Indian Institute of Technology Ropar

MM206

Principles of Extractive Metallurgy
Term Paper

Cost effective process for the recovery of Li from waste batteries

Kavyansh Dhakad
2022mmb1385

Kratin Sharma
2022mmb1385

Rishav Kumar
2022mmb1389

Overview

This presentation outlines a novel approach for economically extracting lithium from lithium-ion batteries, addressing the growing demand for this critical element in renewable energy and electric vehicles. Recognizing the limitations of current extraction methods in terms of cost and environmental impact, our project focuses on developing an innovative technique. We present a detailed methodology encompassing key parameters and experimental data supporting the feasibility of our approach. Through a thorough economic analysis, we demonstrate the potential cost savings and scalability of our method compared to conventional techniques. Moreover, we emphasize the importance of considering environmental implications and discuss measures to mitigate adverse effects. Despite challenges, ongoing research efforts are directed towards optimizing the extraction process for enhanced efficiency and sustainability. In conclusion, our project underscores the urgent need for economical and environmentally conscious solutions in the extraction of lithium, crucial for the advancement of renewable energy technologies.

What are Li-ion Batteries?

Li-ion batteries are rechargeable energy storage devices commonly used in portable electronics, electric vehicles, and renewable energy systems. They operate based on the movement of lithium ions between positive and negative electrodes during charging and discharging cycles.

Li-ion battery includes a positive electrode (cathode) made of a lithium-containing material such as

- lithium cobalt oxide
- lithium manganese oxide
- lithium iron phosphate

Negative electrode (anode) usually composed of graphite
And an electrolyte that facilitates the movement of lithium ions between the electrodes while preventing direct contact between them.

When a Li-ion battery is charged, lithium ions move from the positive electrode through the electrolyte and are stored in the negative electrode. During discharge, the lithium ions move back to the positive electrode, generating electric current that can power various devices.

Advantages and Disadvantages

Lithium-ion Battery	
Advantages	**Disadvantages**
Light-weight	Involves risk of bursting
Have higher energy density than other rechargeable batteries	Costly, compared to other batteries
Rate of charge loss is less	Complete discharge damage the battery
Have a greater number of charge and discharge cycles	Extremely sensitive to high temperatures (degrades very quickly, if exposed to heat)
Need not be discharged completely (due to absence of memory effect)	Very short lifespan (2 to 3 years from the date of manufacturing, even if not in use)
Operates at higher voltage than other rechargeable batteries (approx. 3.7 volt)	Not available in standard cells sizes (AA, C, and D) like others

Advantages over other types of batteries, including

- high energy density
- lightweight design
- relatively low self-discharge rates

Limitations such as

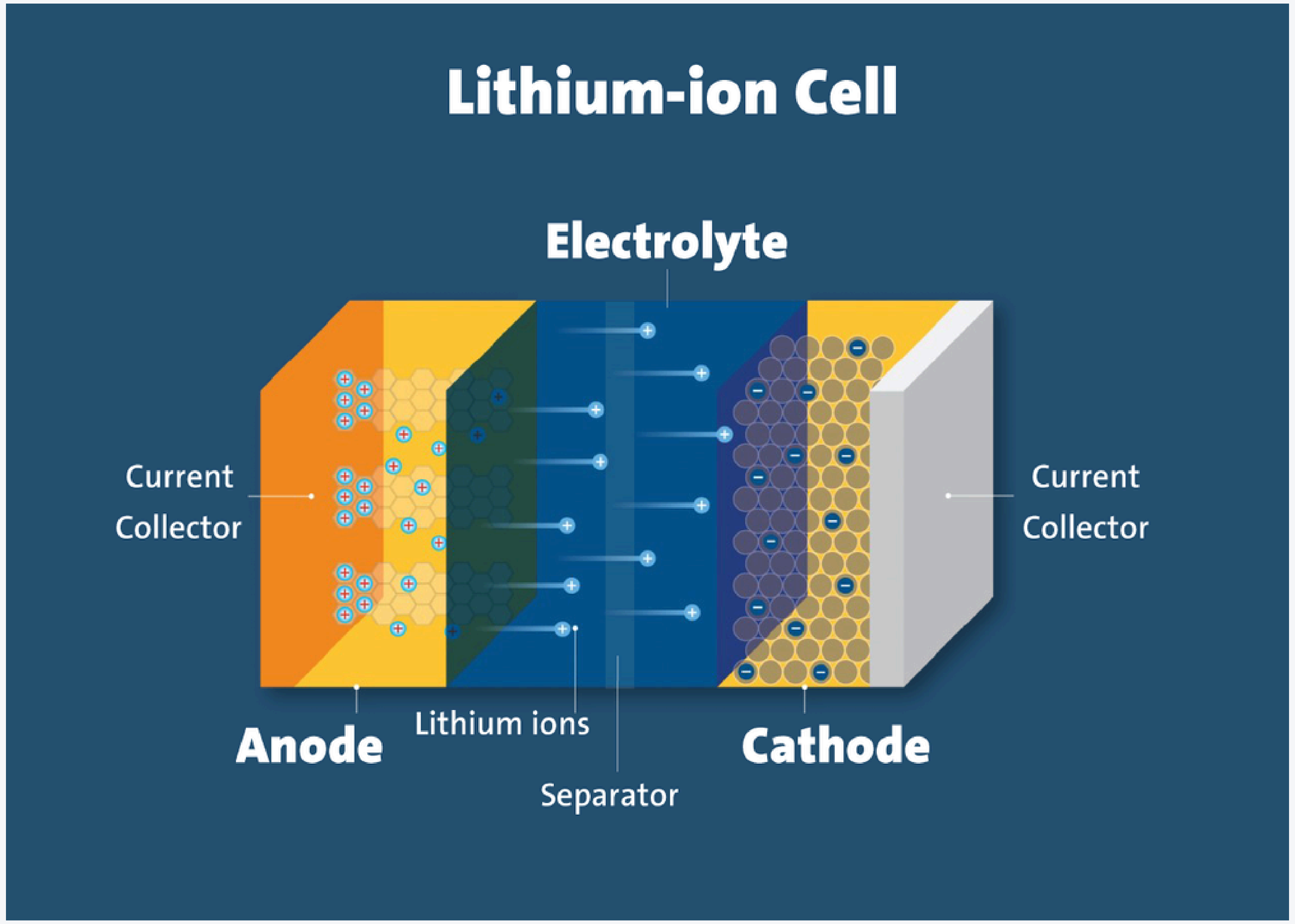
- limited lifespan
- sensitivity to high temperatures, and the potential for thermal runaway under certain conditions.

Source: https://ul.org/research/electrochemical-safety/getting-started-electrochemical-safety/what-are-lithium-ion

https://www.researchgate.net/figure/Advantages-and-disadvantages-of-Li-ion-batteries-compared-to-other-rechargeable-batteries_fig7_337012019

How Li-ion Battery works?

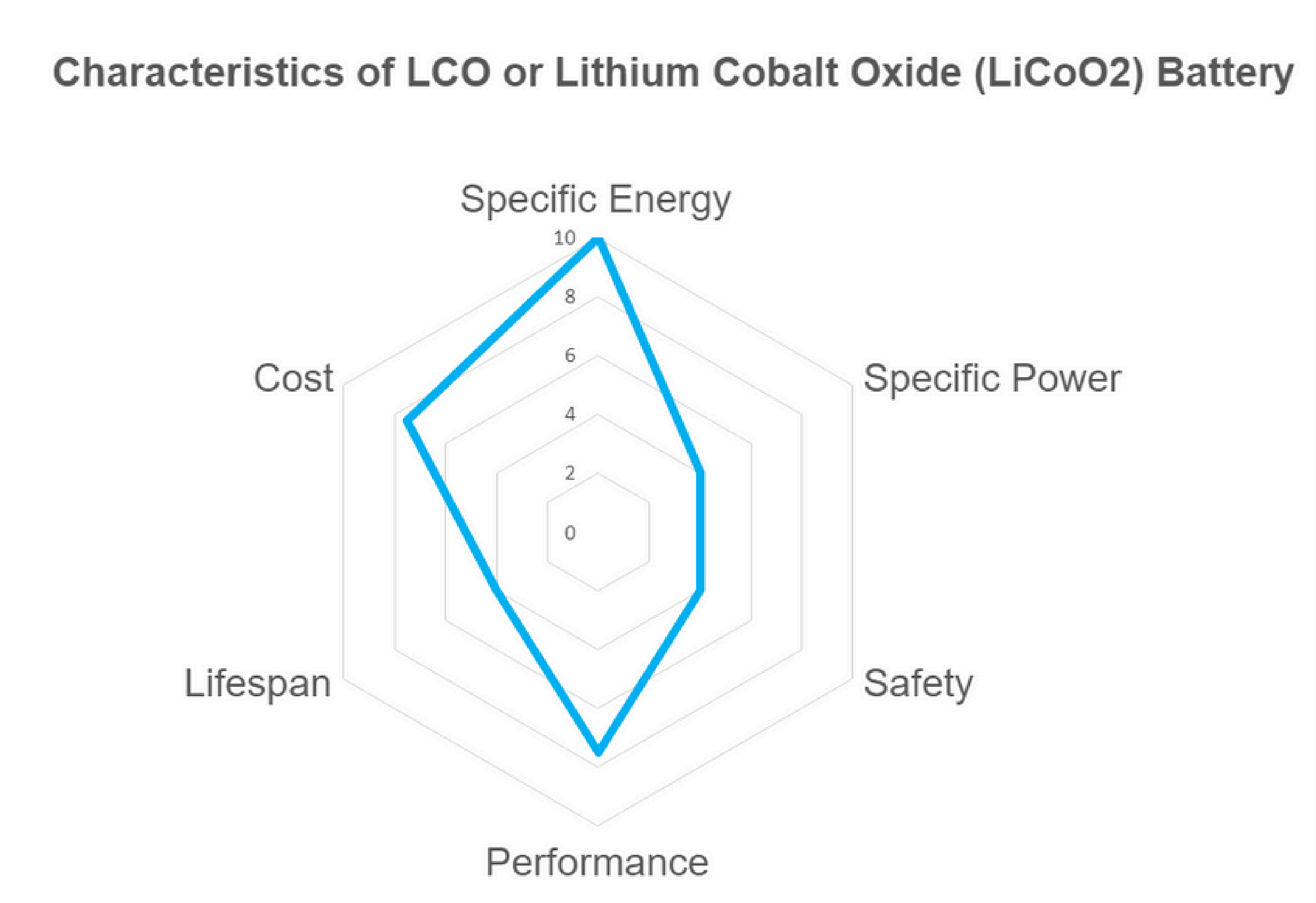
- A lithium-ion battery operates through a process involving its key components: positive and negative electrodes, separated by an electrolyte.
- During charging, lithium ions move from the positive electrode (cathode) to the negative electrode (anode) through the electrolyte, driven by an applied voltage.
- This process involves the release of electrons at the positive electrode and their acceptance at the negative electrode, generating stored energy.
- When discharging, this flow of ions reverses, with lithium ions moving back to the positive electrode, creating an electric current that powers devices.
- This reversible movement of ions enables the battery to be rechargeable. However, factors like electrode degradation can affect its efficiency over time.



Source : https://ul.org/research/electrochemical-safety/getting-started-electrochemical-safety/what-are-lithium-ion

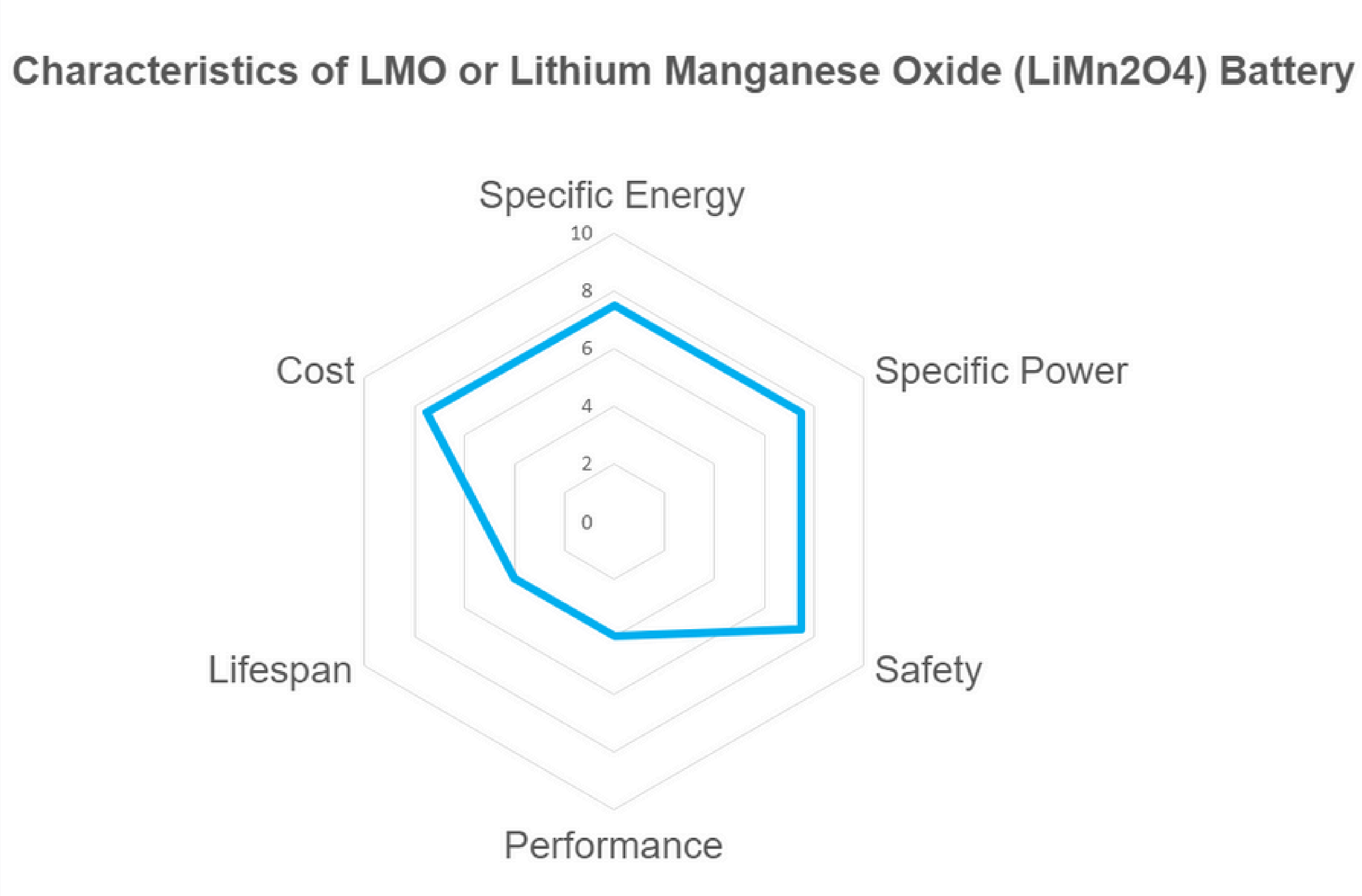
Types of Li-ion Batteries

- **LCO or Lithium Cobalt Oxide (LiCoO2)**



Applications : Cameras, laptops, mobile phones, and tablets.

- **LMO or Lithium Manganese Oxide (LiMn2O4)**

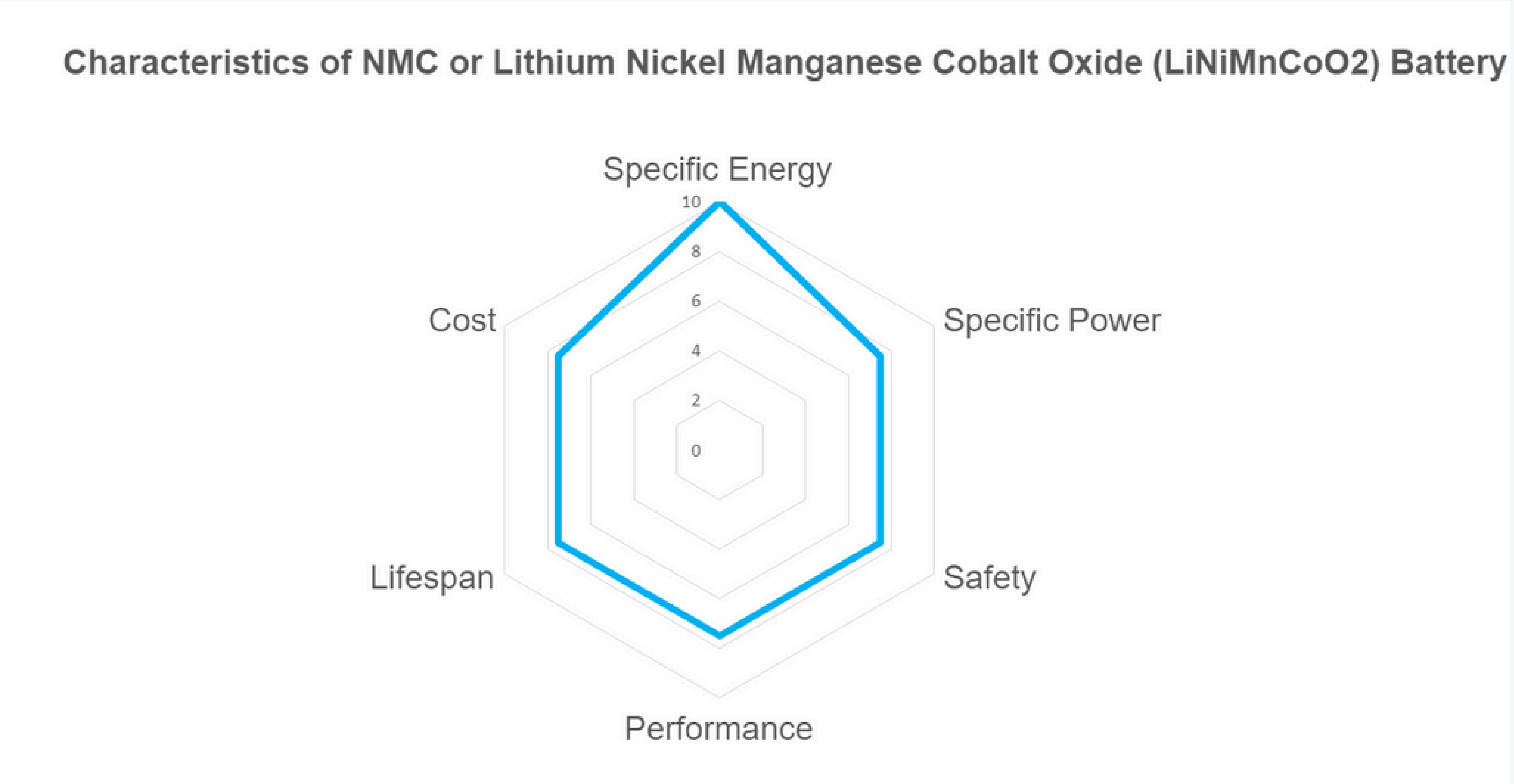


Applications : Medical devices, portable power tools, hybrid and electric vehicles, and powertrains.

Source :https://www.blackridgeresearch.com/blog/what-is-a-lithium-ion-battery-what-are-the-types-of-lithium-ion-battery-chemistries

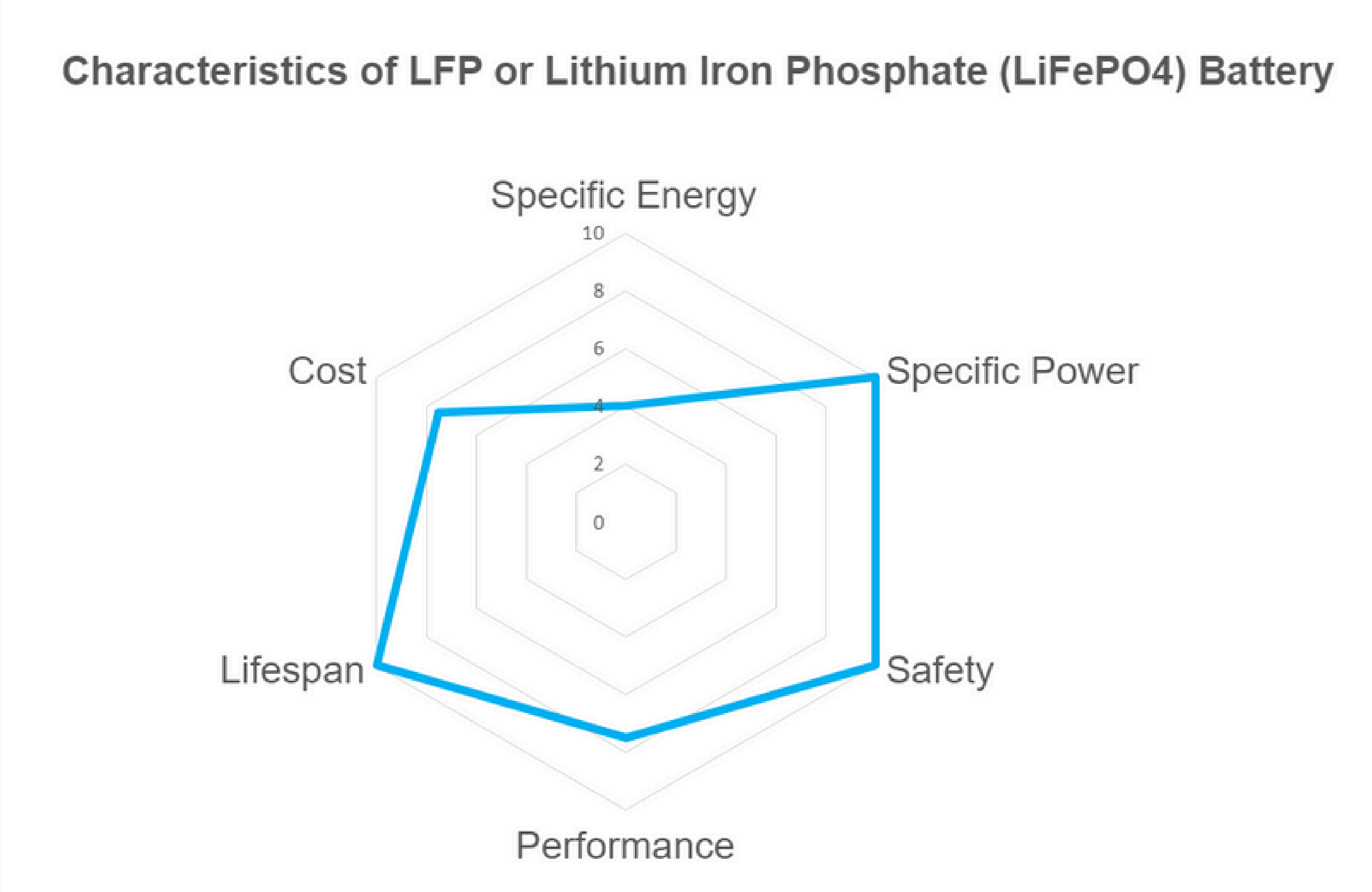
Types of Li-ion Batteries

- **NMC or Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO2)**



Applications: E-bikes, EVs, medical devices, and industrial.

- **LFP or Lithium Iron Phosphate (LiFePO4)**

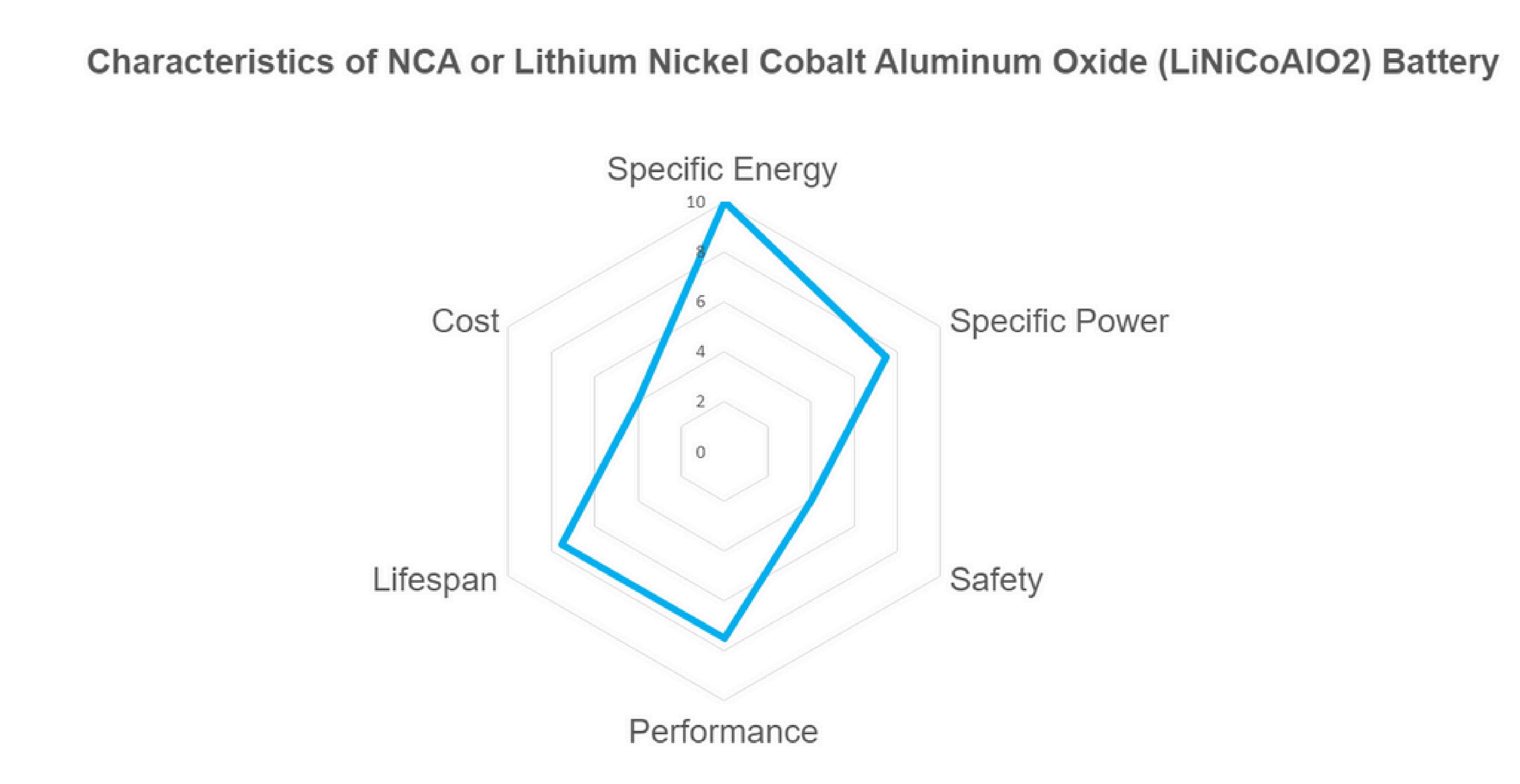


Applications: Mainly stationary applications with high endurance like UPS.

Source :https://www.blackridgeresearch.com/blog/what-is-a-lithium-ion-battery-what-are-the-types-of-lithium-ion-battery-chemistries

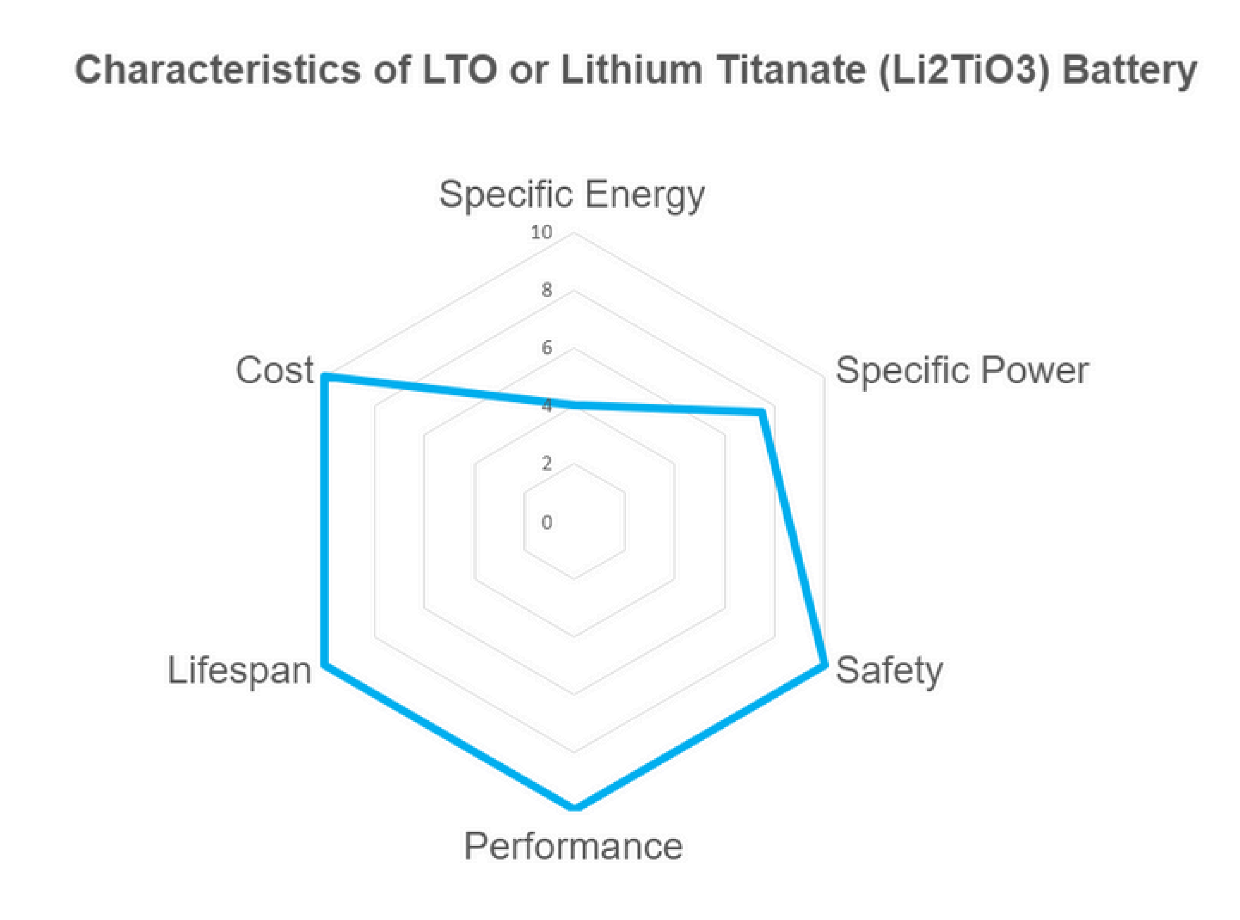
Types of Li-ion Batteries

- **NCA or Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO2)**



Applications: EVs, electric powertrains, medical devices, and industrial.

- **LTO or Lithium Titanate (Li2TiO3)**



Applications: Aerospace and military equipment, EVs, electric powertrains, solar-powered street lighting, telecommunications systems, and UPS.

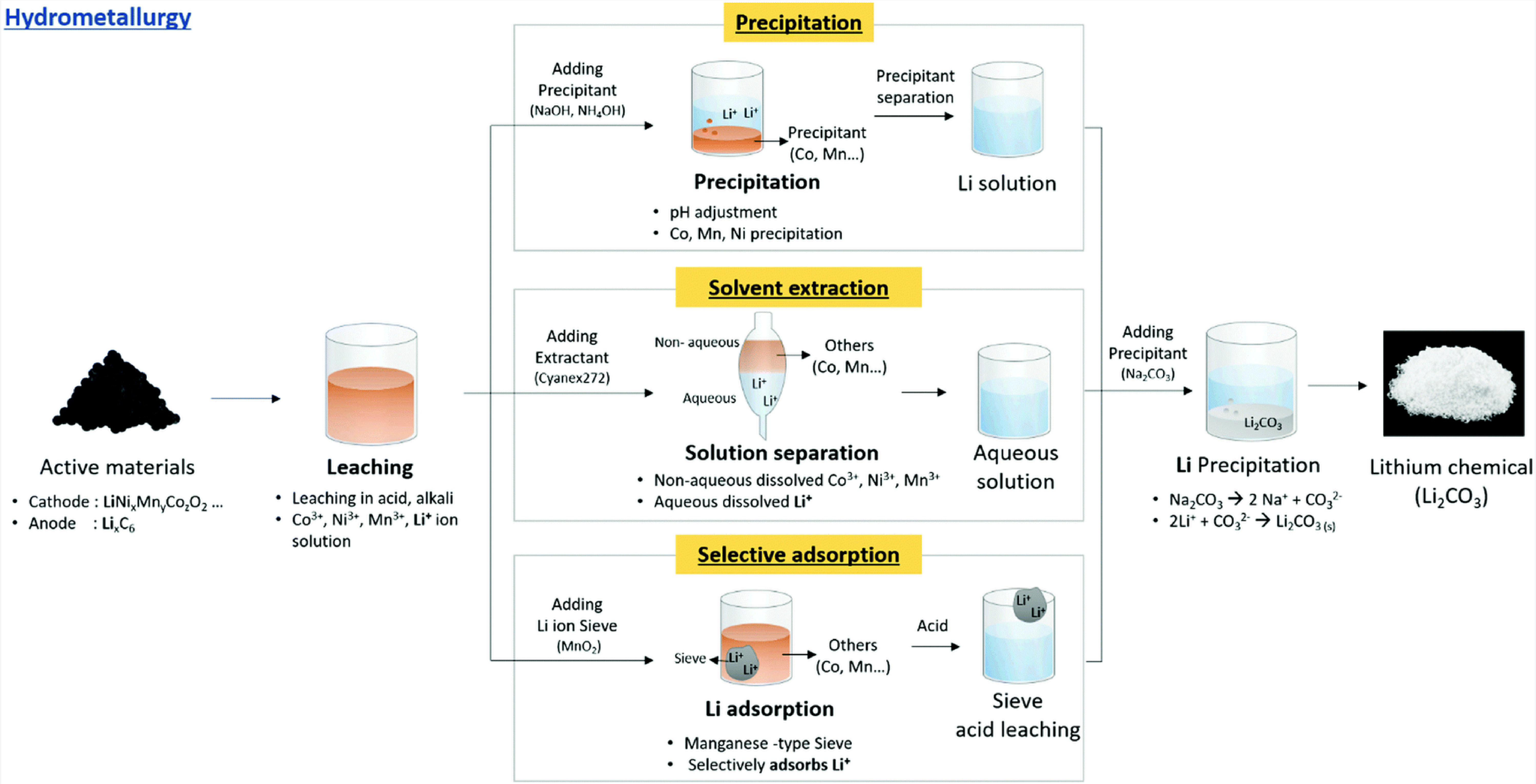
Source :https://www.blackridgeresearch.com/blog/what-is-a-lithium-ion-battery-what-are-the-types-of-lithium-ion-battery-chemistries

Extraction Of Li from Li-ion battery by Hydrometallurgy

Hydrometallurgy stands as the predominant method for lithium extraction from waste Li-ion batteries, owing to its effectiveness in ionizing lithium from pre-treated battery materials through the use of acids or bases, followed by leaching to obtain Li+ solutions. The process involves a series of steps and utilizes various chemicals to facilitate lithium extraction and purification.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy Flow-Chart



source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy

1. Leaching with Acids and Bases: In the initial stages, the battery materials undergo ionization with acids such as sulfuric acid, hydrochloric acid, or nitric acid, or with bases like sodium hydroxide or sodium carbonate. Redox reactions may be employed using agents like hydrogen peroxide (H_2O_2) to enhance leaching efficiency.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy

2. Precipitation Method: Following leaching, lithium is separated from the solution by precipitating it as compounds such as lithium carbonate (Li2CO3) or lithium phosphate (Li3PO4). This is achieved by adjusting the pH and temperature to induce precipitation. Commonly used precipitants include sodium hydroxide (NaOH), sodium phosphate (Na3PO4), and sodium carbonate (Na2CO3). Precipitation is deemed a safe, economical, and efficient method, with high lithium retrieval efficiency reported in several studies.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy

3. Solvent Extraction: Alternatively, lithium can be separated using a solvent extraction process, which involves a two-phase system. Nonpolar extractants are utilized to selectively separate valuable metals like cobalt (Co), nickel (Ni), and manganese (Mn) from the solution, leaving lithium behind. Popular extractants include Cyanex272, PC-88a, and D2EHPA. While shorter compared to precipitation, solvent extraction necessitates additional chemicals and meticulous control of conditions.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy

4. Selective Adsorption: Another method, selective adsorption, employs lithium-ion sieves to selectively absorb dissolved lithium from the solution. These sieves, typically made of lithium manganese oxide, are extremely selective for lithium ions and allow for low contamination. However, they require costly materials and additional leaching processes for lithium recovery.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Hydrometallurgy

Despite its efficacy in achieving high recovery rates, hydrometallurgy entails significant chemical usage for leaching, leading to added costs for chemical procurement and disposal. Nevertheless, its efficiency makes it a popular choice in laboratory settings and brings it close to commercialization. Continued research and development in this area aim to optimize processes and reduce environmental impact while maximizing lithium recovery from waste Li-ion batteries.

source :https://pubs.rsc.org/en/content/articlehtml/2021/ma/d1ma00216c

Extraction of Li

- Li in the solution is converted into Li salt products by precipitation method.
- Due to the solubility of lithium carbonate in water (1.33 g/100 g H_2O), the final recovery rate of lithium is low, so it is difficult to reach the expected goal.

Extraction of Li

- The effluent of the spent LIBs used in this study was stripping solution after the recovery of Ni, Mg, and other metals. The main ions are shown in Table 1

Table 1. Main composition of the effluent.

Ions	Li	Na	Co	Mg	SO_4^{2-}	pH
g/L	3.61	42.5	8.75×10^{-5}	8.78×10^{-6}	72.5	5.8
mol/L	0.52	1.85	1.48×10^{-6}	3.61×10^{-6}	2.26	

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

- The reagent used is 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid (HA)

The synthesis method of the extractant 2-ethylhexyl hydrogen {[bis(2-ethylhexyl)amino]methyl} phosphonate acid (HA) was based on the report of Garifzyanov et al.

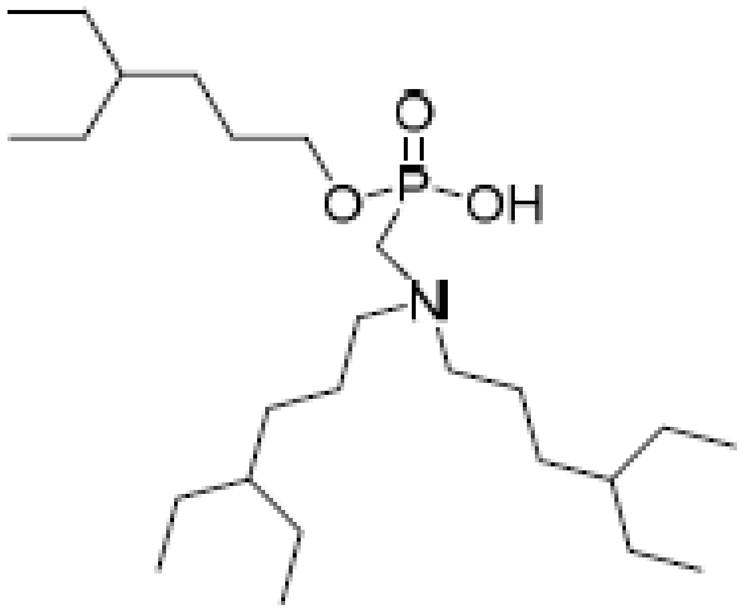


Figure 1. The structure of HA.

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

- Preparation of 1 mol/L extractant involved dissolving the HA (presumably a complexing agent or extractant) in sulfated kerosene.
- The prepared extractant underwent saponification with 5 mol/L NaOH, likely to enhance its ability to extract lithium.
- A 20 mL equilibrium tube was used for the extraction process, with 3 mL each of the organic and aqueous phases.
- The tube was shaken at 25°C for 30 minutes to ensure thorough mixing and achieve phase equilibrium.

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid[[
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

- After equilibrium was reached, the pH and metal ion concentration in the aqueous phase were determined, indicating the extent of lithium extraction.
- The process followed a specific scheme outlined in Figure 2, guiding the steps from preparation to analysis.
- Extraction efficiency (E%) was calculated as the ratio of the metal ion concentration extracted into the organic phase to the total metal ion concentration, providing a measure of the effectiveness of the extraction process.

$$E\% = \frac{C_i - C_e}{C_i} \times 100\%$$

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

3.4. Extraction Mechanism

The extractant HA was first saponified to produce NaA. The extraction of Li^+ with NaA can be expressed by the following equation:

$$Li^+{}_{(a)} + (1+x)NaA_{(o)} \rightleftharpoons LiA{\cdot}xNaA_{(o)} + Na^+{}_{(a)} \tag{5}$$

where A is the extractant anion. "a" represents the aqueous phase, and "o" represents the organic phase. The equilibrium constant K_{ex} of this reaction can be written as:

$$K_{ex} = \frac{[LiA{\cdot}xNaA]_{(o)} \cdot [Na^+]_{(a)}}{[Li^+]_{(a)} \cdot [NaA]_{(o)}^{(1+x)}} \tag{6}$$

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

The distribution ratio D_{Li} can be expressed as follows:

$$D_{Li} = \frac{[LiA \cdot xNaA]_{(o)}}{[Li^+]_{(a)}} \tag{7}$$

Therefore, Equation (6) can be simplified as:

$$K_{ex} = \frac{D_{Li} \cdot [Na^+]_{(a)}}{[NaA]_{(o)}^{(1+x)}} \tag{8}$$

By taking the logarithm of both sides of Equation (8), Equation (9) can be obtained:

$$\lg D_{Li} = (1+x)\lg[NaA]_{(o)} + \lg K_{ex} - \lg[Na^+]_{(a)} \tag{9}$$

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

To investigate the extraction mechanism of lithium, a series of experiments were carried out by varying the concentration of the extractant. The relationship between $\lg D_{Li}$ and $\lg[NaA]_{(o)}$ is depicted in Figure 6 and revealed a slope of approximately "1.07" for Li^+, implying that the value of "$1 + x$" was equal to "1". In addition, the value of $\lg K_{ex}$ could be calculated to be 0.196 by the intercept "−0.132". The experimental results indicated that one molecule of extractant formed a complex with a Li^+ ion during the extraction process. Thus, the extraction mechanism of Li^+ with NaA can be written as follows:

$$Li^+{}_{(a)} + NaA_{(o)} \rightleftharpoons LiA_{(o)} + Na^+{}_{(a)} \tag{10}$$

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid

Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

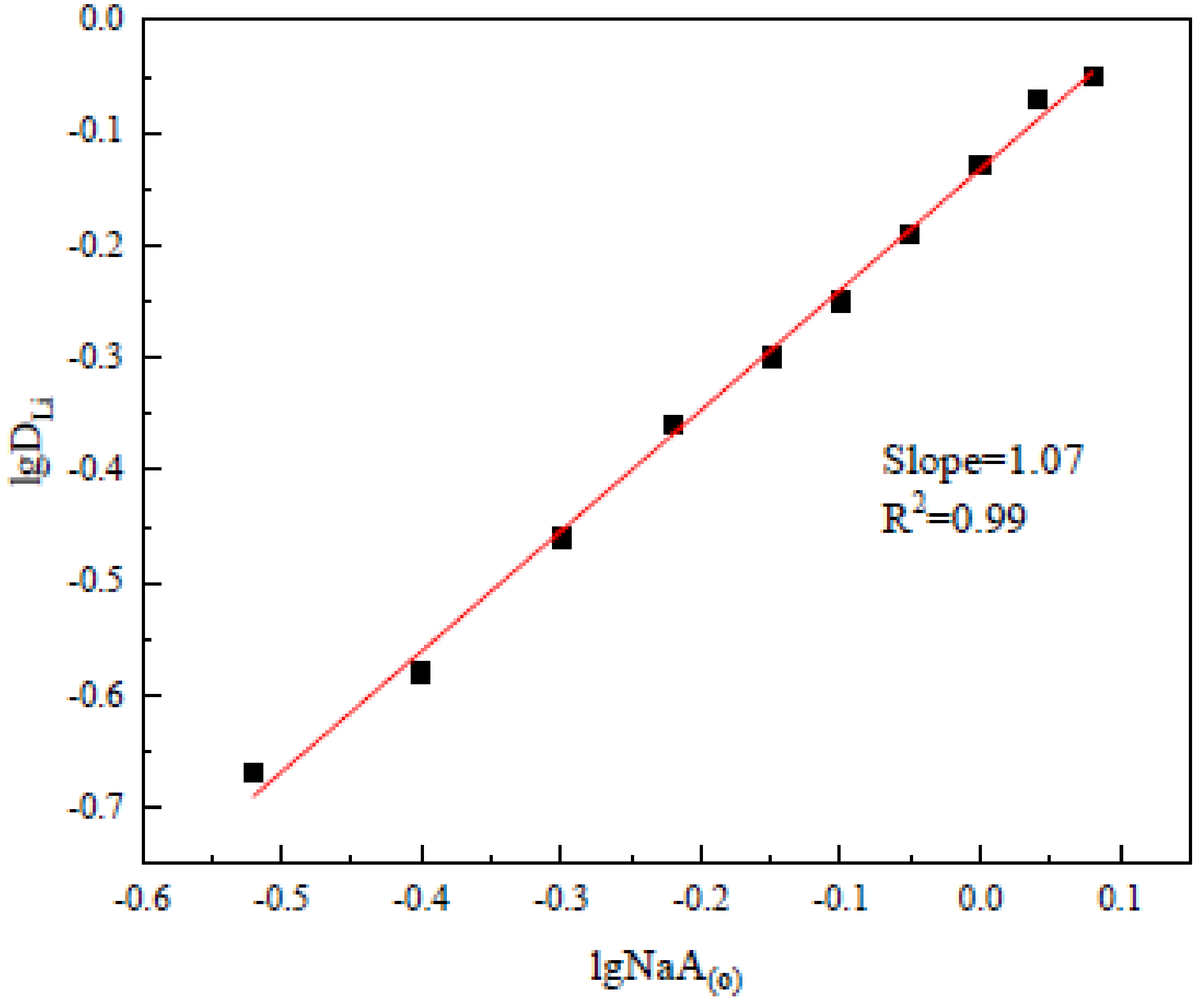


Figure 6. Effect of equilibrium concentration of NaA on lithium extraction. $[Li^+]$ = 3.6 g/L, pH = 8.5, saponification ratio = 70%, O:A = 1:1, 25 °C, t = 30 min.

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid

Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

- pH values in the aqueous phase strongly influence lithium extraction efficiency.
- Initial pH range of 5.8—12.0 showed low lithium extraction efficiency, while significantly increased in the range of 12.0—13.0.
- Difference between initial acidity and equilibrium acidity due to replacement of hydrogen ions by lithium ions during extraction.
- Higher extraction efficiency observed at increased equilibrium acidity.
- Saponification with 5 mol/L NaOH enhances metal ion extraction efficiency by promoting cation exchange reactions.

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Extraction of Li

- Relationship between saponification degree and lithium-ion extraction efficiency at pH 8.5 demonstrated increasing efficiency with higher degrees of saponification.
- Optimal saponification degree for lithium extraction efficiency determined to be 70%.
- Investigation of saponified organic phase on lithium ion extraction efficiency under different pH conditions revealed gradual increase in efficiency within pH range of 8.5—11.0.

Source : Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid
Xiaoqin Wang, Zhulin Zhou, Xuting Si, Youcai Lu * and Qingchao Liu *

Saponification

- Saponification is a chemical reaction in which ester bonds are hydrolyzed in the presence of a strong base (such as sodium hydroxide or potassium hydroxide) to produce soap and alcohol. In the context of the text you provided, saponification is used to modify the extractant by reacting it with sodium hydroxide, which enhances its ability to extract lithium ions during the extraction process. This modification likely involves the conversion of certain functional groups in the extractant molecule, making it more effective for the desired extraction.

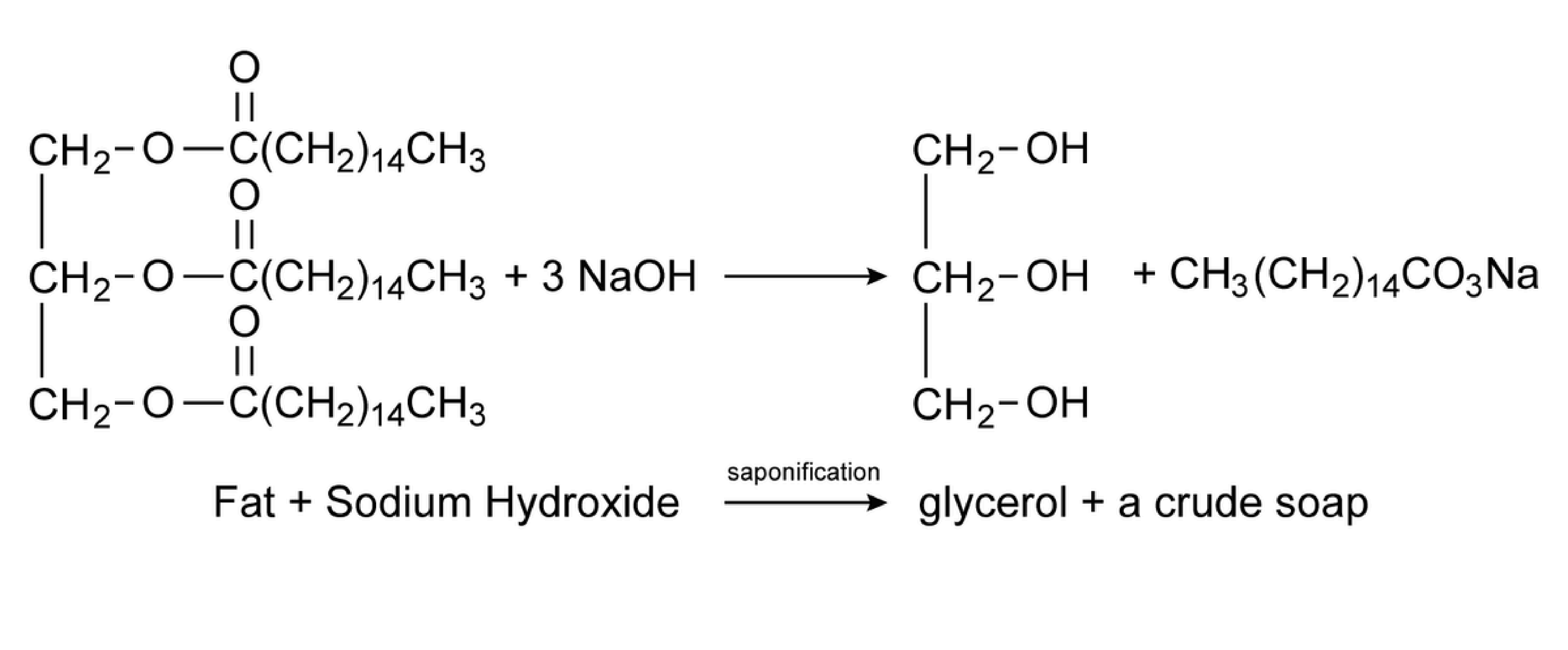
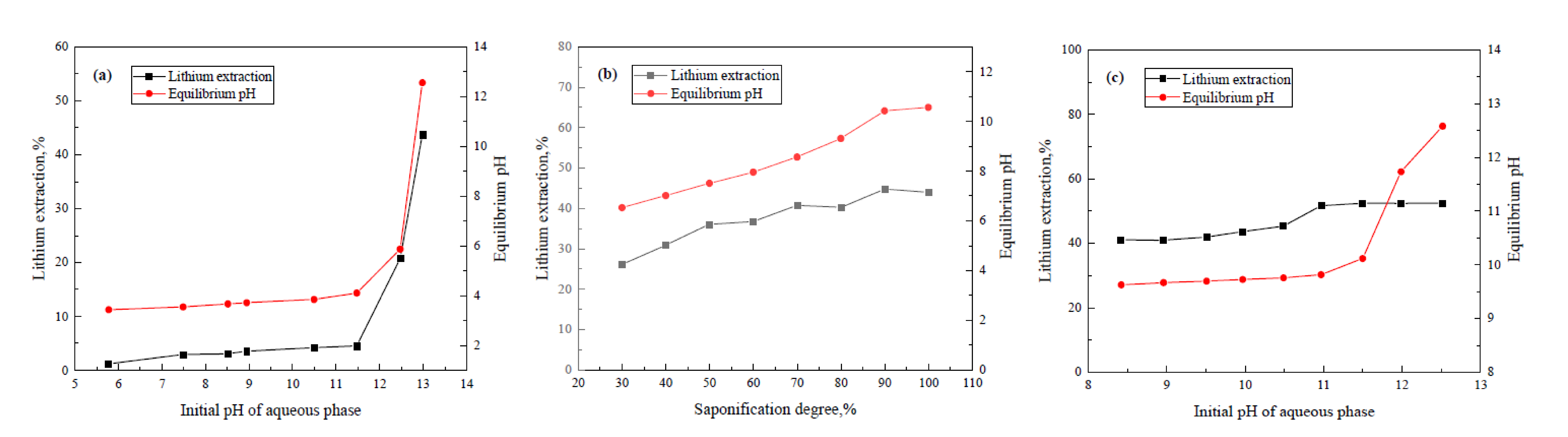


Image source : https://www.thoughtco.com/definition-of-saponification-605959
https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.thoughtco.com%2Fdefinition-of-saponification-605959&psig=AOvVaw1sTXwriPvQvbmewOj1lSWb&ust=1713842504504000&source=images&cd=vfe&opi=89978449&ved=0CBIQjRxqFwoTCJD805zv1IUDFQAAAAAdAAAAABAE

Extraction of Li

Saponification significantly enhanced lithium ion extraction efficiency and expanded the applicable acidity range of the extractant.

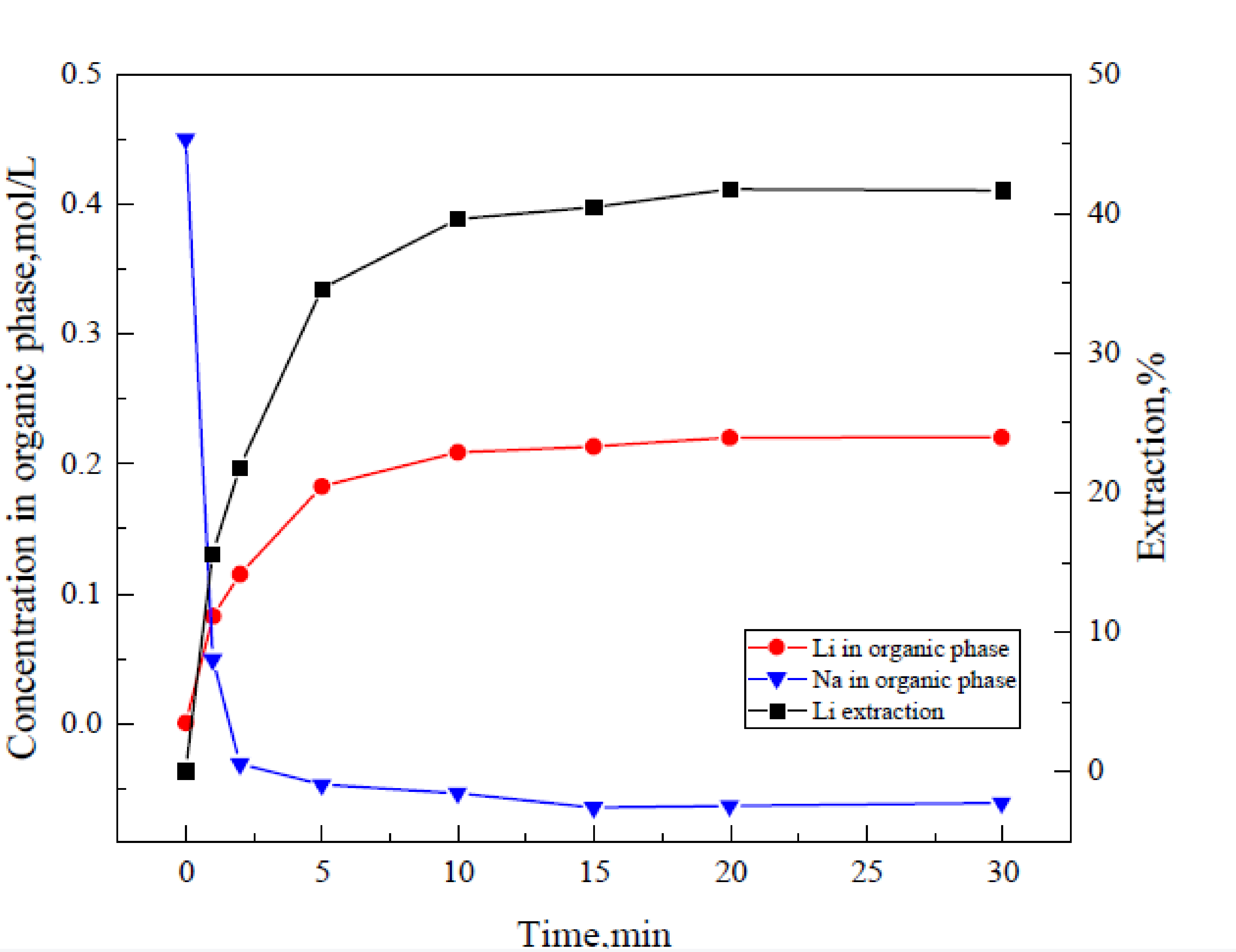


Your Figure 3. (a) Effect of pH on lithium extraction, (b) Effect of saponification degree, (c) Effect of pH value on lithium extraction by saponified organic.

Extraction of Li

Effect of Extraction Time

- Extraction time significantly influences lithium-ion extraction efficiency.
- Under the conditions of a 1 mol/L organic phase with 70% saponification and O:A ratio of 1:1, lithium extraction efficiency reaches equilibrium in approximately 10 minutes, achieving around 40% efficiency.
- Concentration of lithium ions increases in the organic phase while sodium ions decrease due to replacement by lithium ions.
- A 30-minute extraction time is employed to ensure complete equilibrium in subsequent experiments.
- Prolonged extraction times may lead to increased transfer of sodium ions to the organic phase due to their high concentration in the aqueous phase.

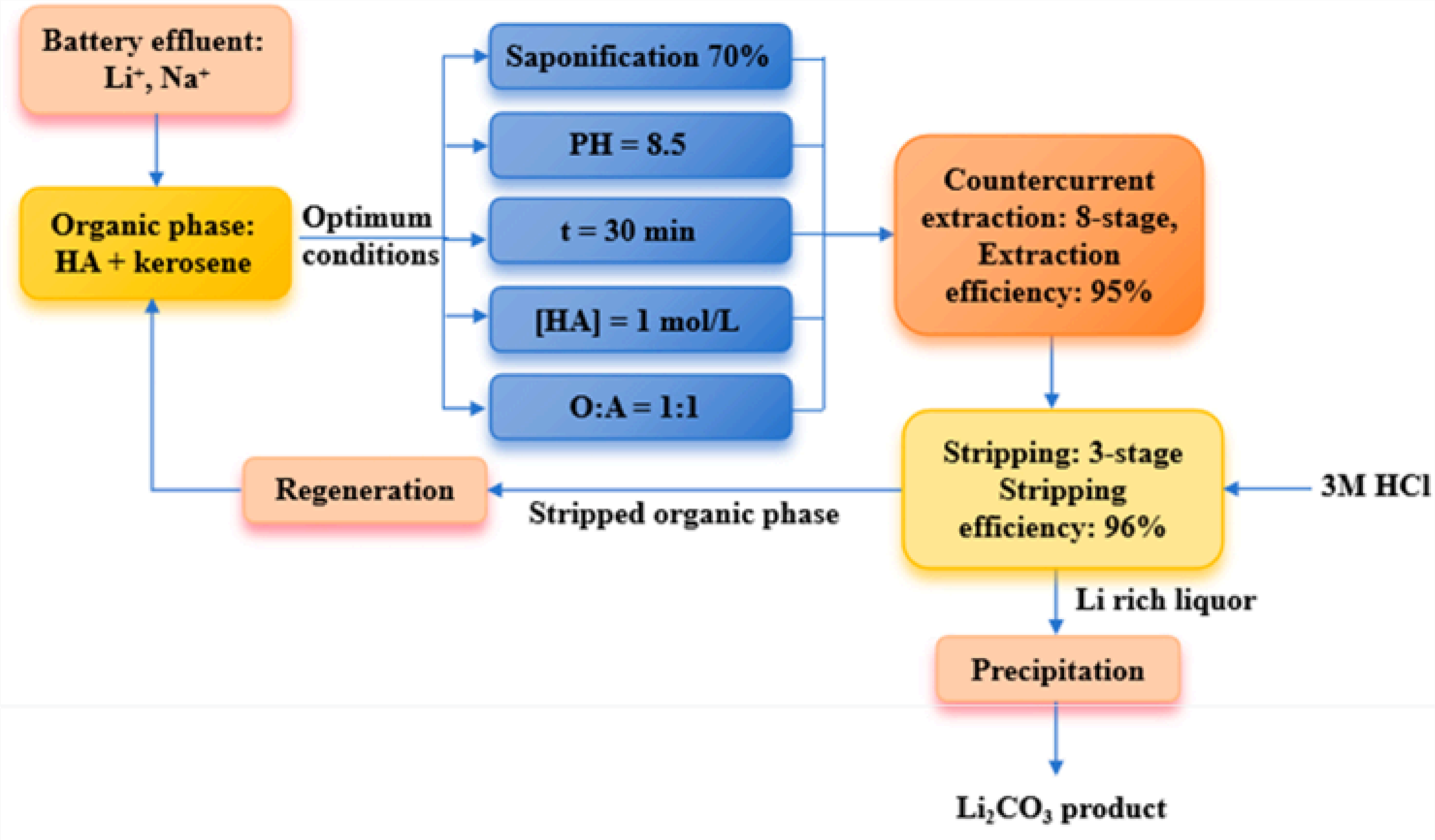


Effect of extraction time on lithium extraction. Extraction conditions: [Li +] = 3.6 g/ L,
[HA] = 1 mol/L, pH = 8.5, saponification ratio = 7000, O:A = 1: 1, 25 oc.

Whole Process of Li Recovery

- Based on the above studies, a whole process was designed to recover lithium from the spent LIB effluent, involving **saponification, extraction, stripping, precipitation, and regeneration.** The whole process flowchart is shown The experimental results showed that over **95% of lithium was successfully recovered in the extraction stage**, and almost all of the lithium in the organic phase was stripped into the aqueous phase in the stripping stage. Meanwhile, the overall recovery efficiency of lithium during the entire process exceeded 90%. It is worth noting that throughout the operation, spanning over three months, the entire recovery process demonstrated stable extraction performance, with rapid phase separation and a clear interface between the two phases. By means of this process, we successfully recovered lithium from the spent LIB effluent. This process not only improved the recovery efficiency of lithium, but also helped to mitigate the environmental impact of spent batteries. In the future, we plan to further refine this process, enhance the efficiency of lithium recovery, and explore its potential applications in industrial production.

Whole Process of Li Recovery



Conclusion

- Introduction of a novel extractant, HA, for lithium extraction from spent lithium-ion batteries (LIBs) effluent.
- Investigation of the extraction mechanism using slope methods and FT-IR spectral analysis.
- Study of the effects of acidity and time on lithium extraction efficiency with HA.
- Demonstrated good chemical stability and cyclic regenerability of the extraction system over 10 reuse cycles.
- Utilization of countercurrent extraction to achieve over 95% lithium extraction into the organic phase.
- Stripping of lithium from the organic phase to form a concentrated lithium solution.
- Precipitation of lithium carbonate (Li_2CO_3) from the concentrated solution using saturated Na_2CO_3 solution.
- Presentation of an efficient method for lithium recovery from spent LIBs effluent.

Thank you!