

Recycling Cathode-Active Materials from Lithium-Ion Batteries with Supercritical Fluids — Review of Current and Alternative Methods

Daniel Ren

Abstract

Lithium-ion batteries (LIBs) are widely used in the electric vehicle and smartphone industries, hailed as an alternative to fossil fuels. However, the mining of lithium and cobalt, the most common metals used in LIBs, is associated with miner exploitation and environmental damage. Therefore, an efficient recycling initiative must be implemented in order to ethically continue the production of LIBs.

In this Review, we examine the current industrial recycling procedures (pyrometallurgy and hydrometallurgy) by their yield and externalities. Despite their high recovery rates, we find that both methods are associated with wasteful usage of energy and materials. Then, we analyze a third method of metal recovery involving supercritical fluid (SCF) extraction. The impact of certain additives (hydrogen peroxide, ethanol, polymers) and operating conditions (temperature, pressure, reaction time) are summarized. We find that SCF extraction is effective and practical on a small scale while using moderate amounts of energy and materials. Lastly, we propose future experiments to further optimize the effects of additives and operating conditions of SCF extraction.

Keywords: recycling, lithium-ion battery, cobalt, supercritical fluid extraction

(1) Introduction

The first lithium-containing battery was created in the 1970s, following an U.S. oil embargo from the Organization of Petroleum Exporting Countries (OPEC) [1] [2]. This incident, known as the 1973 American Oil Crisis, spurred Exxon's Stanley Whittingham to create the first lithium-containing battery. The battery was made of titanium sulfide intercalated with lithium metal, placed in lithium perchlorate electrolyte [1]. The potential of the battery was around two volts, but rendered unusable due to the explosivity of lithium metal [3].

This was just the beginning. John Goodenough from Bell Labs was the first to experiment with cobalt oxide (CoO_2) with intercalated lithium ions, producing a potential of four volts. He later went on to investigate the effectiveness of other transition metals in batteries [4]. From his work, the first lithium-ion battery (LIB) for commercial production would be created by Akira Yoshino

and utilized by Sony Corporation. Whittingham, Goodenough, and Yoshino would go on to win the Nobel Prize in 2019 for their discoveries [1].

In general, batteries must be light and energy-dense in order to be widely produced. Lithium fulfills this requirement due to its low molecular weight (6.94 g/mol) and high electropositivity (-3.04 V compared to a standard hydrogen electrode, which is assigned the arbitrary value of zero) [3]. Therefore, lithium batteries have the highest energy density compared to other batteries available today. Following growing concern of fossil fuel consumption in the transportation industry, LIBs have been used in 40 million on-road electric vehicles (EVs) [5] [6]. LIBs are also used in smartphones, of which 1.166 billion units were sold in 2023 [7]. Lastly, LIBs have become the standard in the renewable energy industry due to their high energy densities [8].

There are five categories of LIB cathodes: LiCoO_2 (LCO), LiNiMnCoO_2 (NMC), LiNiCoAlO_2 (NCA), LiFePO_4 (LFP), and LiMn_2O_4 (LMO). The first manufactured battery was an LCO battery, and they continue to be the most common LIB today [9].

A structure of a typical lithium cobalt oxide (LCO) battery is shown in Figure 1. The defining feature of an LCO battery is its cathode, created from crystalline cobalt (III) oxide separated by lithium ion layers.

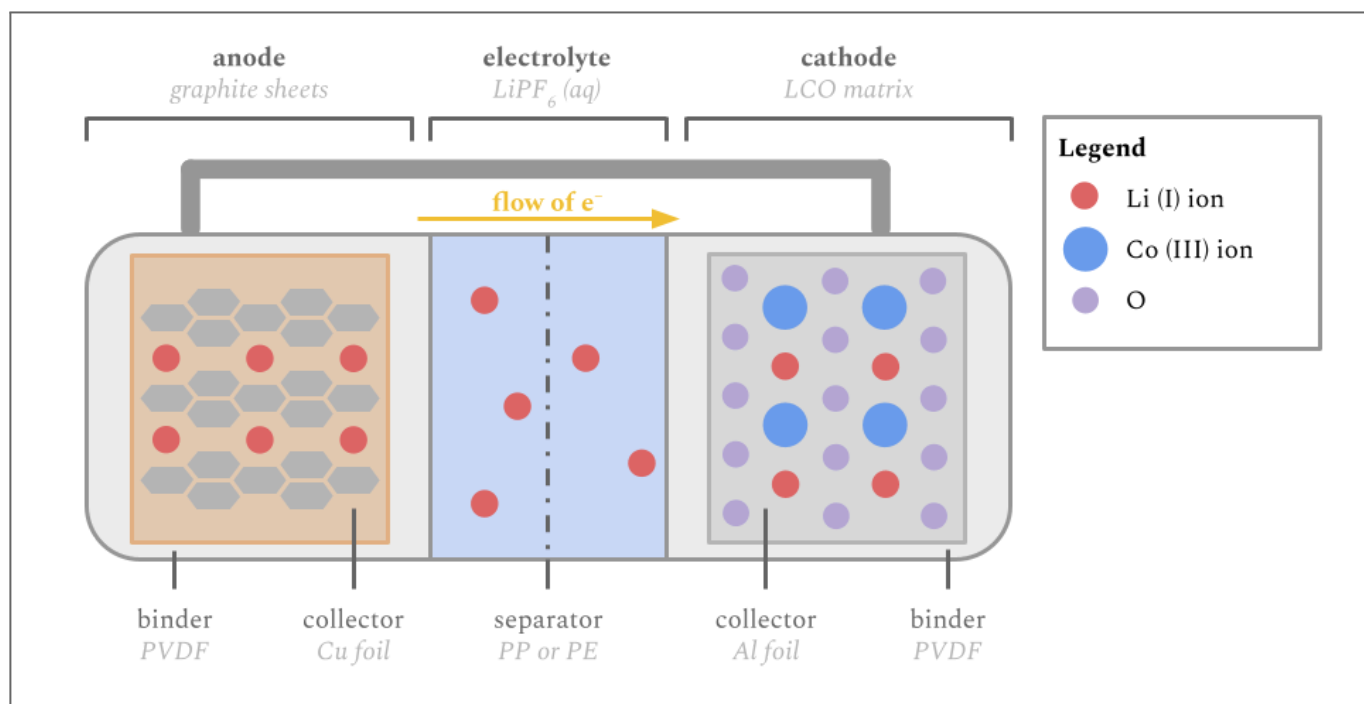
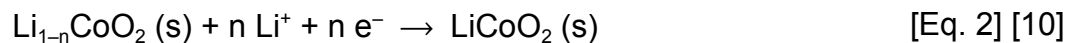


Figure 1: The structure of a typical LCO battery

The most common anode is created from lithiated graphite (LiC_6). When the battery is turned on, the anode decomposes and the lithium is oxidized:



Then, the lithium ions migrate through the electrolyte, usually a lithium hexafluorophosphate (LiPF_6) dissolved in organic solvent. In the cathode, the ions react with the LCO matrix:



To recharge the battery, electricity is sent from the cathode to the anode, reversing the reactions above.

Unfortunately, the processes by which to make the cathodes, lithium mining and cobalt mining, are unsustainable and risky. To produce 1 ton of lithium metal, 250 tons of spodumene ore ($\text{LiAlSi}_2\text{O}_6$) or 750 tons of mineral brine must be obtained [11]. Also, the excess ionic salts created from precipitation of lithium carbonate are released into the environment, leaching into water systems and disrupting the local flora and fauna [12]. Cobalt is the bigger problem; more than half of the world's Co production comes from the Democratic Republic of the Congo. A study conducted in DRC shows that those who live close to artisanal mines have a higher concentration of Co in their blood, which is linked to oxidative DNA damage [13]. Child labor and exploitation has also led to a decrease in education levels for those living close to artisanal mines [14]. Put simply, due to environmental and humanitarian concerns relating to mining, our sources of cobalt are not sustainable in the long term. Recycling cathode materials can help alleviate these concerns.

This paper reviews the separation of cobalt and lithium from the cathode-active material, excluding any organic binders or metal foil attached to the cathode. We will mainly look at LCO batteries with a minor focus on NMC batteries. This paper will first overview the current methods of separation—namely, pyrometallurgical and hydrometallurgical methods. Then, this paper will review the emerging method supercritical fluid (SCF) extraction, which uses less resources and produces less toxic chemicals compared to the previous methods. Finally, the feasibility and possibilities of further experiments are evaluated.

(2) Current Methods

(2.1) Pretreatment

As seen in Figure 2, before the cathode-active material can be separated into Li and Co, the extraneous components of the entire LIB must be removed. This is done with a variety of chemical and physical processes, altogether called *pretreatment*.

It is quite dangerous to perform any chemical reactions on an LIB when it still has electrical capacity. Therefore, the LIB is first discharged by soaking in an aqueous solution of sodium chloride. There is one major drawback; in contact with water, LiPF_6 electrolyte will react to form corrosive hydrofluoric acid:



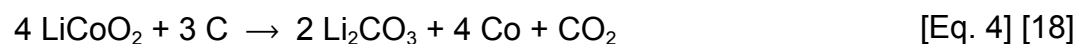
The LIB is dismantled so only the cathode remains. Then, to get rid of the organic binders and aluminum foil attached to the cathode, the cathode is soaked in a solvent. Currently, the most effective one is *N*-methylpyrrolidone (NMP), while *N,N*-dimethylformamide (DMF) seems to be a low cost, reusable alternative [16] [17].

After pretreatment, only the cathode active materials remain. They can go through one of two major chemical processes—pyrometallurgy or hydrometallurgy.

(2.2) Pyrometallurgy

Pyrometallurgy is a branch of metallurgy that involves the extraction of metals with thermal energy. Applications of pyrometallurgy can start as early as pretreatment, where the battery's binders and solvents can be removed via incineration [18].

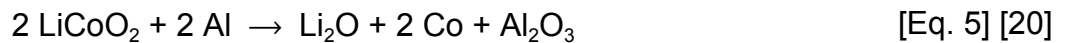
When pretreatment is finished, the cathode-active materials are heated to below their melting point in the presence of elemental carbon, called **roasting**. While it is technically possible to roast with nitrogen gas, oxygen gas plays an important role by transforming the carbon into carbon monoxide and dioxide. At relatively low temperatures, the reaction is as follows:



Li et al. [19] conducted a roasting experiment with end-of-life LCO batteries. LCO and graphite were put into a tube furnace and roasted for 30 minutes at a temperature under 1000°C . The resulting cobalt metal was separated via wet magnetization technology. The authors achieved a

total recovery rate of 90.07% Co and 94.95% Li. Clearly, roasting is an effective separation technique that can be carried out at industrial scales.

Alternatively, the cathode-active materials can be raised above their melting points in a process called **smelting**, obtaining elemental metal in the process. First, the temperature is raised to evaporate the electrolyte and combust the organic binders, which provides energy for the whole reaction. Then, aluminum metal is added and the following reaction occurs:



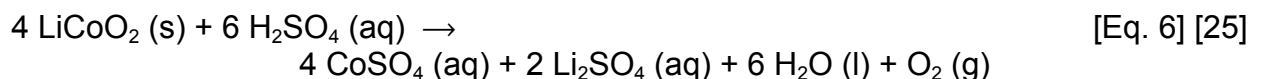
This reaction is highly exothermic, so the net energy of smelting is not as high as it might seem. The aluminum is in the form of an oxide and cannot be recovered. In any case, once the metal oxides or alloys are recovered, they can be separated via solvent extraction, chemical precipitation, or (in the case of alloys) selective liquidation.

The major flaw of all pyrometallurgy is the high temperatures required. These processes need a large energy input and trigger the creation of toxic gases. In particular, hydrogen fluoride (HF) and organic dioxins are common toxins produced from the decomposition of electrolytes, separators, and binder materials [21]. Any sulfur-based batteries will release sulfur dioxide upon combustion as well. These gases pollute the environment and induce damage to human respiratory and immune systems [22] [23] [24].

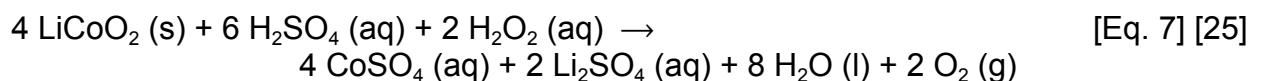
(2.3) Hydrometallurgy

Hydrometallurgy is a branch of metallurgy that uses aqueous solutions to isolate and extract metal ions. After pretreatment, the cathode-active materials are treated with acid and converted in aqueous form in a hydrometallurgical process called acid leaching. The most common reagents are:

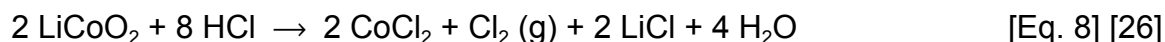
(i) sulfuric acid



(ii) sulfuric acid with hydrogen peroxide



(iii) hydrochloric acid



Acid leaching with hydrochloric acid tends to produce harmful chlorine gas. By contrast, sulfuric acid methods produce no harmful substances.

Mantuano et al. conducted a metal extraction experiment via liquid-liquid techniques [27]. The LIBs were ground into dust and leached with sulfuric acid at a temperature of 80°C with a 1:30 solid-to-liquid ratio (g/mL). They found that out of the 5.11 g Co and 0.71 g Li originally in the battery dust, a mere 37% of cobalt and 55% the lithium was successfully retrieved.

Research has proven that reducing agents play a major role in hydrometallurgy. An experiment from Kang et al. using 6% v/v hydrogen peroxide (H₂O₂) and typical conditions yielded a very high recovery rate—98% Co and 97% Li [28]. Another experiment from Zhao et al. using 5% v/v ethanol (EtOH) yielded recovery rates of over 99% for both metals [29]. In general, H₂O₂ and EtOH reduce the Co (III) into Co (II), which is more easily extracted.

Although industrial processes typically leach with inorganic acids due to their relative affordability, organic acids seem to be just as effective without producing toxic gas. Li et al. used 1.25 M citric acid and 1% v/v H₂O₂ to obtain recovery rates of 91% Co and 99% Li, although withholding the use of H₂O₂ significantly diminishes the recovery rates to 25% Co and 54% Li [30]. The same authors also used 1.5 M malic acid and 2% v/v H₂O₂ to achieve a recovery rate of 93% Co and 99% Li [31]. As seen here, the performance of organic acids coupled with hydrogen peroxide can rival that of inorganic acids. In any case, once the acid leaching is done, the metals can be separated by solvent extraction (some extractants include Cyanex 272, Versatic 10, D2EHPA, LIX 84-I, etc.) or chemical precipitation [32] [33] [34].

The primary drawback of a purely hydrometallurgical method is the large volume of reagents needed. Both the leaching and solvent extraction processes require high quantities of highly concentrated strong acids and bases, which are corrosive and dangerous to handle. Processes involving precipitation need their volume and pH to be controlled very carefully, and the metal recovery suboptimal due to incomplete precipitation.

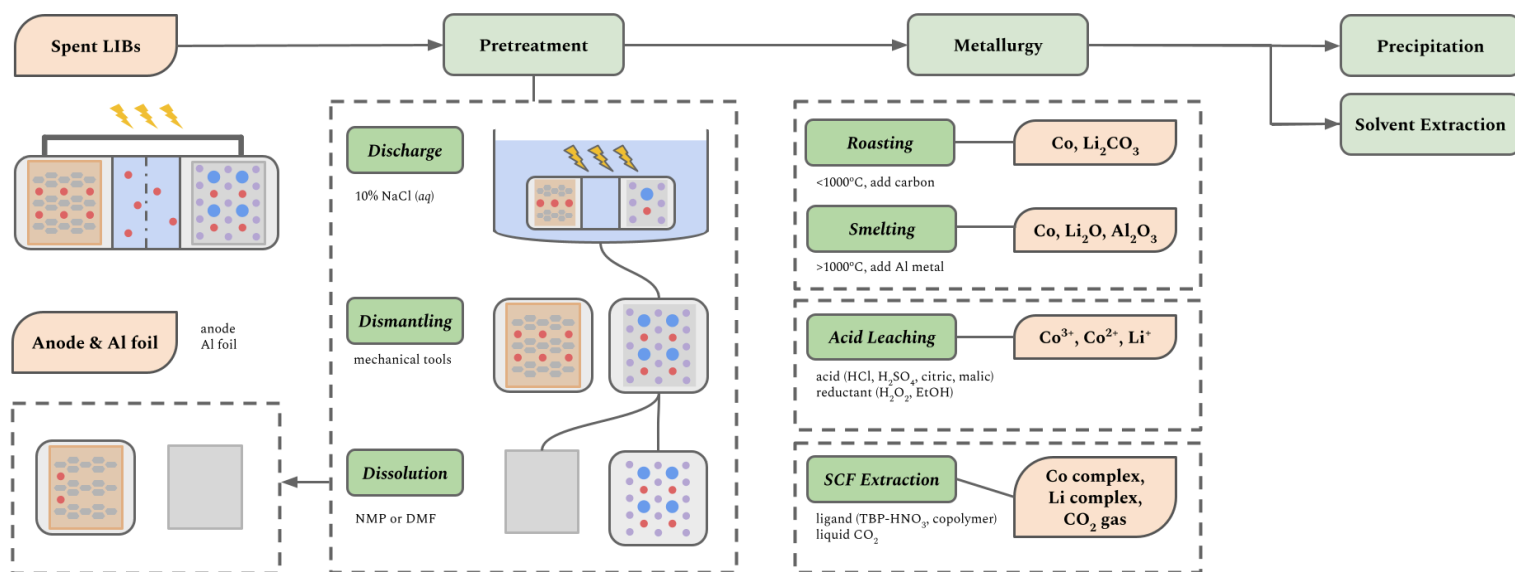


Figure 2: A flowchart detailing possible processes used to recycle LIBs.

(3) Supercritical Fluid Method

(3.1) Overview

Pyrometallurgical and hydrometallurgical methods of treating cathode-active materials are effective and scalable, so they are both used industrially. However, roasting and smelting require excessive energy consumption, which can release toxic fumes and carbon dioxide into the atmosphere. Meanwhile, acid leaching requires a large volume of corrosive chemical reagents. As an attempt to solve these problems, metal extraction via supercritical fluids (SCF) uses a low volume of reagents and energy, while achieving high recovery rates of cobalt and lithium.

The basic premise of SCF extraction is as follows: the cathode-active material is obtained and pulverized via the same pretreatment process as outlined in Section 2.1. Then, it is put into a high-pressure reactor along with a ligand. The solvent (usually water or carbon dioxide) is injected into the reactor, and the temperature/pressure is adjusted to bring it to supercritical condition, which also triggers a complexation reaction between the powder and ligand. Once the metal complex dissolves in the solvent, the pressure is relieved, leaving behind a precipitate and gaseous solvent. That precipitate should be a mixture of cobalt and lithium complexes, which can be further separated via solvent extraction.

The recovery rate of a certain metal M is defined by the parameter R_M :

$$R_M = \frac{\text{weight of metal } M \text{ in extracted sample}}{\text{weight of metal } M \text{ in un-extracted sample}} \times 100\%.$$

We will observe the effects of six major variables that can be adjusted in SCF extraction:

- (a) Presence of hydrogen peroxide (H_2O_2)
- (b) Presence of ethanol (EtOH)
- (c) Presence of polyvinyl chloride (PVC)
- (d) Reaction time
- (e) Temperature
- (f) Pressure

(3.2) Properties of SCFs

For some amount of CO_2 in a closed container, at $31^\circ C$, no matter how much the pressure is increased, it can never become a liquid. Likewise, at 74 bar, no matter how much the temperature is increased, it can never become a gas [35]. That set of conditions is called the *critical point* of CO_2 . Once the temperature and pressure is increased beyond the critical point, the CO_2 enters an in-between state of matter—a *supercritical fluid*.

Table 1: The physical properties of CO_2 (sc) as compared to CO_2 (g) and CO_2 (l) [36].

Property	CO_2 (g)	CO_2 (sc)	CO_2 (l)
Density (kg/m^3)	0.6-2	200-900	600-1000
Dynamic viscosity ($mPa \cdot s$)	0.01-0.3	0.1-0.3	0.2-3
Diffusivity $\times 10^6$ (m^2/s)	10-40	0.07	0.0002-0.002
Surface tension ($dyne/cm^2$)	-	-	20-40

As seen in Table 1, properties of CO_2 (abbreviated to $scCO_2$) are in-between that of gaseous and liquid CO_2 . Similar to both, $scCO_2$ has low polarity as well. Therefore, it must be used in conjunction with other solvents to give it the necessary properties for extraction [37]:

- methanol (CH_3OH) or ethanol (CH_3CH_2OH) to increase polarity
- toluene ($C_6H_5CH_3$) to increase aromaticity
- tributyl phosphate (TBP, $(CH_3CH_2CH_2CH_2O)_3PO$) to increase solubility of metal complexes

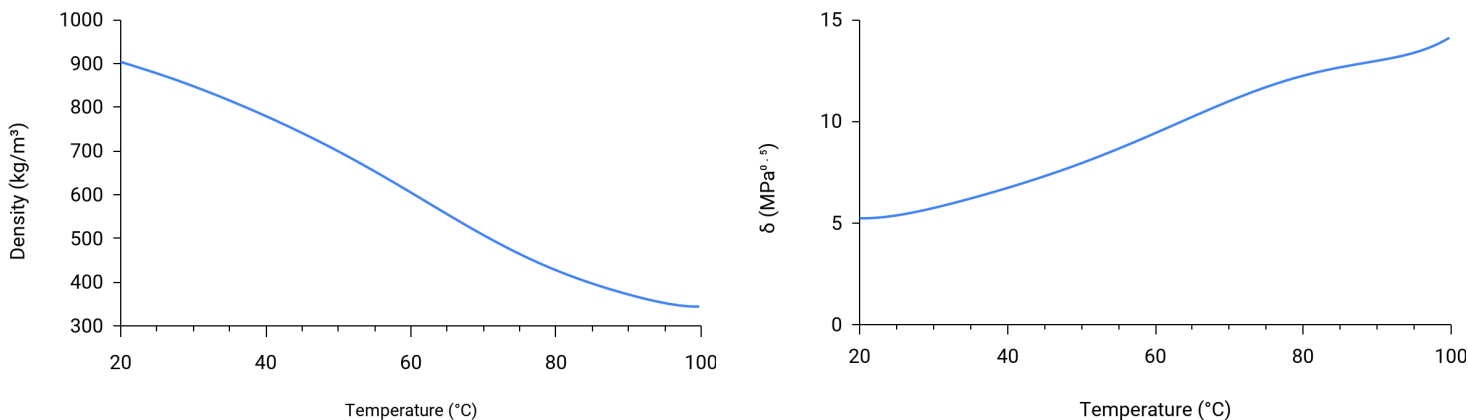


Figure 3: The correlation between density (left) and the Hildebrand solubility parameter δ (right) of scCO_2 vs. temperature at 150 bar [36].

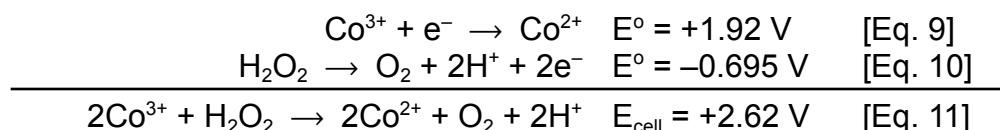
Supercritical fluids are very sensitive to external conditions. At high pressures, various properties of scCO_2 are monotonically related to temperature, as seen in Figure 3. This allows us to precisely adjust the properties of scCO_2 —most notably metal solvation power—by changing the reactor temperature [37]. Additionally, scCO_2 extraction methods have already proven to be effective in decaffeination of coffee, pasteurization of milk, and production of pigments [38] [39] [40]. Therefore, we can separate metals or metal complexes from solution selectively by fine-tuning the temperature of the supercritical fluid.

Supercritical water (abbreviated to scH_2O) is a solvent that behaves similarly to scCO_2 . The critical point for water is 374°C and 221 bar, so it takes more energy to push water above its supercritical state. While scH_2O molecules are still polar, the weakening of hydrogen bonds causes it to dissolve nonpolar compounds [41].

(3.3) Effect of Additives

From extensive research in hydrometallurgy, we infer that the addition of reductants and acids increase the recovery rate of lithium and cobalt. We will discuss three major additives that appear periodically throughout many studies: hydrogen peroxide, ethanol, and polyvinyl chloride.

Hydrogen peroxide is very commonly used in hydrometallurgical processes due to its power as a reducing agent. Specifically, the following half-reactions takes place when H_2O_2 is added to cobalt in the +3 oxidation state [42]:

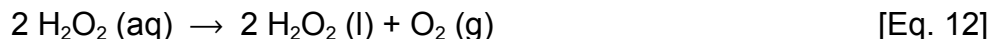


In general, cobalt complexes are more soluble in scCO₂ when the central atom is in a +2 oxidation state. Additionally, the reduction of Co³⁺ breaks the bonds in the LCO matrix, allowing Li⁺ to complex with the ligands added. The result is a higher recovery rate of both cobalt and lithium from spent LIBs when cobalt is first reduced to the +2 form.

This claim is supported by a study conducted by Zhang and Azimi which investigated scCO₂ extraction for two types of NMC batteries [43]. In it, the cathode-active material is ground into powder and placed into a 100 mL high-pressure reactor. A ligand consisting of aqueous nitric acid and tributyl phosphate (TBP-HNO₃) was added, along with liquid CO₂. Then, 4 mL of 21% v/v H₂O₂ was added in some trials to test the effects of hydrogen peroxide. When the complexation reaction finished, the reactor was depressurized to precipitate out the metal complexes. The products were dissolved in aqua regia and characterized with inductively-coupled plasma optical-emission spectroscopy (ICP-OES). The study found that the metal extraction rates peaked at around 74% Co & 70% Li without H₂O₂, and 90% Co & 89% Li in the presence of H₂O₂. Upon analysis with X-ray photoelectron spectroscopy (XPS), the study found a significantly lower concentration of Co³⁺ in the trial with H₂O₂ in it, further showing that H₂O₂ is an effective reducing agent even in supercritical conditions.

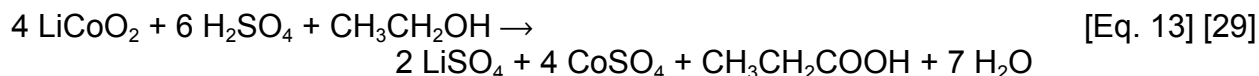
However, if the volume and concentration of H₂O₂ increases past a certain value, the recovery rates of both metals start to decrease instead. Bertuol et al. conducted an experiment combining scCO₂ and acid for the best results [44]. A positive control with typical 2 M H₂SO₄ leaching and varying concentrations of H₂O₂ achieved up to 98% Co recovery rates. Then, the same leaching tests were performed with scCO₂ at much higher pressures, which yielded cobalt and lithium in the form of salts. Lastly, the cobalt metal was extracted via electrowinning (electrochemical reaction from charged metal to neutral metal) while the now-gaseous CO₂ was recaptured and reused. The study found a high cobalt recovery rate of 98% in the positive control, 95.5% Co in scCO₂ with 4% v/v H₂O₂, and 70% in scCO₂ with 8% v/v H₂O₂.

This can be explained by the extra water in the system whenever H₂O₂ (aq) is used, as well as the decomposition of hydrogen peroxide to form water. Too much water will capture some of the cobalt and lithium ions originally in the scCO₂ solvent, lowering the amount of cobalt and lithium complexes created.



In systems with macro-ligands such as p(VBPDA-co-FDA), excess water cannot be accommodated in the water-scCO₂ microemulsion system, thus forming heterogeneous media with large water droplets. Those macro-ligands can aggregate onto the droplet's surfaces instead of forming metal complexes, further lowering the recovery rates of cobalt and lithium [45].

Ethanol (CH₃CH₂OH or EtOH) can also act as a reducing agent when reacting with LCO. The acetic acid also contributes as an organic leachant.



In supercritical conditions, the same conditions apply; with the right operating conditions, ethanol is fully miscible in scCO₂.

Vauloup investigated the effects of H₂O₂ and EtOH on SCF extraction systems imbued with p(VBPDA-co-FDA). As seen in Figure 4, this copolymer consists of phosphonate groups that act as an acid leaching agent and metal complexation agent, optimizing several parts of the metal extraction process in one go. Additionally, the acetate ion can act as a polar co-ligand, solubilizing the metal complexes in the faintly-polar scCO₂ medium.

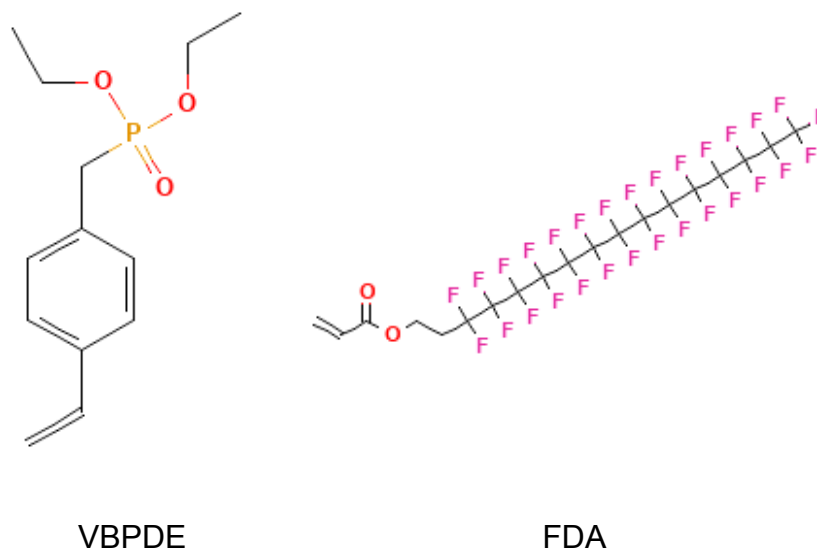


Figure 4: The skeletal structures of 4-vinylbenzylphosphonate (VBPDE) and 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA)

A positive control—solvent extraction with the cathode-active material, copolymer, trifluorotoluene (TFT), and methanol—was established, achieving recovery rates of 90% Co and 87% Li. Then, scCO₂ extraction was run with the exact same chemicals, achieving recovery rates of ~60% for both metals. Notably, when a small amount of 96% v/v EtOH was added to the second experiment, the recovery rates increased to 75% Co and 71% Li. This shows that the reduction of Co³⁺ to Co²⁺ does take place in some capacity, increasing the solubility of the cobalt metal complexes and yielding more precipitate.

Polyvinyl chloride (PVC) is a common plastic used in piping and wire insulation, favored for its chemical stability and hardness. Unfortunately, PVC recycling is notoriously difficult, since the chlorine in the vinyl chloride monomer reacts with hydrogen and is released upon incineration. This study makes use of the HCl in aqueous form with leaching. When PVC is brought to sufficiently high temperatures (>250°C), it will undergo the following reaction:

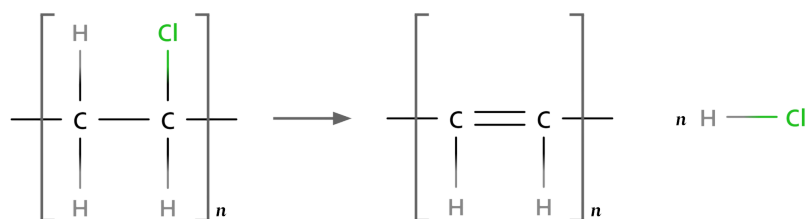


Figure 5: The reaction pathway for the pyrolysis of PVC [46].

The HCl serves as a leaching agent, breaking apart the LCO matrix as with Eq. 8. The reaction detailed in Figure 5 occurs far beyond the critical temperature for CO₂ (31°C), so PVC can only be utilized alongside supercritical water, with a much higher critical temperature (374°C).

Liu and Zhang explored the potential of sub- and supercritical water as a solvent for metal extraction, simultaneously incorporating a safe method of dechlorination of PVC [47]. In their experiments, they placed the cathode-active material, PVC powder, and deionized water into a 100 mL reactor. Then, they varied the temperature between 150°C and 400°C at a constant pressure, completed the reaction, separated the remaining solid with vacuum filtration, and characterized the product with ICP-OES. Their results are summarized in Figure 6, where they found that the leaching efficiency of PVC climbed sharply at temperatures above 200°C, peaking at around 350°C. At 374°C, the leaching efficiency started to decline, along with the recovery rates of both metals. This suggests that metal extraction with water works best when it is subcritical (i.e. above 100°C but kept liquid by pressure) rather than supercritical.

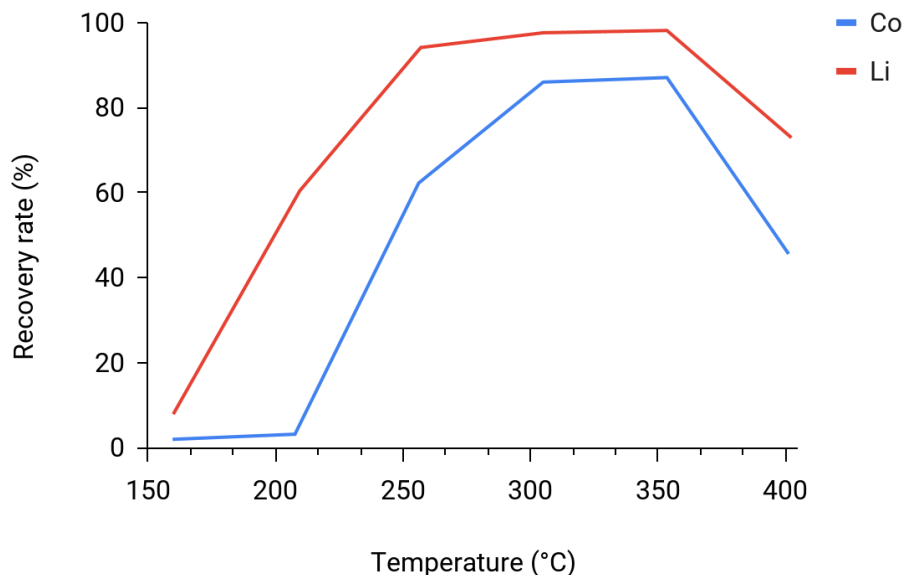


Figure 6: The effects of temperature on the recovery rates of cobalt and lithium in scH_2O , under the following experimental conditions—solid:liquid ratio = 1:63 g:mL and time = 60 min. Adapted from Liu and Zhang [47].

PVC is also successful at separating the LCO matrix, as shown by Barros et al. [48]. In this experiment, the cathode-active material, PVC, sulfuric acid, and deionized water were inserted into a reactor, in a similar fashion to the previous study. (Some trials forewent PVC powder and acted as a control group.) This time, the temperature was raised to 450°C at 240 bar, conditions which are moderately higher than the critical point of water. For the scH_2O experiment, this study finds near-perfect recovery rates of ~100% for both metals. Without PVC, the LCO matrix mainly broke into solid cobalt (II) oxide and lithium carbonate. With PVC, the cobalt was found in the form of cobalt (II) chloride, which is soluble in water. This indicates that PVC solubilizes cobalt ions in water, positively impacting recovery rates.

We conclude that adding PVC has the same effect of adding strong acid in the reaction. The main benefit of these methods is the recycling of both PVC and LIBs without any dangerous byproducts, like HF or HCl.

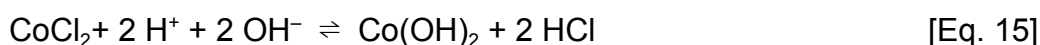
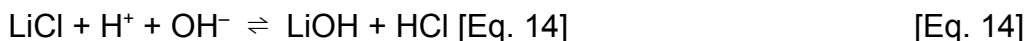
(3.4) Effect of Operating Conditions

Next, we will discuss the operating conditions that affect recovery rate: temperature, pressure, and reaction time.

Temperature can affect a supercritical system in a number of ways, depending on the extraction method used.

In scCO_2 , temperature can affect a supercritical system by destabilizing the metal complexes created. Lithium ions have small coordination numbers due to their +1 oxidation state, so not many ligands can attach themselves to each ion. Conversely, cobalt's +2 or +3 oxidation state gives it a high coordination number. A change in temperature is far more likely to destabilize a lithium-centric complex compared to a cobalt-centric one, exacerbating the reduction of lithium recovery rates [43]. Since addition of H_2O_2 brings cobalt's oxidation state from +3 to +2, further studies should be conducted on the joint effect of H_2O_2 and temperature on lithium recovery rate.

In Liu and Zhang's study with scH_2O , lithium and cobalt were recovered as chlorides (LiCl and CoCl_2) in the liquid product [47]. Optimal recovery rates occurred at 350°C , when the water was still in a subcritical state; raising the temperature lowered the recovery rates drastically (Co: 86.9% to 45%; Li: 98.6% to 70%). As the temperature rose, the autoionization of water produced more H^+ and OH^- ions, destabilizing the metal chlorides:



Only the liquid product was characterized at the end of Liu and Zhang's study. Therefore, it is likely that the majority of the cobalt and lithium precipitated out of the medium as hydroxides, ending up as solid residue.

In Bertuol et al.'s study, we see scH_2O remain effective at up to 450°C , far greater than the value we see in the previous study. This discrepancy can be explained with the second study's use of sulfuric acid, which increases the metal recovery rates no matter the temperature.

Pressure does not seem to affect the recovery rate of either metal. In Zhang and Azimi's study, changing the pressures from 207 bar to 310 bar, well above the critical point of CO_2 , had little to no effect on the ending results [43]. A paper cited by the study finds that the solubility of organometallic complexes in scCO_2 starts low near the critical point, rises steeply as pressure increases, and tapers off at a sufficiently high pressure. Zhang and Azimi's study seems to prove the insignificance of pressure above ~ 200 bar.

In the study conducted by Bertuol et al., the pressure was set to 75 bar, barely above scCO₂'s critical point, and yet the recovery rate of both metals exceeded 95%. This discrepancy can once again be explained with the addition of sulfuric acid.

Reaction time seems to be a major factor in the extraction efficiency for both methods. Most SCF extraction processes seem to take less than an hour to complete, with the shortest one taking only 5 minutes to reach optimal conditions. There is a very short window of time in which recovery rates maximize, followed by a sharp decline in both directions.

In Bertuol et al.'s study, cobalt recovery rate reached around 80% in the 1st minute of scCO₂ extraction. It was optimized at 95.5% at 5 minutes before dropping sharply to 57% after 10 minutes. This sudden drop can be explained by the degradation of H₂O₂ at high temperatures shown in Eq. 12. The reaction progresses over time, lowering the amount of H₂O₂ that can effectively reduce Co³⁺ to Co²⁺. The water produced by H₂O₂ degradation also dissolves the metal ions in more water, reducing the amount of Co-Li found in the solid product.

In Liu and Zhang's study concerning scH₂O extraction, a similar phenomenon occurs; the optimal recovery rates of >96% for both metals were achieved at a 30 min reaction time. In the next 30 minutes, the recovery rate of lithium is almost 100%, but that of cobalt decreases to around 85%. Further reaction time shows recovery rate decreases in both metals. The authors attribute this to the reaction between the HCl, Co-Li, and metal wall of the reactor.

Table 2: Summary of all studies reviewed in this paper.

Method	Agents	T (°C)	P (bar)	time (min)	s:l (g:ml)	R _{Co} (%)	R _{Li} (%)	Ref
roasting	n/a	1000	-	30	-	95.7	98.9	[19]
inorg. acid leaching	H ₂ SO ₄	80	-	60	1:50	37	55	[27]
inorg. acid leaching	2M H ₂ SO ₄ , 6% H ₂ O ₂	60	-	60	1:10	98	97	[28]
inorg. acid leaching	3M H ₂ SO ₄ , 5% EtOH	90	-	160	1:50	99	99	[29]
org. acid leaching	1.25M citric, 1% H ₂ O ₂	90	-	30	1:50	91	99	[30]
org. acid leaching	1.5M malic, 2% H ₂ O ₂	90	-	40	1:50	93	99	[31]
scCO ₂ extraction	TBP-HNO ₃	40	310	30	1:5	74	70	[43]
scCO ₂ extraction	TBP-HNO ₃ , 21% H ₂ O ₂	40	310	30	1:5	90	89	[43]
inorg. acid leaching	2M H ₂ SO ₄ , 8% H ₂ O ₂	75	-	60	1:20	98	-	[44]
scCO ₂ extraction	2M H ₂ SO ₄ , 4% H ₂ O ₂	75	75	5	1:20	95.5	-	[44]

solvent extraction	p(VBPDA-co-FDA), TFT/ MeOH, 30% H ₂ O ₂	60	-	240	-	90	87	[45]
scCO ₂ extraction	p(VBPDA-co-FDA), 30% H ₂ O ₂	60	250	60	-	~60	~60	[45]
scCO ₂ extraction	p(VBPDA-co-FDA), 96% EtOH	60	250	240	-	75	71	[45]
sch ₂ O extraction	PVC	350	>221	60	1:63	86.9	98.6	[47]
sch ₂ O extraction	PVC	400	>221	60	1:63	45	70	[47]
sch ₂ O extraction	PVC	450	240	≤120	-	100	100	[48]

(4) Conclusion

This Review gave a brief recapitulation of the composition of LIBs, as well as an overview of the pretreatment process. Then, three extraction processes were evaluated by their yield and externalities.

The two current recycling methods used today are pyrometallurgy and hydrometallurgy. While both methods are scalable and yield high recovery rates (>90%), pyrometallurgy consumes high amounts of energy while hydrometallurgy utilizes large volumes of corrosive reagents. Meanwhile, SCF extraction is a quick but demanding process, with optimal recovery rates ranging from 70% to 100%. Currently, experimentation has only been performed at a laboratory scale.

Reductants like hydrogen peroxide (H₂O₂) and ethanol (EtOH), as well as strong acids (like HCl from PVC) bolster the recovery rate of cobalt and lithium by breaking apart the LCO matrix. Temperature and reaction time need to be very specific to achieve optimal metal extraction, while pressure seems to have no significant effect once it is sufficiently high.

Taking these three methods into account, it is clear that SCF extraction holds great value in the future of LIB recycling. It is a fast, efficient, cost-effective, and environmentally-friendly process, outdoing pyrometallurgical and hydrometallurgical processes in all areas except recovery rates. It will add significant industrial value once it is scaled up for commercial use, but this method requires further experimentation and reevaluation at that time.

Acknowledgements

The author would like to thank Siddharth Rajupet for his guidance and input on this manuscript. The author also thanks Dr. Eric Schelter from the University of Pennsylvania for providing general reading materials on this topic during the Chemistry Research Academy (2024) that inspired this manuscript.

References

- J. B. Goodenough, M. S. Whittingham, and A. Yoshino, "The Nobel Prize in Chemistry 2019". [1]
- "Milestones in the History of U.S. Foreign Relations - Office of the Historian." Accessed: Oct. 17, 2024. [Online]. Available: <https://history.state.gov/milestones/1969-1976/oil-embargo> [2]
- J.-M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, no. 6861, pp. 359–367, Nov. 2001, doi: [10.1038/35104644](https://doi.org/10.1038/35104644). [3]
- M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, "Lithium insertion into manganese spinels," *Materials Research Bulletin*, vol. 18, no. 4, p. 461, 1983. [4]
- K. A. Vishnumurthy and K. H. Girish, "A comprehensive review of battery technology for E-mobility," *Journal of the Indian Chemical Society*, vol. 98, no. 10, p. 100173, Oct. 2021, doi: [10.1016/j.jics.2021.100173](https://doi.org/10.1016/j.jics.2021.100173). [5]
- "Trends in electric cars – Global EV Outlook 2024 – Analysis - IEA." Accessed: Oct. 17, 2024. [Online]. Available: <https://www.iea.org/reports/global-ev-outlook-2024/trends-in-electric-cars> [6]
- M. Huang, "Press Center - Global Quarterly Smartphone Production Jumps 12.1% in 4Q23; Annual Total Drops 2.1% Down to 1.166 Billion Units, Says TrendForce | TrendForce - Market research, price trend of DRAM, NAND Flash, LEDs, TFT-LCD and green energy, PV," TrendForce. Accessed: Oct. 17, 2024. [Online]. Available: <https://www.trendforce.com/presscenter/news/20240311-12070.html> [7]
- B. Diouf and R. Pode, "Potential of lithium-ion batteries in renewable energy," *Renewable Energy*, vol. 76, pp. 375–380, Apr. 2015, doi: [10.1016/j.renene.2014.11.058](https://doi.org/10.1016/j.renene.2014.11.058). [8]
- A. Väyrynen and J. Salminen, "Lithium ion battery production," *The Journal of Chemical Thermodynamics*, vol. 46, pp. 80–85, Mar. 2012, doi: [10.1016/j.jct.2011.09.005](https://doi.org/10.1016/j.jct.2011.09.005). [9]

- [10] “Li-ion batteries: basics, progress, and challenges - Deng - 2015 - Energy Science & Engineering - Wiley Online Library.” Accessed: Oct. 17, 2024. [Online]. Available: <https://scijournals.onlinelibrary.wiley.com/doi/full/10.1002/ese3.95>
- [11] “Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review - ScienceDirect.” Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0304386X14002278>
- [12] “Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing - ScienceDirect.” Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0048969718318746>
- [13] C. Banza Lubaba Nkulu *et al.*, “Sustainability of artisanal mining of cobalt in DR Congo,” *Nat Sustain*, vol. 1, no. 9, pp. 495–504, Sep. 2018, doi: [10.1038/s41893-018-0139-4](https://doi.org/10.1038/s41893-018-0139-4).
- [14] M. Malpede, “The Dark Side of Batteries: Education and Cobalt Mining in the Democratic Republic of the Congo,” Apr. 16, 2021, *Social Science Research Network, Rochester, NY*: 3680730. doi: [10.2139/ssrn.3680730](https://doi.org/10.2139/ssrn.3680730).
- [15] W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang, and Z. Sun, “A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries,” *ACS Sustainable Chem. Eng.*, vol. 6, no. 2, pp. 1504–1521, Feb. 2018, doi: [10.1021/acssuschemeng.7b03811](https://doi.org/10.1021/acssuschemeng.7b03811).
- [16] L. Li *et al.*, “Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process,” *Journal of Power Sources*, vol. 262, pp. 380–385, Sep. 2014, doi: [10.1016/j.jpowsour.2014.04.013](https://doi.org/10.1016/j.jpowsour.2014.04.013).
- [17] Y. Xu *et al.*, “A simple solvent method for the recovery of Li_2CoO_2 and its applications in alkaline rechargeable batteries,” *Journal of Power Sources*, vol. 252, pp. 286–291, Apr. 2014, doi: [10.1016/j.jpowsour.2013.11.052](https://doi.org/10.1016/j.jpowsour.2013.11.052).
- [18] J. Mao, J. Li, and Z. Xu, “Coupling reactions and collapsing model in the roasting process of recycling metals from LiCoO_2 batteries,” *Journal of Cleaner Production*, vol. 205, pp. 923–929, Dec. 2018, doi: [10.1016/j.jclepro.2018.09.098](https://doi.org/10.1016/j.jclepro.2018.09.098).

- [19]
“Environmentally-friendly Oxygen-free Roasting/Wet Magnetic Separation Technology for in situ Recycling Cobalt, Lithium Carbonate and Graphite from Spent LiCoO₂/graphite Lithium Batteries | Request PDF.” Accessed: Oct. 17, 2024. [Online]. Available: [https://www.researchgate.net/publication/282388687_Environmentally-friendly_Oxygen-free_RoastingWet_Magnetic_Separation_Technology_for_in_situ_Recycling_Cobalt_Lithium_Carbonate_and_Graphite_from_Spent_LiCoO₂graphite_Lithium_Batteries](https://www.researchgate.net/publication/282388687_Environmentally-friendly_Oxygen-free_RoastingWet_Magnetic_Separation_Technology_for_in_situ_Recycling_Cobalt_Lithium_Carbonate_and_Graphite_from_Spent_LiCoO2graphite_Lithium_Batteries)
- [20]
G. Ren *et al.*, “Recovery of valuable metals from spent lithium ion batteries by smelting reduction process based on FeO–SiO₂–Al₂O₃ slag system,” *Transactions of Nonferrous Metals Society of China*, vol. 27, no. 2, pp. 450–456, Feb. 2017, doi: [10.1016/S1003-6326\(17\)60051-7](https://doi.org/10.1016/S1003-6326(17)60051-7).
- [21]
“Recycling of cathode from spent lithium iron phosphate batteries - ScienceDirect.” Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0304389420310578>
- [22]
“Hydrofluoric Acid: Burns and Systemic Toxicity, Protective Measures, Immediate and Hospital Medical Treatment - PMC.” Accessed: Oct. 17, 2024. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC6290397/>
- [23]
O. US EPA, “Learn about Dioxin.” Accessed: Oct. 17, 2024. [Online]. Available: <https://www.epa.gov/dioxin/learn-about-dioxin>
- [24]
“Sulfur Dioxide | Medical Management Guidelines | Toxic Substance Portal | ATSDR.” Accessed: Oct. 17, 2024. [Online]. Available: <https://wwwn.cdc.gov/TSP/MMG/MMGDetails.aspx?mmgid=249&toxid=46>
- [25]
D. A. Ferreira, L. M. Z. Prados, D. Majuste, and M. B. Mansur, “Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries,” *Journal of Power Sources*, vol. 187, no. 1, pp. 238–246, Feb. 2009, doi: [10.1016/j.jpowsour.2008.10.077](https://doi.org/10.1016/j.jpowsour.2008.10.077).
- [26]
Z. Takacova, T. Havlik, F. Kukurugya, and D. Orac, “Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach,” *Hydrometallurgy*, vol. 163, pp. 9–17, Aug. 2016, doi: [10.1016/j.hydromet.2016.03.007](https://doi.org/10.1016/j.hydromet.2016.03.007).
- [27]
“Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid–liquid extraction with Cyanex 272 - ScienceDirect.” Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378775306000437>

- [28]
J. Kang, G. Senanayake, J. Sohn, and S. M. Shin, "Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272," *Hydrometallurgy*, vol. 100, no. 3, pp. 168–171, Jan. 2010, doi: [10.1016/j.hydromet.2009.10.010](https://doi.org/10.1016/j.hydromet.2009.10.010).
- [29]
J. Zhao *et al.*, "Hydrometallurgical recovery of spent cobalt-based lithium-ion battery cathodes using ethanol as the reducing agent," *Environmental Research*, vol. 181, p. 108803, Feb. 2020, doi: [10.1016/j.envres.2019.108803](https://doi.org/10.1016/j.envres.2019.108803).
- [30]
L. Li, J. Ge, F. Wu, R. Chen, S. Chen, and B. Wu, "Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant," *Journal of Hazardous Materials*, vol. 176, no. 1, pp. 288–293, Apr. 2010, doi: [10.1016/j.jhazmat.2009.11.026](https://doi.org/10.1016/j.jhazmat.2009.11.026).
- [31]
L. Li, J. Ge, R. Chen, F. Wu, S. Chen, and X. Zhang, "Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries," *Waste Management*, vol. 30, no. 12, pp. 2615–2621, Dec. 2010, doi: [10.1016/j.wasman.2010.08.008](https://doi.org/10.1016/j.wasman.2010.08.008).
- [32]
S. Donegan, "Direct solvent extraction of nickel at Bulong operations," *Minerals Engineering*, vol. 19, no. 12, pp. 1234–1245, Sep. 2006, doi: [10.1016/j.mineng.2006.03.003](https://doi.org/10.1016/j.mineng.2006.03.003).
- [33]
S. Kurşunoglu, "EXTRACTION OF NICKEL FROM A MIXED NICKEL-COBALT HYDROXIDE PRECIPITATE," *Bilimsel Madencilik Dergisi*, pp. 45–52, Mar. 2019, doi: [10.30797/madencilik.537644](https://doi.org/10.30797/madencilik.537644).
- [34]
C. Cheng and M. D. Urbani, "The recovery of nickel and cobalt from leach solutions by solvent extraction: Process overview, recent research and development," *Proceedings of ISEC 2005*, pp. 503–526, Jan. 2005.
- [35]
S. Nowak and M. Winter, "The Role of Sub- and Supercritical CO₂ as 'Processing Solvent' for the Recycling and Sample Preparation of Lithium Ion Battery Electrolytes," *Molecules*, vol. 22, no. 3, p. 403, Mar. 2017, doi: [10.3390/molecules22030403](https://doi.org/10.3390/molecules22030403).
- [36]
P. Cattaneo, F. D'Aprile, V. Kapelyushko, P. Mustarelli, and E. Quartarone, "Supercritical CO₂ technology for the treatment of end-of-life lithium-ion batteries," *RSC Sustain.*, vol. 2, no. 6, pp. 1692–1707, Jun. 2024, doi: [10.1039/D4SU00044G](https://doi.org/10.1039/D4SU00044G).
- [37]
K. Li and Z. Xu, "A review of current progress of supercritical fluid technologies for e-waste treatment," *Journal of Cleaner Production*, vol. 227, pp. 794–809, Aug. 2019, doi: [10.1016/j.jclepro.2019.04.104](https://doi.org/10.1016/j.jclepro.2019.04.104).

- [38]
I. De Marco, S. Riemma, and R. Iannone, "Life cycle assessment of supercritical CO₂ extraction of caffeine from coffee beans," *The Journal of Supercritical Fluids*, vol. 133, pp. 393–400, Mar. 2018, doi: [10.1016/j.supflu.2017.11.005](https://doi.org/10.1016/j.supflu.2017.11.005).
- [39]
G. V. Amaral *et al.*, "Dairy processing using supercritical carbon dioxide technology: Theoretical fundamentals, quality and safety aspects," *Trends in Food Science & Technology*, vol. 64, pp. 94–101, Jun. 2017, doi: [10.1016/j.tifs.2017.04.004](https://doi.org/10.1016/j.tifs.2017.04.004).
- [40]
A. A. F. Zielinski, A. del P. Sanchez-Camargo, L. Benvenuti, D. M. Ferro, J. L. Dias, and S. R. S. Ferreira, "High-pressure fluid technologies: Recent approaches to the production of natural pigments for food and pharmaceutical applications," *Trends in Food Science & Technology*, vol. 118, pp. 850–869, Dec. 2021, doi: [10.1016/j.tifs.2021.11.008](https://doi.org/10.1016/j.tifs.2021.11.008).
- [41]
"Water under Supercritical Conditions: Hydrogen Bonds, Polarity, and Vibrational Frequency Fluctuations from Ab Initio Simulations with a Dispersion Corrected Density Functional | ACS Omega." Accessed: Oct. 17, 2024. [Online]. Available: <https://pubs.acs.org/doi/10.1021/acsomega.7b02036>
- [42]
S. D. Cramer and B. S. Covino, Eds., "Electrochemical Series," ASM International, 2005, pp. 665–671. doi: [10.31399/asm.hb.v13b.a0006542](https://doi.org/10.31399/asm.hb.v13b.a0006542).
- [43]
"Recycling of lithium, cobalt, nickel, and manganese from end-of-life lithium-ion battery of an electric vehicle using supercritical carbon dioxide - ScienceDirect." Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S092134492200461X>
- [44]
D. A. Bertuol, C. M. Machado, M. L. Silva, C. O. Calgaro, G. L. Dotto, and E. H. Tanabe, "Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction," *Waste Management*, vol. 51, pp. 245–251, May 2016, doi: [10.1016/j.wasman.2016.03.009](https://doi.org/10.1016/j.wasman.2016.03.009).
- [45]
"Lithium and cobalt extraction from LiCoO₂ assisted by p(VBPDA-co-FDA) copolymers in supercritical CO₂ - ScienceDirect." Accessed: Oct. 17, 2024. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0956053X24001673>
- [46]
J. Wu *et al.*, "Kinetic Study of Polyvinyl Chloride Pyrolysis with Characterization of Dehydrochlorinated PVC," *ACS Sustainable Chem. Eng.*, vol. 12, no. 19, pp. 7402–7413, May 2024, doi: [10.1021/acssuschemeng.4c00564](https://doi.org/10.1021/acssuschemeng.4c00564).

[47]

K. Liu and F.-S. Zhang, “Innovative leaching of cobalt and lithium from spent lithium-ion batteries and simultaneous dechlorination of polyvinyl chloride in subcritical water,” *Journal of Hazardous Materials*, vol. 316, pp. 19–25, Oct. 2016, doi: [10.1016/j.jhazmat.2016.04.080](https://doi.org/10.1016/j.jhazmat.2016.04.080).

[48]

T. V. Barros *et al.*, “Recovery of lithium and cobalt from lithium cobalt oxide and lithium nickel manganese cobalt oxide batteries using supercritical water,” *Environmental Pollution*, vol. 359, p. 124570, Oct. 2024, doi: [10.1016/j.envpol.2024.124570](https://doi.org/10.1016/j.envpol.2024.124570).