Optimizing the Hydro-metallurgical Extraction of Supply-Chain Critical Metals from Emulated Spent Lithium-Ion Batteries

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***Abstract*—Lithium-ion batteries are an integral part of today's society, powering ubiquitous rechargeable devices. However, only 5% of all lithium-ion batteries are recycled, resulting in 8 million tons of waste being dumped in landfills [1]. This poses a risk to the environment and requires new metal to be mined. Improving the recycling process for lithium-ion batteries can have a large impact even in small communities like Plano, where over a ton of valuable metal can be extracted from lithium-ion batteries every year. There are several methods that can be used to recycle lithium-ion batteries, but they are largely inefficient and expensive. This paper aims to outline the optimization of the efficiency of hydro-metallurgical processes to extract metal from spent lithium-ion batteries. The proposed process has three steps - filtration, chelation, and electrolysis. Filtration removes the insoluble debris from the solution, chelation will be used to remove select metals like iron from the solution, and electrolysis can be used to extract the rest of the valuable metals. The data collected from the experiment indicated that the methods used were successful in improving the efficiency of the whole extraction. However, work still needs to be done to improve the efficiency on a commercially viable scale.**

Keywords - Sustainability, Lithium-ion, recycling, hydro-metallurgy

I. Introduction

Lithium-ion batteries (LIBs) are a fundamental pillar that helps power various electronic devices and appliances. However, the world power consumption is increasing at a rate that will put strain on the supply chain of LIBs in the long term [2]. LIB consumption is expected to grow 5x in the next two decades, primarily due to the proliferation of electric vehicles (EVs). Creating a secondary supply chain from recycling used LIBs can be an effective way to sustain the world's energy needs. Additionally, recycling LIBs removes the need to mine new metals and materials and prevents environmental concerns that come with improper treatment of batteries in landfills. The goal of this project was to optimize the hydro-metallurgical extraction of various supply-chain critical metals from emulated spent LIBs.

Figure 1 indicates that the demand for LIBs have skyrocketed in the past few years due to various car companies' introduction of hybrid and fully electric cars into the automobile industry. In 2022, the demand for lithium significantly exceeded the available supply despite the near twofold increase in production since 2017 [3]. With the reliance on LIBs only expected to increase in the coming years, it is important to quickly create a method to sustain the world energy requirements in the long term. Simply mining new metal will eventually result in the lack of available resources, so it is important to focus on reusing material that has already been disposed of.

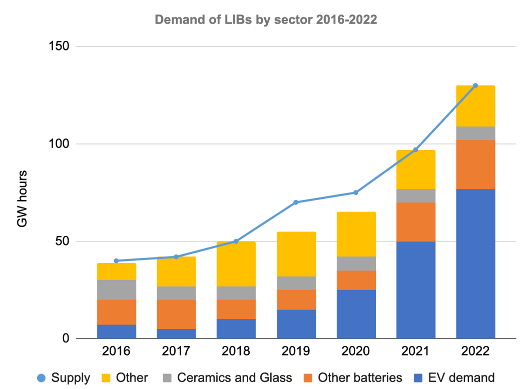

Fig 1. Overall supply/demand of lithium for batteries by sector, 2016-2022

II. Background

A. Requirement for Emulation

A Li-ion battery is made out of three essential components: the cathode, anode, and electrolyte. Many valuable metals are found within a battery, with some of the most prevalent being copper (~15%), iron (~4%), and cobalt (~4%). Materials like cobalt are toxic and lithium can ignite if not treated properly. In order to prevent any safety concerns, the battery was emulated using stable compounds that can be dissolved in aqueous mediums. The salts were put by ratio of weight corresponding to the ratio of the actual metals in a battery. To emulate the debris of a battery, polystyrene balls were put into the solution. Figure 2 indicates the typical composition of a lead acid and lithium-ion battery [4].

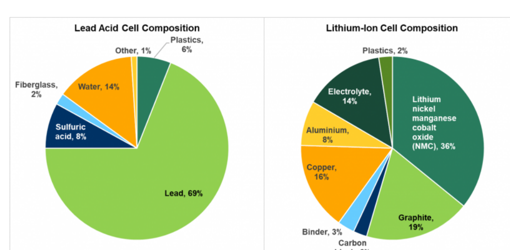

Figure 2: Composition of lead acid and lithium-ion battery.

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B. Methods of Separation

The overall process of recycling a lithium-ion battery is categorized into three steps: the physical, chemical, and electrical method.

The physical method is usually filtration, where the nonmetal portion of the battery is separated from other materials like plastic and paper. The separated materials then go through their own specific recycling processes. A physical method is generally used at the start of a recycling process as it is an easy way to get rid of inert debris from the rest of the battery.

The chemical method is used to selectively extract certain heavy metals from a metal solution. Chemical methods involve using compounds that bind to the heavy metal enabling easy separation in the form of precipitates. Due to the chemical method's selective extraction, it is commonly used after the physical method to remove the most valuable metal from the solution.The chemical method is inherently an efficient process, due to its exothermic nature. However, these chemical methods may not be efficient in extracting all of the metal content in the solution.

The electrical method, usually electrolysis, is where an electric current is passed through a liquid electrolyte inducing a chemical reaction, and the metal deposits onto the cathode of the setup. Figure 3 indicates the fundamental concept of electrolysis with a cathode, anode and electrolyte[5]. Electrolysis is a very energy-intensive process but can be used to extract various metals from the solution. It is generally used last due to its ability to extract multiple metals if given enough time.

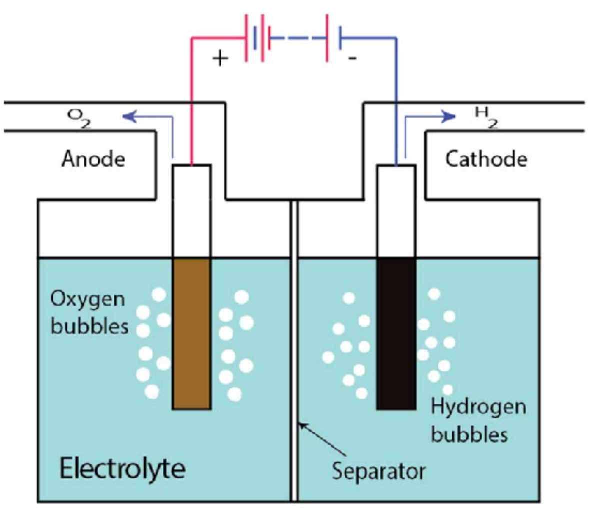

Figure 3: Electrolysis concept.

C. Hydro-metallurgy

Hydro-metallurgy is one of the most mainstream methods of recycling lithium-ion batteries. The method involves using chemical reactions to selectively extract individual metal compounds from a multi-metal compound solution. Different chemicals and concentrates are used depending on the type and composition of the lithium-ion battery, but the process is generally very energy-efficient and chemically intensive. The side-products of hydro-metallurgy can also be potentially dangerous depending on the chemicals used to extract the metal [6].

D. Catalyst Concentration

A catalyst is something that boosts the rate of a chemical reaction. Catalysts work by lowering the activation energy required for a chemical reaction to take place, allowing the process to use less energy to achieve the same result. The higher the concentration of a catalyst, the faster the reaction will be, until the maximum saturation is reached.

E. Temperature Modulation

Temperature modulation is another very common way of increasing the rate of a chemical reaction. Often times, there is a peak temperature in which the reaction is at its fastest, and the exact optimal value varies depending on the materials used and the proportions in which they are in the reaction. If the temperature of a reaction strays too far from the optimal point, the reaction can be significantly slowed or stopped altogether.

III. Experimental Procedure

A. Experimental Setup

The emulation of the battery setup used a combination of Ferrous Sulfate Heptahydrate, Nickel Chloride Hexahydrate, and Copper Sulfate Pentahydrate. The choice of the compounds were determined by water-soluble compounds of the critical metals of a lithium-ion battery. However, lithium and cobalt were not used due to their hazardous nature since the experiment was not conducted in a laboratory environment. Figure 4 shows the typical metals which can be found in a li-ion battery.

Material	Co	Fe	Ni	Cu	Al	Other
Percent	7%	9%	4%	10%	15%	55%

Figure 4: Composition of a typical lithium-ion battery

Polystyrene balls were used to emulate the plastics and nonmetals that are in a lithium-ion battery. In actual lithium-ion recycling, the battery is shredded into many small pieces, which makes using several small balls more appropriate than a large piece of plastic or paper.

B. Filtration

Filtration is done by the straining of the aqueous solution by a physical filter. Using the filters, the liquid solution was separated from the polystyrene balls. The porosity of the physical filters should be that the physical debris can be separated out from the rest of the solution. Once the plastic balls are separated, they can be put through their own specific recycling process.

C. Chelation

After the solution without debris is decanted into a separate beaker, chelation was used to selectively extract certain heavy metals. The two chelates used in this experiment were Ethylenediamine Tetraacetic Acid (EDTA) and L-Glutamine, both well-known chelates to extract metals like iron. Identical solutions underwent chelation using the different chelates to test which materials were extracted and the varying efficiency of extraction. A molar ratio of 2:1 was used as the optimal chelate to metal ratio [7]. After the reaction was finished, a solid precipitate was at the top of the solution. Using physical filtration, the solid precipitate was separated and evaluated. Figure 5 shows the basic mechanism of chelation.

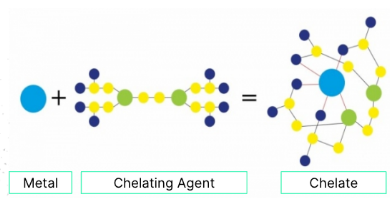

Figure 5: Chelation Process

$$Fe(S0_4) \cdot 7H_2O + Na_2(EDTA) \rightarrow Fe(EDTA) + Na_2(SO_4) + 7H_20$$

D. Electrolysis

The final step to remove the metals from the solution is electrolysis. This experiment used a Wanptek 30V 10A power supply as a source. The electrodes (zinc and graphite) were chosen based on inertness and effectiveness for electrolysis. The potential difference of the setup was set to be greater than the electrochemical potential of the half-cell used in the process (1V). Using the decanted solutions that underwent chelation, electrolysis was used to extract any residual metal. The base rates of electrolysis were recorded for each sample, and the samples underwent further testing to study the impacts of catalysts and temperature on electrolysis efficiency. The current through the electrolyte is used as a proxy for electrolysis efficiency. A higher current reading equates to a higher efficiency.

1) Catalyst Concentration

Citric acid and tartaric acid are two commonly used catalysts for electrolysis [8]. The electrolysis efficiency was recorded at regular intervals until saturation was reached.

2) Temperature Modulation

Temperature modulation is the final method used in this experiment to increase the efficiency of metal extraction. The temperature was slowly increased in the sample in which the catalyst was added, and the current was regularly measured.

E. Composite Results

The results of catalyst concentration and temperature modulation can be combined to compare and contrast to the baseline electrolysis efficiency before and after optimization. Data can be recorded depending on the individual increases in extraction rate based on the solutions/chelates used.

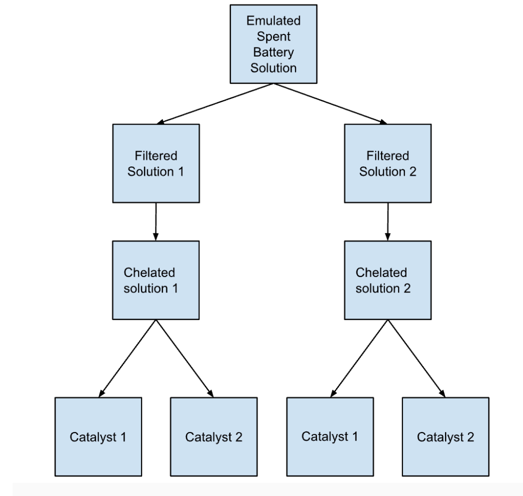

Figure 6: Flow Diagram of Experimental Procedure

IV. Results and Interpretations

A. Filtration

Filtration was shown to be an effective method to remove the solid particles away from the liquid solution. However, the effectiveness of the filtration process depends on the porosity of the filter.

B. Chelation

Chelation was also shown to be an effective way to selectively extract heavy metals from liquid solutions. While both EDTA and L-Glutamine were able to properly react with the metals in the solution, EDTA generated about three times as much precipitate as L-Glutamine (3g vs 1g). Additionally, EDTA likely extracted both iron and nickel, while L-Glutamine only extracted iron.

C. Electrolysis

Electrolysis proved to be able to extract various metals from the metal solution, and the extraction rate was able to be optimized through catalyst concentration and temperature modulation.

1) Catalyst Concentration

Citric acid and tartaric acid were both shown to have an positive effect on the rate of electrolysis. Figures 7 and 8 show the effect of catalysts on electrolysis for various chelates.

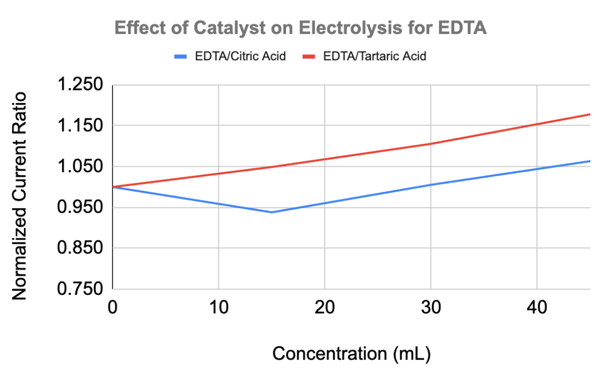

Figure 7: Effect of Catalyst on Electrolysis for EDTA

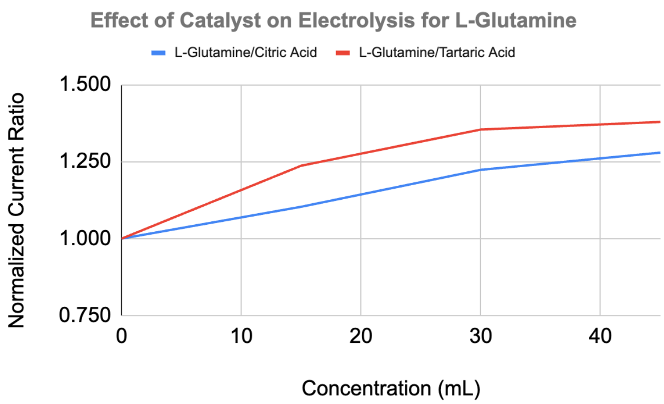

Figure 8: Effect of Catalyst on Electrolysis for L-Glutamine

Measured data indicates that tartaric acid was a more effective catalyst with a 30% increase compared to the baseline while citric acid produced a 20% increase in the electrolysis efficiency.

2) *Temperature Modulation*

Modulating temperature allowed for a very significant increase in the rate of electrolysis, ranging around a 100% increase in efficiency at the optimal heat when compared to room temperature [9]. Experimental observations indicate significant fluctuations in the electrolysis efficiency when the boiling point of the electrolytic solution was reached. Figure 9 shows the effect of temperature on the rate of electrolysis.

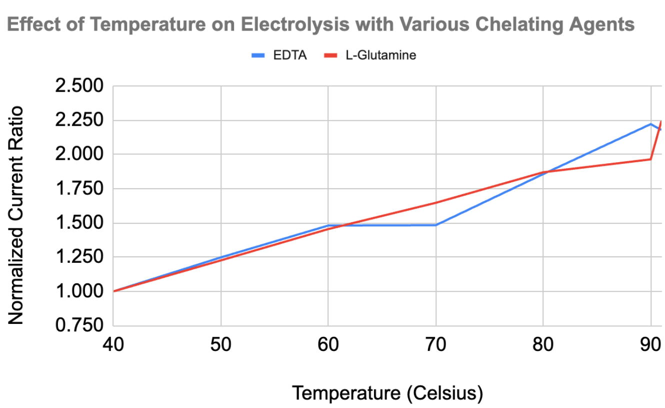

Figure 9: Effect of temperature on Electrolysis

3) *Total Efficiency*

The combination of L-Glutamine and Tartaric acid proved to be the most efficient method of electrolysis extraction for the metals in the solution. When combining the catalysts and temperature together, the result ranged from around 1.9-2.6 times baseline efficiency. While mechanisms can be incorporated to improve the efficiency of the recycling process, the impact of recycling also depends on consumer awareness and the collection process of spent lithium-ion batteries. Figure 10 shows the composite results of all chelate and catalyst combinations.

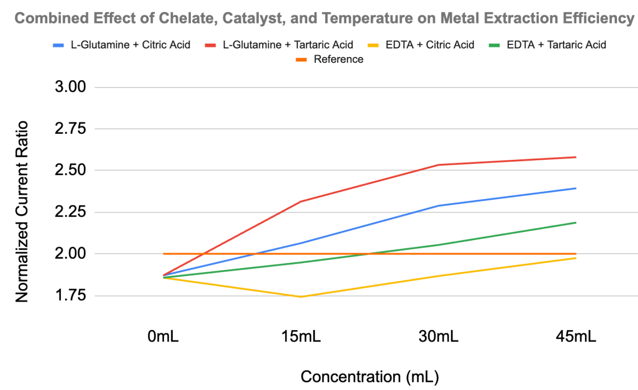

Figure 10: Combined Effect of Chelate, Catalyst and Temperature

4) *Energy Analysis*

The analysis of a typical electrolysis setup was done to calculate the absolute energy efficiency of the process. 26g of ferrous sulfate was dissolved in water, which equates to about 5.2 grams of iron. In a baseline electrolysis setup, 1g of iron was extracted in 105 minutes, resulting in an overall efficiency of 19.2%. This indicates that 13.585 Wh of energy was expended to extract 1g of iron. Up to 900,000 tons of iron can be extracted from recycled lithium-ion batteries in 2022. The power required to extract the iron out of batteries using the above setup is estimated to be over 12,500 GWh, which is more than the worldwide yearly energy production. This clearly shows that the energy efficiency of an extraction process needs to be improved by several orders of magnitude to have a commercially viable recycling process. Commercial viability needs to be studied in depth to ensure that the recycling process is self-sustaining in the long-term.

V. Economics

Startup costs	**Low range cost ($**	**High range cost ($**
Land	200000	1000000
Automated battery reycling machinerny	1000000	4000000
Permits and licences	10000	50000
Safety equipment and waste management	10000	500000
Construction of facility	500000	50000000
Security measures	75000	150000
Transportation vehicles	100000	2000000
Advertising	50000	100000
Total	1745000	56800000
Revenue per metric tonne ($)	5000	
Operating cost per metric tonne ($)	1560	
Average capacity of a 10,000 sq ft facility (metric tonnes	3000	
Revenue stream from 10,000 sq ft facility	15000000	15000000
Cost of operating a 10,000 sq ft facility	4680000	4680000
Depreciation of startup costs	349000	11360000
Profit	9971000	-1040000

Figure 11: Economics of Lithium-ion Recycling

A. *Reasoning*

The lack of working lithium-ion recycling plants throughout the world can be accredited due to the difficulty in maintaining profitability. Operating large-scale recycling mechanisms come with significant fixed costs which in many cases poses a significant barrier to commercial viability. Figure 11 represents the cost-return analysis of a lithium-ion recycling plant.

Recycling plants also can create large amounts of toxic waste and gas, meaning that a more sustainable way or recycling and disposing of waste must be made in lithium-ion recycling as well. Figure 9 illustrates the operation details of the cost involved in a typical lithium-ion recycling plant [10].

VI. Conclusion

A. Synopsis

The three-step process including filtration, chelation, and electrolysis was shown to be an effective method in extraction of various metals from an emulated spent lithium-ion battery. The combined electrolysis process led to a 1.9-2.6x increase in efficiency compared to a baseline setup. Even with the improvement, the results indicate that there must be tremendous improvements in energy efficiency in order to scale up the setup to be commercially viable.

B. Limitations

The experiment used a chemical emulation of a spent battery, assuming a certain composition of materials. Deviation from this assumption could impact results. Variables such as anode corrosion, cathode and anode separation. ambient temperature fluctuation, and the scaling of the experimental setup could pose limitations and can cause errors in the eventual results analysis.

C. Future Work

Improving the scalability of the hydro-metallurgical process will be a prime research area in the future for sustainable lithium-ion recycling. While hydro-metallurgy is popular in lithium-ion recycling, alternate methods such as pyrometallurgy have been gaining more prominence to improve the efficiency of the recycling process. Alternate methods for energy storage such as sand batteries, hydrogen fuel cells, and carbon nano-tube batteries provide energy storage mechanisms that may be more environmentally friendly than lithium-ion batteries. Additionally, while improving the extraction efficiency of spent lithium-ion batteries is very important, it is equally important to increase the procurement and identification efficiency of used lithium-ion batteries to solve the “first-mile” problem associated with lithium-ion battery recycling.

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References

1. Team, C. S. (2022, September 22). *Lithium Ion Battery Recycling*. CAS. https://www.cas.org/resources/cas-insights/lithium-ion-battery-recycling
2. Degen, F., Winter, M., Bendig, D., & Tübke, J. (2023, September 28). Energy consumption of current and future production of lithium-ion and post lithium-ion battery cells. Iea. (n.d.).
3. Trends in batteries – global EV outlook 2023 – analysis. IEA. https://www.iea.org/reports/global-ev-outlook-2023/trends-in-batteries
4. FOTW #1128, April 6, 2020: Innovations in Automotive Battery Cell Composition | Department of Energy. (n.d.). https://www.energy.gov/eere/vehicles/articles/fotw-1128-april-6-2020-innovations-automotive-battery-cell-composition
5. The basics of electrolysis. Shalom Education. (2024, February 14). https://www.shalom-education.com/courses/gcsechemistry/lessons/chemical-changes/topic/the-basics-of-electrolysis/
6. Hydrometallurgy. Hydrometallurgy - an overview | ScienceDirect Topics. (n.d.). https://www.sciencedirect.com/topics/engineering/hydrometallurgy
7. Lithium recovery from spent lithium-ion batteries leachate by chelating agents facilitated electrodialysis - Zheng Xing, Madhavi Srinivasan, Chemical Engineering Journal, 15 October 2023
8. Effect of citric acid on electrochemical properties of liquid electrolytes. (n.d.). https://www.researchgate.net/publication/351636367_Effect_of_Citric_Acid_on_Electrochemical_Properties_of_Liquid_Electrolytes
9. Cesiulis, H.; Tsyntsaru, N. Eco-Friendly Electrowinning for Metals Recovery from Waste Electrical and Electronic Equipment (WEEE). Coatings 2023, 13, 574. https://doi.org/10.3390/coatings13030574
10. How much does it cost to open a battery recycling facility?. FinModelsLab. (2023, October 5). https://finmodelslab.com/blogs/startup-costs/battery-recycling-startup-costs