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Low-acid leaching of lithium-ion battery active materials in Fe-catalyzed Cu- H_2SO_4 system



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ABSTRACT

Leaching of active cathode materials of Li-ion batteries (LIB) is a hotly contested topic. In the published literature, the best processes utilize concentrated acid (e.g. 2–3 M H₂SO₄) and elevated temperatures for waste LIB leaching, along with unstable reduction reagents such as H₂O₂. In this study, we demonstrate the dissolution of LiCoO₂ (LCO) in a low-acid leaching system that utilizes typical battery elements which can be found in impure, recycled black masses; Fe²⁺ as a reducing agent towards LCO, and Cu as a reducing agent towards Fe³⁺. We show for the first time that the Cu-Fe²⁺-H₂SO₄ system can provide an excellent performance in dissolving LCO materials at low acid environment and near-room temperature (T = 30 °C), even to the point where the acidity of the solution decreases to pH = 1.89 while reaching Co extraction of 92%. To the best of our knowledge, such high leaching efficiency has not been previously reported under such mild conditions. Nowadays, recyclability of the process waters may also be important, and herein we highlighted the influence of Na₂SO₄ on leaching of LCO active materials as well in this system. Minimization of the lixiviant concentration and temperature is beneficial in allowing decrease in chemical and energy consumption. High pH operation also can support further downstream processing, helping to avoid the problem of sodium accumulation towards the end-stage where lithium is recovered.

1. Introduction

There is a strong on-going push towards electrification of society. Recently, Tesla produced their millionth electric vehicle (EV), with the other automotive makers are following in suit, and lithium-ion batteries (LIB) are playing a key-role in this revolution. The rapid adaptation of LIBs in EVs, stationary storage applications and vast array of consumer products, such as mobile phones, laptops and other electronics, have opened new opportunities to businesses. This has also given a new responsibility to hydrometallurgists: these batteries and their components need to be recycled, this most likely requires hydrometallurgical expertise at some part of the recycling process if the components are downcycled back to reagents (Fan et al., 2020; Harper et al., 2019). Present industrial activities are focused in particular on recycling of Co and Ni, found in lithium-cobalt oxide (LCO) and nickel-manganese-cobalt oxide (NMC) types of batteries (Chagnes and Swiatowska, 2015). These metals are the most valuable components in the batteries, whereas Li is often lost. This can be considered a tragedy, as most of the components in the batteries have to undergo extensive and energy-intensive manufacturing and refining processes - only to be discarded later. In the present study LCO is being investigated as it has been in the past the dominating Li-ion battery chemistry in the mobile applications, and is currently entering the recycling operators in large amounts. In 2013, 32,000 t of LCO cathode materials had already been produced (Chagnes and Swiatowska, 2015).

In leaching of spent LIBs, strong mineral acids with relatively high concentrations, and at slightly elevated temperatures, have been used along with strong oxidizing and reducing agents in the state-of-the-art literature. Nan et al. suggested that the reaction by which LCO dissolves in sulfuric acid is as per Eq. (1) (Nan et al., 2005):

$$4LiCoO_2 + 6H_2SO_4 = 2Li_2SO_4(aq.) + 4CoSO_4(aq.) + O_2(g) + 6H_2O$$
(1)

In turn, it has been suggested that the dissolution is driven by delithiation, as was suggested by Peng et al. (2018) in reactions (Eqs. (2)-(3)),

$$LiCoO_2 + xH^+ \rightarrow xLi^+ + Li_{1-x}CoO_2 + xe^-$$
⁽²⁾

$$Li_{1-x}CoO_2 + 4H^+ + (1+x)e^- \rightarrow (1-x)Li^+ + Co^{2+} + 2H_2O$$
 (3)

These results relating to the importance of delithiation were further confirmed by the extensive study of Billy et al. (2018), highlighting the complex chemistry and internal charge transfer reactions that can occur in these materials under leaching conditions. In the published research of the active materials leaching, sulfuric acid has been particularly popular, due to its widespread industrial application throughout the minerals processing industry (Ferreira et al., 2009). However, in order to obtain great yields of Co, Ni and Mn, high concentrations of the acids, such as 2–4 M H₂SO₄ or HCl, have generally been required (Lv et al., 2018). From process perspective, this is challenging: high concentration ensures that the solution remains acidic even after leaching,

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Technical Note



or has a high sulfate content. Use of high acid concentration can necessitate employment of a large quantity of neutralization chemicals before the recovery and solution purification stages of battery metals, which typically occur at the pH range from 4 to 9, i.e. $[H^+] < 10^{-4}$ M.

Furthermore, the sulfuric acid by its own is not enough: a reductant is commonly required in order to reach high metal extractions from the active cathode materials (Vieceli et al., 2018). Reducing agents, such as hydrogen peroxide (H_2O_2), have been commonly utilized in the leaching. The purpose of H_2O_2 is to provide electrons to higher valence metals in the active material oxide, enabling the destabilization of the stable oxide structure, and enabling their dissolution according to Eq. (4) (Ferreira et al., 2009):

$$4LiCoO_2 + 6H_2SO_4 + 2H_2O_2 \rightarrow 2Li_2SO_4(aq.) + 4CoSO_4(aq.) + 2$$
$$O_2(g) + 8H_2O$$
(4)

However, H₂O₂ is an unstable chemical, with relatively high oxidizing power, and in presence of common battery metals and impurities, such as metallic Cu, it will also act as an oxidizing agent. Furthermore, there are several reactions that may cause catalytic decomposition of H₂O₂, however it is not clear whether they can occur under leaching conditions, for instance in case of Fe (Fritz et al., 1934). Due to these factors, it is important to better understand the dissolution behavior and search for more effective leaching strategies. In preceding studies others have shown how the common impurities in the battery recycling may help dissolve active material oxides (Peng et al., 2019; Joulié et al., 2017). In our latest study, we utilized these impurities (Fe and Cu) in efficient, near-room temperature leaching of LCO without any H₂O₂ (Porvali et al., 2020). Small quantities of dissolved iron were shown to be able to catalyze the transfer of electrons from metallic Cu to solid lithium cobalt oxide (LiCoO₂), allowing its efficient dissolution according to Eq. (5):

$$2LiCoO_2 + Cu + 8H^+ \xrightarrow{Fe_2 + /Fe_3 +} 2Li^+ + 2Co^{2+} + 4H_2O + Cu^{2+}$$
(5)

Although we showed that the dissolution can work efficiently in a catalytic system of H₂SO₄-LiCoO₂-Cu-Fe²⁺/Fe³⁺, the work was performed at constant initial acid concentration of 2 M. This concentration was chosen because of the previous literature showing it being optimal in terms of extraction (Nan et al., 2005; Lv et al., 2018; Meshram et al., 2015a). Therefore, in our previous work the effect of acid concentration was not studied, nor was the influence of additives such as Na₂SO₄, wherein Na, a commonly accrued element due to neutralization, may influence the recyclability of the process solutions. In this work the study on H₂SO₄-LiCoO₂-Cu-Fe²⁺/Fe³⁺-H₂O leaching system was investigated in terms of acid concentration as well as added sodium sulfate concentration. Billy et al. showed that with NMC type active materials, there is a formation of O^-/O_2^{2-} on the surface of the active material which precedes its release as O₂(g) (Billy et al., 2018). A hypothesis for the results is proposed, and we suggest further investigative pathways for this promising idea of low acid leaching of LIB active materials that are traditionally challenging to dissolve.

2. Materials & methods

A 500 mL round-bottom glass leaching reactor with a jacket (Lasilaite, Finland) was utilized in leaching experiments. The reactor was attached to a thermostatically controlled water bath (Lauda A100, Germany) which was used to maintain a constant temperature of T = 30 °C in all experiments. The reactor was sealed with glass stoppers, silicon gasket and steel clamp, along with a glass condenser in order to prevent evaporation, and that any gasses would be able to escape the reactor. In all synthetic solution experiments, a rotameter (LH-ZC50-HR, Kytölä, Finland) was utilized in N₂ purging (0.5 L/min) in order to evacuate the dissolved atmospheric O₂(g) from the solution that might influence the dissolution of Cu in the leaching system as per reaction (6) (Lu and Graydon, 1954):

Table 1	
Table of LCO dissolution experiments and	the investigated parameters

Experimental	H_2SO_4	FeSO ₄ ·7H ₂ O	Na_2SO_4
Code	(M)	(g)	(M)
A1	0.34	1.054	0
A2*	0.5	1.054	0
A3*	1	1.054	0
A4*	1.5	1.054	0
A5	2	1.054	0
A6	2.5	1.054	0
A7	3	1.054	0
A8	0.5	0.527	0
A9	3	0.527	0
A10*	0.5	1.054	0.5
A11*	1	1.054	0.5
A12*	1.5	1.054	0.5
A13*	1	1.054	0.25
A14*	1	1.054	0.25
A15*	1	1.054	0.25
A16*	0.5	1.054	0.25
A17*	1.5	1.054	0.25

The amount of Cu utilized in each experiment was in 1/1 (mol/mol) ratio in respect to Eq. (5), i.e. 2.167 g. 6.68 g LCO was utilized in each experiment. The experiments marked with star were part of the DOE with H₂SO₄ (0.5–1.5 M) and Na₂SO₄ (0–0.5) as parameter ranges. T = 30 °C in all experiments.

$$2Cu + 4H^{+} + O_2(g) \to 2Cu^{2+} + 2H_2O$$
(6)

4 M stock H_2SO_4 was prepared from 95 to 97% H_2SO_4 (VWR Chemicals) and acid-base titration (Phenolphthalein, 1%, FF-Chemicals, Inidicator; 2.0 N NaOH, standardized solution, Alfa-Aesar) was used in ensuring the quality of the 4 M stock solution. Solutions with required acid concentrations were then obtained by diluting this stock solution. LiCoO₂ was of battery grade purity (99.5%, Alfa-Aesar). Ferrous sulfate (FeSO₄·7H₂O, > 99%) was dissolved into the lixiviant before LCO addition, as was the Na₂SO₄ (Thermo Fisher Scientific, > 99%). Cu powder (< 425 µm, 99.5%, Alfa-Aesar) was added before LCO addition as well. In all the experiments, the quantity of the pre-diluted acid solution was V = 0.4 L, and the quantity of LCO utilized in all experiments was always 6.68 g.

The performed experiments are detailed in Table 1. Samples of size 2-3 mL were retrieved with a glass pipette and immediately syringe filtered with 0.45 µm polyethylene sulfone (PES) syringe filter membranes. From the filtrate, a sample for atomic absorption spectroscopy (AAS) was retrieved by air displacement pipette and diluted to appropriate concentrations. AAS analysis was performed with Thermo Fisher, ICE 3000, USA. The experiments marked with star were part of the design of experiments (DOE) matrix (Box et al., 1978). Response surface methodology (RSM) was utilized in their analysis by creating an experimental matrix corresponding to a face-centered central composite design (CCF) (Bezerra et al., 2008). The methodology can help 1) reveal interactions of the investigated parameters to the response, which could then be linked to chemical behavior and 2) help identify possible data outliers (i.e. bad data). Error is assumed to be random and normally distributed in these experiments. In the DOE, reaction rate constants were the measured responses and $[Na_2SO_4]$ and $[H_2SO_4]$ concentrations the tested variables. Reaction rate constants (K_c) were obtained by surface reaction controlled cubic rate law (7) (Free, 2013) and final extractions were obtained at t = 2 h. In the experiment (A1) where 0.34 M was utilized, the quantity of acid was carefully considered. The required quantity of acid was calculated based on the stoichiometry of the reaction (5). Assuming no significant side-reactions lead to significant dissolution of Cu, the required amount of acid was estimated based on amount of LCO used in the experiment. LCO, not Cu, was then the limiting factor. The amount of required Cu was calculated based on stoichiometric ratio (1:1) requirement indicated by reaction (5), hence 2.167 g of Cu was utilized. The calculation was done as follows in



Fig. 1. (A) The extraction of Co as a function of acid concentration. (B) The relative molar extraction of Co/Cu as a function of acid concentration. T = 30 °C.

equation.

3. Results & discussion

3.1. The effect of acid concentration

In this study, the effect of acid concentration on LCO leaching was investigated in the leaching system containing dissolved Fe²⁺, metallic Cu and H₂SO₄. The amount of dissolved Cu and Co were both measured as a function of time over 2 h while the amount of initial H₂SO₄ was varied within the range of 0.5-3 M. Also, H₂SO₄ concentration of 0.34 M was studied (A1). The amount of the acid was based on theoretical calculations assuming that if all the Co dissolved according to reaction (5), the final acid concentration in the solution should be close to neutral. Fig. 1A shows that the maximum obtainable extraction for Co was 10 g/L. Also, it can be seen that the system with the lowest acid concentration (0.34 M, A1) performed extremely well for Co extraction. High acid concentration, seems to enhance Co leaching kinetics in the initial phase of the experiment, signified as high Co/Cu mol/mol ratio in Fig. 1B. This suggests that there are different leaching mechanism affecting in the system as a function of acid concentration and time: initially, the Co is being reduced and dissolved by the reaction (1). However, at lower acid concentration, this reaction is not dominant, and it is expected that most of the sulfuric acid is dissociated to either bisulfate or free hydrogen ions. The difference in the leaching mechanism is most likely due to the rate of delithiation being dependent on acid concentration. Billy et al. showed that with NMC materials the delithiation is a strong driver in surface reorganization, and that the acid concentration has significant influence on the rate and extent of delithiation (Billy et al., 2018). Surprisingly, in the current study it was found that and elevated acid concentration (3 M) indicated significant retardation in the dissolution rate. The dissolution rate may be inhibited by several factors, such as structural changes leading to more stable oxide configuration, as was discussed just previously. Regardless, this is purely conjecture and should be regarded as such.

In addition to pure acid concentration, and encouraged by the observed behavior of the singular experiment with 3 M H_2SO_4 , the behavior of variable Fe content was compared at low and high acidity (0.5 vs. 3 M), i.e., the interaction of *[Fe]* and *[H₂SO₄]* was investigated. The results (Fig. 2) clearly indicate that a high acid concentration is not beneficial to overall extraction of Co, and that even small quantity of Fe catalyzes LCO dissolution. This effect more evident at low acid concentration (0.5 M) vs. high acid concentration (3.0 M). This discovery could pave way for recycling processes that utilize inherently low acid concentrations, reducing reagent consumption in neutralization stage



Fig. 2. The effect of acid concentration in conjunction with the effect of iron concentration. All the experiments contained metallic Cu (2 g) as a reductant for Fe³⁺. T = 30 °C.

that follows the leaching.

The reason for the described phenomenon is ambiguous. It is wellknown that at high sulfuric acid concentration the extraction of Co is initially rapid, but will reach equilibrium before significant Co extraction occurs (Co < 50% (Porvali et al., 2020)) and reaction ceases. Higher acid concentration is known to lead to more rapid delithiation in NMC type materials, which in turn leads to surface reorganization (Billy et al., 2018). Earlier, it has been claimed that the dissolution of LCO may stop because of the formation of Co₃O₄ (Ferreira et al., 2009; Joulié et al., 2014), suggesting similar surface reorganization may be occurring in LCO active materials. Co_3O_4 is a p-type semiconductor whose formation on the surface of the LCO particle may inhibit the charge transfer between the bulk particle, Co₃O₄ and surface of the whole particle, leading to decrease in dissolution at higher acid concentrations. It is suggested that the formation of peroxide-like O^{-}/O_{2}^{2-} atoms (Billy et al., 2018) on the surface of active materials could be the reaction step by which the Fe^{2+} is able to enhance dissolution of LCO. Furthermore, we suggest that low acid concentration is helpful in maintaining the presence of these oxygen atoms, as delithiation is more limited in lower acid concentrations, visible already in results of Fig. 1B. It is suggested that in this manner excessive surface reorganization is avoided, therefore enabling a controlled deconstruction of the LCO structure and extraction of Co²⁺, even under relatively mild acid concentrations, which – to the best of the authors' knowledge – has not been demonstrated in prior literature.

The experiment that utilized 0.34 M H₂SO₄ showed an excellent Co extraction (92%), although it had the slowest initial reaction rate. The final pH of the solution was measured to be pH = 1.89, which indicates that high extractions could be achieved even at low acidities, and further that the acidity of the leaching solution is less important parameter in a system with Fe reductant, than suggested by the previous traditional leaching studies (Meshram et al., 2015b). This highlights the importance of understanding the changes in the active materials surface structure, as well as the solution composition and acidity, during the leaching process itself. It is vital to understand that the very stable oxide structure of trivalent Co in LiCoO₂ must be attacked in order to be able to obtain good yields of Co. In the present study, although the mechanism is not unambiguous, we have now shown that Fe²⁺ is particularly efficient in attacking this stable oxide structure, at nearroom temperature, by reducing Co^{3+} to Co^{2+} . We have also shown that low acid leaching under room temperature can provide a higher final yield with a sufficient kinetics compared to high acid leaching. This can also provide further benefits for the further downstream processing as well, as less neutralization chemicals will be required. This reduction could potentially be as much as a factor of 10-100, i.e. if the final pH ranges in 1-2 instead of 0-0.5. This is also of the importance, as it will influence the reusability of the purified lixiviant. Sodium is one of the most commonly accumulating elements in the downstream processes due to the neutralization reactions. For example, Liu et al. (2019) showed that it can be important to consider how the quantity of Na in sulfate medium might influence the downstream recovery processes. Furthermore, reusing of process waters or partially purified process waters in leaching may lead to Na accumulation. Therefore, the influence of Na on dissolution in this catalytic system was investigated next.

3.2. The effect of sodium sulfate

The effect of presence of sodium and sulfate ions was investigated by having sodium sulfate as an additive in the solution. The effect of Na₂SO₄ (0–0.5 M) at initial acidity of 0.5–1.5 of H₂SO₄ was tested with a DOE matrix. DOE matrix was utilized in order to ascertain whether there would be interaction between the acid and sodium sulfate concentration. The kinetic results are presented in Fig. 3. The listed reaction rate constants were the responses given to the DOE matrix. The results show that the addition of Na₂SO₄ decreased the reaction rates by somewhat. Since the solutions were acidic throughout the experiments (pH < 1), it is unlikely that there would be passivation layers forming on the solid Cu. More likely, Na⁺ ions influence the delithiation of LCO.

 Table 2

 ANOVA table of the DOE results involving sulfuric acid and sodium sulfate.

DF	Adj SS	Adj MS	F-value	<i>p</i> -value
1	1.23543	1.23543	28.58	0
1	1.23543	1.23543	28.58	0
1	1.23543	1.23543	28.58	0
9	0.38907	0.04323		
7	0.36846	0.05264	5.11	0.173
2	0.02061	0.01031		
10	1.62449			
	DF 1 1 9 7 2 10	DF Adj SS 1 1.23543 1 1.23543 1 1.23543 9 0.38907 7 0.36846 2 0.02061 10 1.62449	DF Adj SS Adj MS 1 1.23543 1.23543 1 1.23543 1.23543 1 1.23543 1.23543 1 1.23543 1.23543 9 0.38907 0.04323 7 0.36846 0.05264 2 0.02061 0.01031 10 1.62449	DF Adj SS Adj MS F-value 1 1.23543 1.23543 28.58 1 1.23543 1.23543 28.58 1 1.23543 1.23543 28.58 9 0.38907 0.04323 7 7 0.36846 0.05264 5.11 2 0.02061 0.01031 1 10 1.62449

Experiments belonging to this investigation where marked with star in Table 1.

In all experiments, the final extraction at 2-h mark was found to be between 82% and 93% Co extraction.

The ANOVA results are listed in Table 2. Due to statistical insignificance (p > .1), the interaction term and binomial terms had to be eliminated as there were no correlation. This means that the sulfuric acid content did not have further influence on how much sodium sulfate independently influenced the dissolution rate of Co. Furthermore, the sulfuric acid concentration did not influence at all the reaction rate at the investigated acidity range (0.5-1.5 M). It is therefore possible to conclude, as both Na₂SO₄ and H₂SO₄ contain sulfate ions, that the amount of sulfate ions didn't contribute to the dissolution rate in the investigated concentration range, but it is the presence of sodium ions that decreases the kinetics. Only a single main effect, the concentration of Na₂SO₄, was shown statistically to be significant in influencing the reaction rate constants. Na₂SO₄ had an undeniable effect on dissolution rates, which were also naturally reflected upon the final Co yields (at t = 120 min). Decreases in reaction rates were observed, going from $4.5 \cdot 10^{-3}$ to $3.6 \cdot 10^{-3}$ when Na_2SO_4 i.e. Na^+ ion concentration increased from 0 to 1 M, regardless of the sulfuric acid concentration that was utilized. Lack-of-fit had p = .173 and therefore, the null hypothesis "there is lack of fit" can be confidently discarded at confidence level CL = 95%.

As it can be seen from the results, the presence of sodium sulfate is detrimental to leaching rate of LCO at sulfuric acid concentrations 0.5–1.5 M. This suggests that the recycling processes aiming to reutilize industrial process water flows need to consider their sodium sulfate balance in order to avoid decreases in dissolution rates, or take this change into consideration in the process design phase.

3.3. Significance of the low acid leaching to recycling

One of the greater issues in the processing of spent Li-ion batteries is the extent to which the operator must go in adjusting the solution pH.



Fig. 3. Co extraction in the experiments involving DOE matrix, and the reaction rate constants (reported as 10^{-3}). T = 30 °C.

For instance, many suggested processes extract Li alongside other metals to the lixiviant, and only recover Li after solution has been completely purified. Li₂CO₃ - one of the common final Li products - has a very high solubility, which in turn necessitates evaporative crystallization in its production. Most traditional leaching studies have shown that that the active cathode materials require a high initial acid concentration ranging from 1 to 3 M in order to achieve appreciable leaching rates. With this kind of initial concentrations, it is highly possible that the residual acid content ranges anywhere from 0.1 to 2 M. In this study, we show that in LCO-Fe²⁺/Fe³⁺-Cu-H₂SO₄ leaching system, the acid feed can be highly optimized: we obtained excellent Co extraction even though the final pH of the system after reaction was 1.89 (i.e. $[H^+] = \sim 0.0129$ M). Already at this level, the addition of alkaline required for the solution neutralization in the subsequent recovery and purification stages is heavily minimized. Future research in this field of study should focus on implementing these findings as there still remains uncertainty on how the leaching mechanisms are influenced by presence of, e.g., other foreign anions present in the LIB waste (Fluorides and phosphates from the electrolyte residues) and graphite (adsorption of ions). However, it must be recognized that the use of Cu as an additive may be prohibitive, especially if it could be recovered. Also, future research prospects could involve investigation of alternative ways to regenerate Fe^{2+} in the case that Cu is satisfactorily recovered prior to leaching of the impure black mass.

4. Conclusions

In this paper, it was shown that the dissolution of LCO active materials is possible under conditions which have not earlier been presented in the literature. In the state-of-the-art literature, the best results have been obtained with the combination of high temperature and high acid concentration. In contrast, we demonstrate that the dissolution of LCO is possible in a catalytic leaching system containing metallic Cu and dissolved Fe at very low acid concentrations, and simultaneously at low temperature of T = 30 °C. We proved that the Co dissolution proceeds up to 92% extraction in 2 h, even when there is just barely enough acid to stay below pH = 3. We also demonstrated that the dissolution rate of Co is influenced by the presence of sodium. It was hypothesized that this is related to delithiation and replacement of Li by Na in the structure, and this could potentially influence the usability of circulated process water streams in leaching that might contain Na.

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Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., Escaleira, L.A., 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta 76 (5), 965–977. https://doi.org/10.1016/j.talanta.2008.05.019.
- Billy, E., Joulié, M., Laucournet, R., Boulineau, A., De Vito, E., Meyer, D., 2018. Dissolution mechanisms of LiNi1/3Mn1/3Co1/3O2 positive electrode material from lithium-ion batteries in acid solution. ACS Appl. Mater. Interfaces 10 (19), 16424–16435. https://doi.org/10.1021/acsami.8b01352.
- Box, G.E.P., Hunter, W.G., Hunter, J.S., 1978. Statistics for Experimenters. 664 John Wiley and sons New York.
- Chagnes, A., Swiatowska, J., 2015. Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling. Elsevier Science.
- Fan, E., et al., 2020. Sustainable recycling technology for Li-ion batteries and beyond: challenges and future prospects. Chem. Rev. https://doi.org/10.1021/acs.chemrev. 9b00535.
- Ferreira, D.A., Prados, L.M.Z., Majuste, D., Mansur, M.B., 2009. Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent li-ion batteries. J. Power Sources 187 (1), 238–246. https://doi.org/10.1016/j.jpowsour.2008.10.077
- Free, M.L., 2013. Hydrometallurgy: Fundamentals and Applications. John Wiley & Sons, Somerset Incorporated.
- Fritz, H., Joseph, W., Pope, W.J., 1934. The catalytic decomposition of hydrogen peroxide by iron salts. Proc. R. Soc. London. Series A - Math. Phys. Sci. 147 (861), 332–351. https://doi.org/10.1098/rspa.1934.0221.
- Harper, G., et al., 2019. Recycling lithium-ion batteries from electric vehicles. Nature 575 (7781), 75–86.
- Joulié, M., Laucournet, R., Billy, E., 2014. Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries. J. Power Sources 247, 551–555. https://doi.org/10.1016/j.jpowsour.2013. 08.128.
- Joulié, M., Billy, E., Laucournet, R., Meyer, D., 2017. Current collectors as reducing agent to dissolve active materials of positive electrodes from li-ion battery wastes. Hydrometallurgy 169, 426–432. https://doi.org/10.1016/j.hydromet.2017.02.010.
- Liu, F., Peng, C., Porvali, A., Wang, Z., Wilson, B.P., Lundström, M., Sep. 2019. Synergistic recovery of valuable metals from spent nickel-metal hydride batteries and Lithiumion batteries. ACS Sustain. Chem. Eng. https://doi.org/10.1021/acssuschemeng. 9b02863. p. acssuschemeng. 9b02863.
- Lu, B.C.-Y., Graydon, W.F., 1954. The rate of dissolution of copper. Can. J. Chem. 32 (2), 153–163.
- Lv, W., Wang, Z., Cao, H., Sun, Y., Zhang, Y., Sun, Z., May 2018. A critical review and analysis on the recycling of spent lithium-ion batteries. ACS Sustain. Chem. Eng. 6 (2), 1504–1521. https://doi.org/10.1021/acssuschemeng.7b03811.
- Meshram, P., Pandey, D.D., Mankhand, T.R., 2015a. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: leaching and kinetic aspects. Urban Mining 45, 306–313. https://doi.org/10.1016/j.wasman.2015.05.027.
- Meshram, P., Pandey, B.D., Mankhand, T.R., 2015b. Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching. Chem. Eng. J. 281, 418–427.
- Nan, J., Han, D., Zuo, X., 2005. Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction. J. Power Sources 152, 278–284. https://doi.org/10.1016/j.jpowsour.2005.03.134.
- Peng, C., Hamuyuni, J., Wilson, B.P., Lundström, M., 2018. Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system. Waste Manag. 76, 582. https://doi.org/10.1016/j.wasman.2018.02.052.
- Peng, C., Liu, F., Aji, A.T., Wilson, B.P., Lundström, M., 2019. Extraction of Li and Co from industrially produced Li-ion battery waste – using the reductive power of waste itself. Waste Manag. 95, 604–611. https://doi.org/10.1016/j.wasman.2019.06.048.
- Porvali, A., Chernyaev, A., Shukla, S., Lundström, M., 2020. Lithium ion battery active material dissolution kinetics in Fe(II)/Fe(III) catalyzed Cu-H2SO4 leaching system. Sep. Purif. Technol. 236, 116305. https://doi.org/10.1016/j.seppur.2019.116305.
- Vieceli, N., Nogueira, C.A., Guimarães, C., Pereira, M.F.C., Durão, F.O., Margarido, F., 2018. Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite. Waste Manag. 71, 350–361.