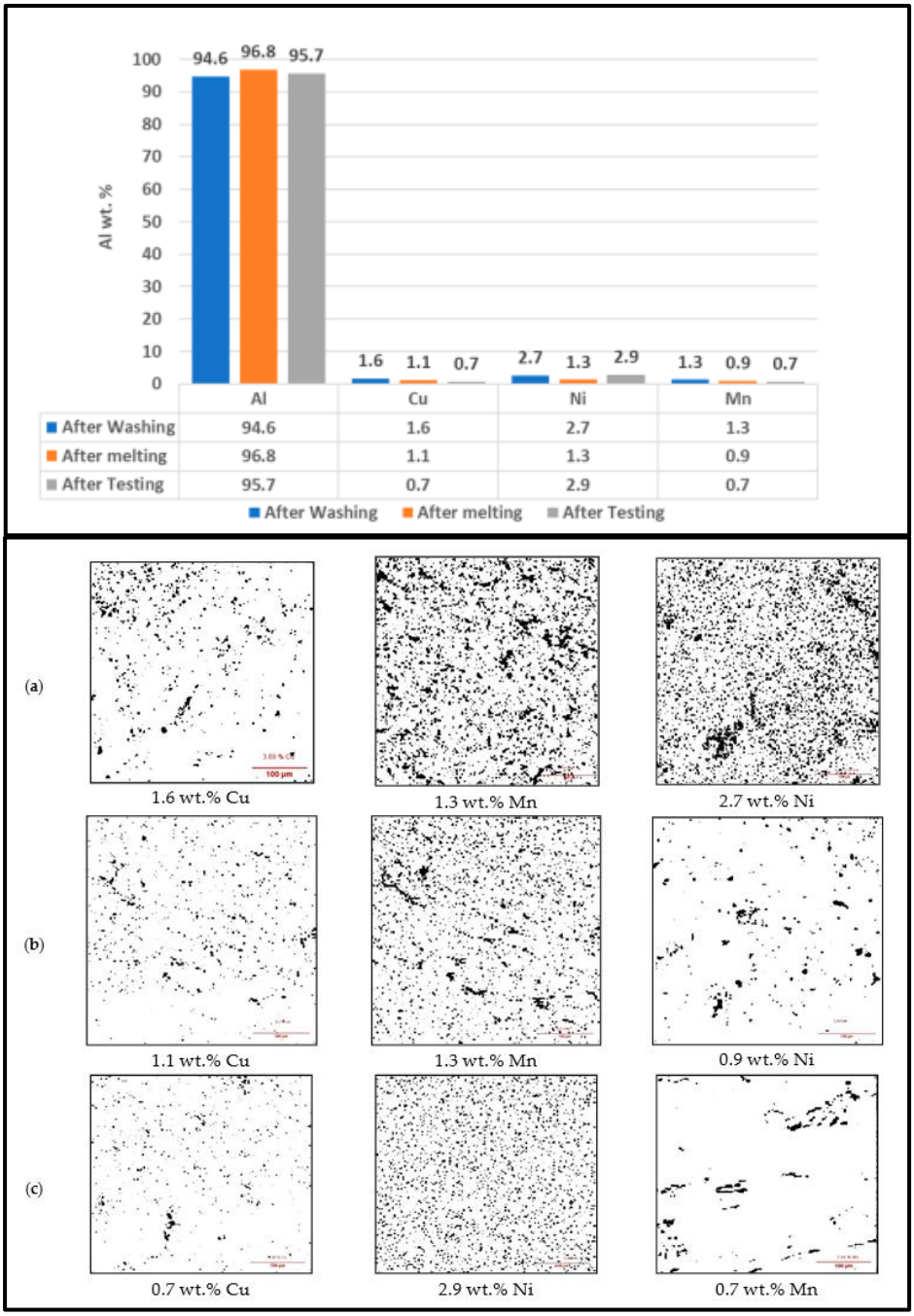


Figure 23: EDX and Elemental mapping for (**a**) As received Al CC from used batteries, (**b**) Al CC from recycled batteries after melting, and (**c**) Al CC from recycled batteries after reuse in new battery and cycling.

It is important to note that all impurities decreased after the thermal treatment of the as-received collectors. Cu content decreased by 0.5 wt.%, nickel by 1.4 wt.%, and manganese by 0.4 wt.%. This drop in impurities proves that the recycling process is capable of reversing impurities in the CCs. Cu and manganese impurities continued to decrease by 0.4 and 0.2 wt.%, respectively, after battery operation. However, nickel content increased by 1.6 wt.%. The increase in nickel impurity after battery operation indicates that some CC degradation occurred along with the loss of active cathode material. Nickel content in impurities is higher than all other elements, especially for as-received CCs (2.7 wt.%) and recycled CCs used in battery testing (2.9 wt.%).

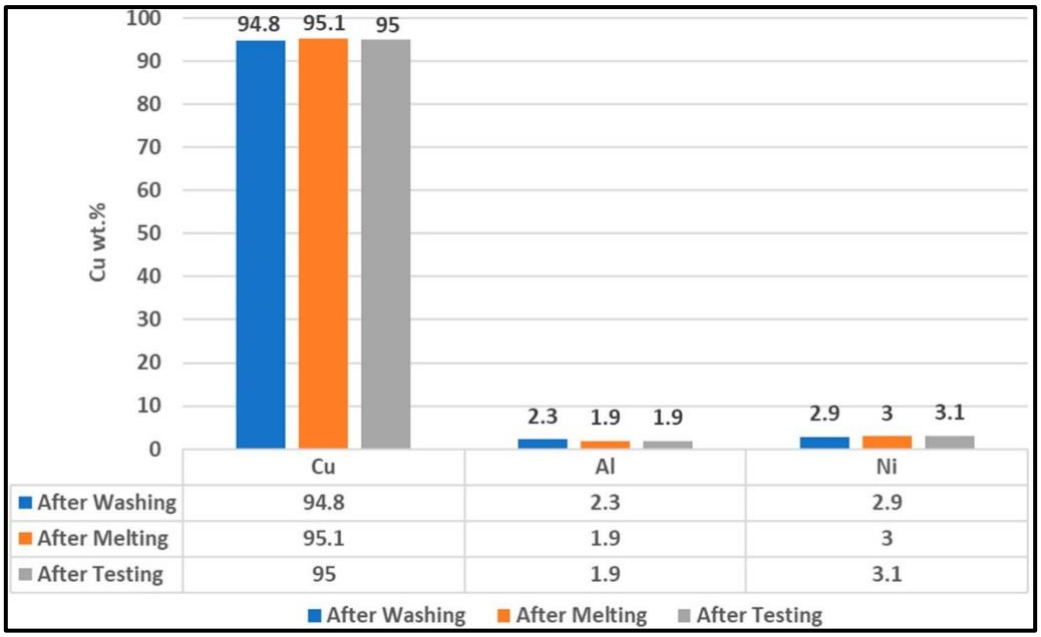


Figure 24: EDX test results on the surface of Cu CCs after washing, melting, and battery testing.

The SEM and elemental assessment results for Cu CCs at the three relevant stages are shown in Figure 25. The impurities found on Cu CCs were Al and nickel. The purity of Cu showed only a slight increase of 0.3 wt.% after recycling and a very small decrease of 0.1 wt.% after battery testing. After recycling, Al impurities decreased by 0.4 wt.%. Contrastingly, nickel impurities increased slightly by 0.1 wt.%.

Battery testing showed no impact on Al content quantities and only slightly increased nickel content by another 0.1 wt.%.

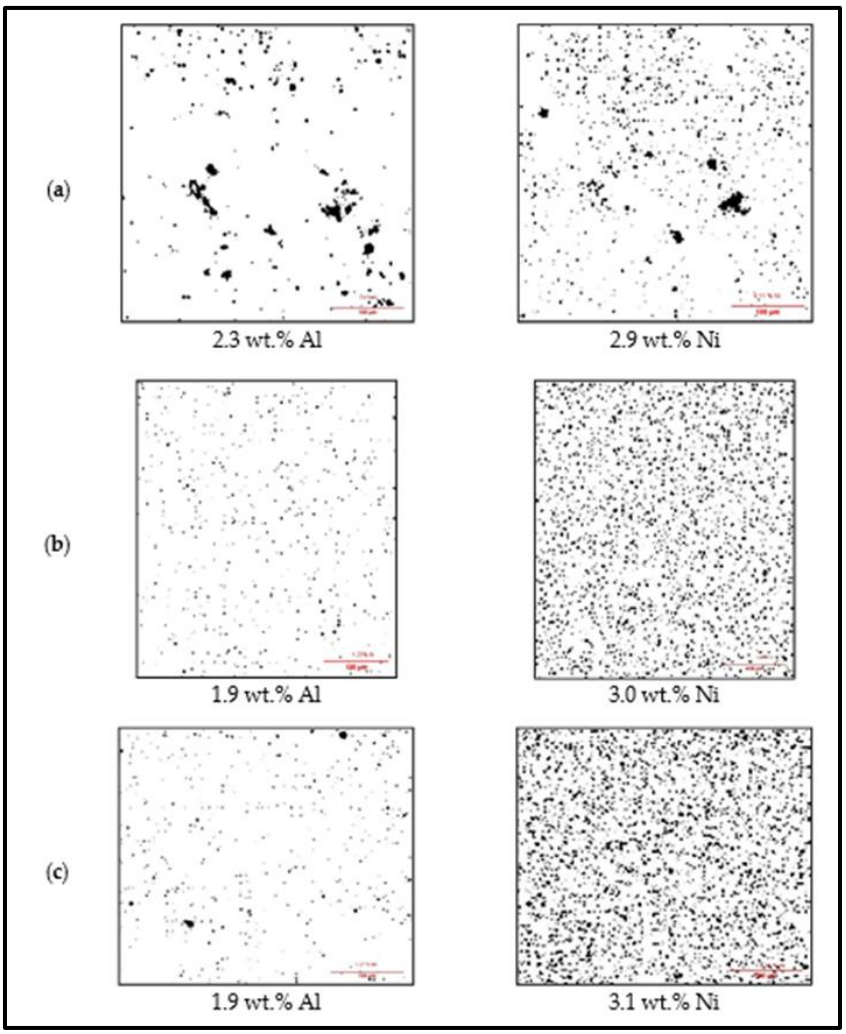


Figure 25**:** Elemental mapping for (**a**) As-received Cu CC from used batteries, (**b**) Cu CC from recycled batteries after melting, and (**c**) Cu CC from recycled batteries after reuse and cycling.

CYCLING PERFORMANCE OF RECYCLED CCS

Results for testing half-cell anodes at a C-rate of C/5 using recycled Cu CCs are shown in Figure 26. After five cycles, the capacity is 312 mAh/g while the capacity after ten cycles is 250 mAh/g. Capacity continues to drop until it reaches 50% after 25 cycles. Contrastingly for testing at a C-rate of C/10, the initial capacity after ten cycles was 255 mAh/g but it dropped to 220 mAh/g after fifteen cycles. The capacity reaches 67% of its initial value after 25 cycles measuring as 170 mAh/g.

(a)

(b)

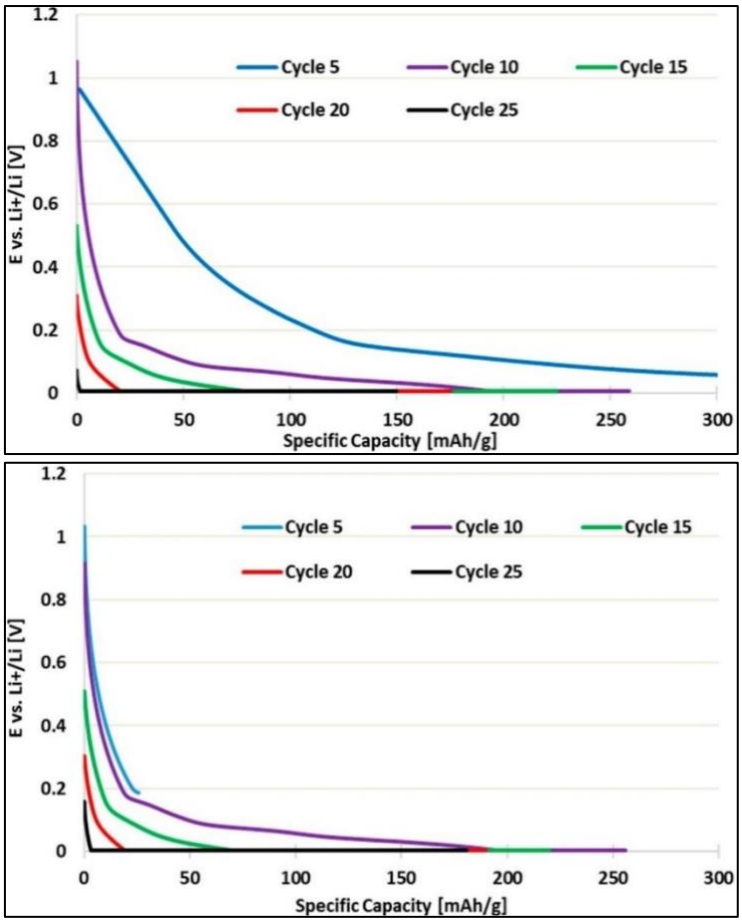
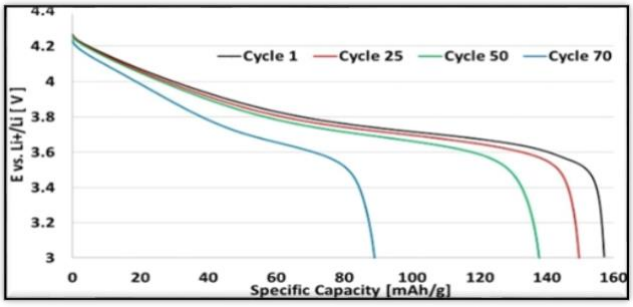


Figure 26: Discharge of anode half-cells with C – rates of (a) C/5, and (b) C/10**:**

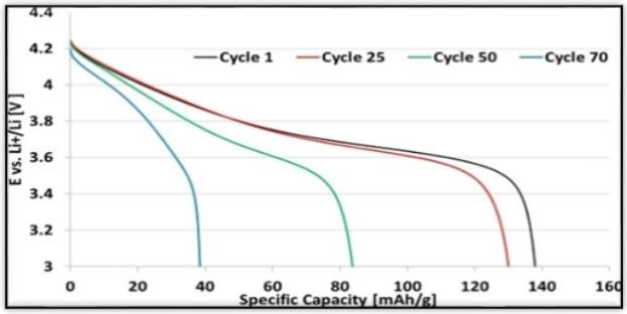
Results for discharging cathode half-cells at C/5 C-rate are shown in Figure 27. After 21 cycles, the capacity is 138 mAh/g. Capacity drops to 85 mAh/g after 52 cycles and finally reaches 39 mAh/g after 71 cycles. Moreover, Figure 24b includes results for discharging half-cell cathodes at C/10 C-rate. This showed an initial

capacity of 157 mAh/g which consistently drops every 25 cycles until reaching a capacity of 130 mAh/g after 50 cycles. After 70 cycles, the capacity is 90 mAh/g which is 57% of the initial capacity. For all tests, specific capacity was normalized by the mass of electrode active material.

The capacity retention of the cathode half-cell tested at both C-rates is shown in Figure 25a along with a comparison to cathodes using fresh Al CC. For C/5, the capacity retention after 50 cycles is 84% while it is 83% for C/10. In contrast, the fresh CC cathode shows a capacity retention of 96%. When compared to the fresh CC cathode, capacity is lower; however, the cathode half-cells still retain more than 80% of the initial capacity. Capacity retention results for anode half-cells are shown in difference in capacity retention.



(a)



(b)

Figure 27: Discharge of cathode half-cells with C-rates of (a) C/5, and (b) C/10.

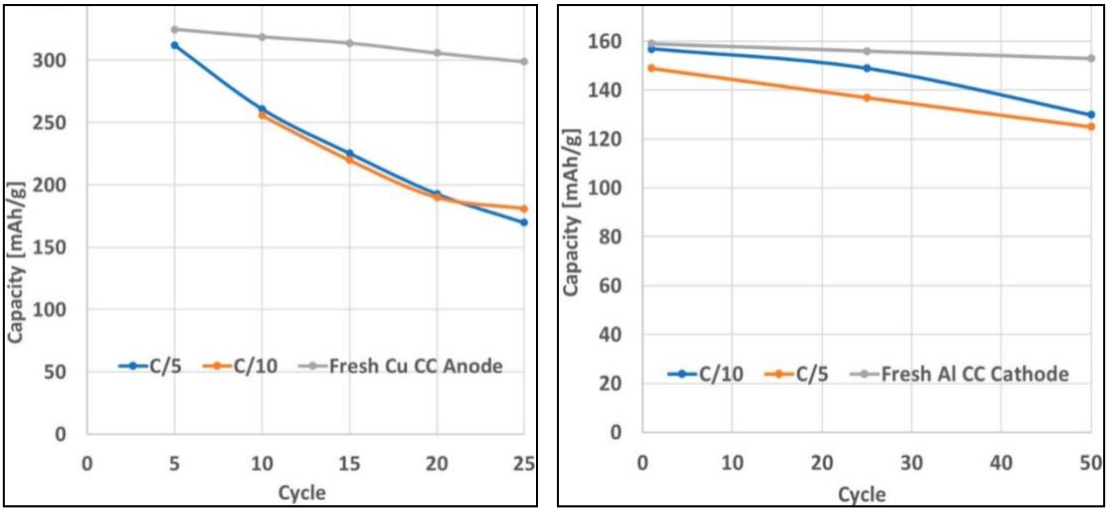


Figure 28: The capacity retention of (**a**) cathode half-cells over 50 cycles and (**b**) anode half-cells over 25 cycles compared to cathodes and anodes made from fresh Al and Cu CC.

CHAPTER IV

CONCLUSIONS

LIBs have been widely used in various applications, including EVs, mobile devices, and renewable energy storage systems, due to their high energy density, long cycle life, and low self-discharge rate. However, the increasing demand for LIBs has raised environmental concerns, including the depletion of natural resources, the generation of hazardous waste, and the emission of greenhouse gases during the manufacturing process. To mitigate these issues, recycling and reusing the valuable materials in LIBs, such as aluminum (Al) and copper (Cu) current collectors (CCs), has attracted great interest in recent years. Al and Cu CCs are critical components in LIBs, as they serve as the electrical contacts for the active materials in the anode and cathode, respectively. These CCs are typically made of high-purity materials, such as Al foil and Cu foil, to ensure good electrical conductivity and corrosion resistance. Therefore, recycling and returning them to the LIB's manufacturing line can significantly reduce the production cost and environmental impact of LIBs, especially in the rapidly growing EV market.

In this thesis, the feasibility of recycling, purification, and reusing Al and Cu CCs from retired LIBs was investigated. The study was conducted in three phases. In the first phase, shredded LIB cells were separated to obtain the components containing Al and Cu CCs. The CCs were then subjected to ultrasonic cleaning using various solvents, and the surface and subsurface impurities were analyzed.

The results showed that ethanol was the most effective solvent for cleaning both Al and Cu CCs, reducing a quarter of surface impurities. In the second phase, the cleaned Al and Cu CCs were recycled via melting and molding, and the impurities were analyzed again. The results indicated that the recycling process was highly effective in purifying the surface of the CCs, as the impurity level was significantly reduced compared to the initial state. However, battery cell testing of the recycled material showed a decrease in capacity retention over time, especially for nickel (Ni) contamination, which may indicate the loss of active cathode material.

In the third phase, anode and cathode half-cells were constructed and tested using the recycled Al and Cu CCs at C-rates of C/5 and C/10 at room temperature. The capacity retention of both cathode and anode half-cells decreased over time, but after 50 cycles of testing, the cathode half-cells showed a capacity retention of above 80%. The battery cell performance testing showed that both anode and cathode half-cells reached below their initial capacities after relatively short cycling periods.

Despite the significant improvement in the purification level of both Al and Cu CCs achieved by the cleaning and melting procedures, the battery cell performance results indicated that the recycled CCs may not be suitable for reuse in new batteries, especially for the Cu CC. Therefore, a more sophisticated purification method should be adopted, which may increase the cost of recycling, or the recycled Al and Cu from retired LIBs should be repurposed in other products/applications where less material purity is acceptable.

Overall, the recycling and reusing of valuable materials in LIBs, such as Al and Cu CCs, is an important strategy for reducing the environmental impact and production cost of LIBs. However, the effectiveness of the recycling and purification methods needs to be carefully evaluated, considering the battery cell performance and material

purity requirements. Future research should focus on developing more efficient and cost-effective recycling and purification technologies to enable the sustainable and circular use of LIBs.

Although we recycled Al and Cu from used batteries through a purification process, we didn't achieve the required level of purity to manufacture new Li-ion batteries. However, we can attempt the process again by increasing the flow of Argon and extending the duration of the process.

With this new information in mind, if we can’t use the aluminum and copper from recycled batteries to remake new LIBs we can use them for other purposes such as use in foundry casting to make parts for different machines or for degassing the steel during the steel making process.

CHAPTER V

RECOMMENDATION FOR FUTURE WORK

To advance the research and development of recycling and reusing copper and aluminum current collectors (CCs) from lithium-ion batteries (LIBs), there are several recommendations for future work. One recommendation is to use a more convenient furnace for melting the recycled CCs. The current furnace used in this study requires a high amount of energy and produces a significant amount of pollution. Therefore, using a more energy-efficient and environmentally friendly furnace could improve the overall sustainability of the recycling process.

Another recommendation is to use a better technique for optimization and characterization of the recycled CCs. Inductively Coupled Plasma (ICP) is a technique that can be used to identify the chemical composition of materials with high accuracy. ICP can provide information on the concentrations of various elements in the CCs, such as copper, aluminum, and impurities. This information can be used to optimize the purification process and improve the quality of the recycled CCs. Additionally, ICP can be used to characterize the performance of the recycled CCs in new LIBs and provide insights into how to further improve the recycling process.

Overall, these recommendations can help advance the recycling and reuse of CCs from LIBs, contributing to the development of a more sustainable energy system. By using more energy-efficient and environmentally friendly techniques and improving the characterization of recycled CCs, researchers and industry professionals can work towards creating a more circular and efficient system for LIB production and disposal.

Another suggestion is to conduct economic research on the recycling of aluminum and copper from lithium batteries, aiming to gain a better understanding of the significance of battery recycling. This research complements our previous discussions on the high electricity consumption associated with aluminum extraction.

One way to enhance the purity of aluminum and copper obtained from battery recycling is by incorporating high-purity materials, thereby elevating the overall purity of the recycled materials.

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