

Proceeding Paper

Application of the Chemical Leaching Method for the Recovery of Li and Co Contained in Spent Li-Ion Batteries [†]

Weronika Urbańska ^{1,*} , Magdalena Osiał ²  and Sławomir Wilczewski ^{2,3} 

¹ Faculty of Environmental Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

² Institute of the Fundamental Technological Research, Polish Academy of Sciences, Pawińskiego 5B, 02-106 Warsaw, Poland

³ Faculty of Chemical Technology and Engineering, Bydgoszcz University of Science and Technology, Seminaryjna 3, 85-326 Bydgoszcz, Poland

* Correspondence: weronika.urbanska@pwr.edu.pl

[†] Presented at the Innovations-Sustainability-Modernity-Openness Conference (ISMO'22), Białystok, Poland, 26–27 May 2022.

Abstract: Waste batteries and accumulators are a group of waste, the amount of which is constantly increasing every year. A particular weight gain of this type of waste is observed for lithium-ion batteries used in various electronic devices and modern passenger vehicles. Due to the complex chemical composition and the content of different valuable metals, used Li-ion batteries should be subjected to appropriate recycling methods, the purpose of which is to separate the individual raw materials included in the battery. Regarding the demand for innovative technologies for processing spent Li-ion batteries, a concept of laboratory experiments was developed in the field of hydrometallurgical recovery of Li and Co contained in the battery powder obtained from this type of waste. As a result, it was shown that it is possible to effectively recover the tested metals with an adequately designed leaching process.

Keywords: Li-ion batteries; leaching; recovery of metals; waste management; environmental engineering



Citation: Urbańska, W.; Osiał, M.; Wilczewski, S. Application of the Chemical Leaching Method for the Recovery of Li and Co Contained in Spent Li-Ion Batteries. *Environ. Sci. Proc.* **2022**, *18*, 12. <https://doi.org/10.3390/environsciproc2022018012>

Academic Editors: Iwona Skoczko, Dorota Anna Krawczyk and Ewa Szatyłowicz

Published: 31 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Waste batteries and accumulators are a source of many raw materials, including metals necessary for producing various electrical and electronic equipment. Currently, the most popular type of batteries used in small-size portable electronic devices, as well as hybrid and electric vehicles, are lithium-ion batteries (Li-ion; LiBs), in which lithium and cobalt are included. These elements are also considered critical raw materials because they are indispensable components of the most modern technologies used worldwide and thus are overexploited forms of natural resources. As a result, such actions may lead to their rapid depletion, and the production of new products containing lithium and cobalt will be at risk. The solution to this problem is the use of secondary metallic materials contained in polymetallic waste, an example of which are spent Li-ion batteries. In industrial and laboratory practice, various techniques are used to recover metals in waste LiBs, including hydrometallurgical methods involving the leaching of elements from the battery powder into solution [1–5]. Thanks to the use of appropriate process parameters (i.e., the concentration and type of leaching and reducing agents, the ratio of solid to liquid phase, temperature, and the duration of experiments), it is possible to achieve high (over 95%) rates of metal recovery, including for Li and Co [5–12].

Considering the increased demand for the recovery of critical metallic raw materials (Li and Co) included in the waste Li-ion batteries, the concept of laboratory experiments in this field was developed.

2. Materials and Methods

The research material was anode–cathode battery powder obtained due to the manual dismantling and fragmentation of spent Li-ion batteries contained in laptops of various brands. The tested powder was subjected to mineralization digestion in the presence of 65% HNO₃, and the initial content of individual metals in the received solution was determined by the ICP-OES method.

For the separation of metals (namely, lithium and cobalt), the acidic reductive leaching method was applied. The conducted leaching experiments were performed in the presence of inorganic and/or organic leaching agents (i.e., sulfuric acid (H₂SO₄), lactic acid (C₃H₆O₃), and formic acid (CH₂O₂)). In addition, hydrogen peroxide (H₂O₂) and glutaric acid (C₅H₈O₄) were used as reducing agents. A list of other process parameters is presented in Table 1.

Table 1. Determined parameters of the leaching process.

Sample	Leaching Agent	Reducing Agent	Temperature	Solid/Liquid Ratio	Time
1	1.5 M sulfuric acid	3 mL H ₂ O ₂	90 °C	1/10	120 min
2	1.5 M sulfuric acid	3 mL H ₂ O ₂ + 5 g glutaric acid			
3	5 M lactic acid	3 mL H ₂ O ₂			
4	5 M lactic acid	3 mL H ₂ O ₂ + 5 g glutaric acid			
5	5 M formic acid	3 mL H ₂ O ₂			
6	5 M formic acid	3 mL H ₂ O ₂ + 5 g glutaric acid			

After leaching, the samples were vacuum filtered, obtaining solutions in which the content of tested metals was determined (ICP-OES method) and powdery leach residues, the latter of which were dried for 24 h at 105 °C.

3. Results and Discussion

As a result of the leaching of the electrode powder from spent Li-ion batteries, acidic polymetallic solutions with a color from light pink to raspberry were obtained. The achieved results of the ICP-OES analyses are presented in Figure 1 in the form of percentage rates of metal recovery in relation to their initial content in the battery powder.

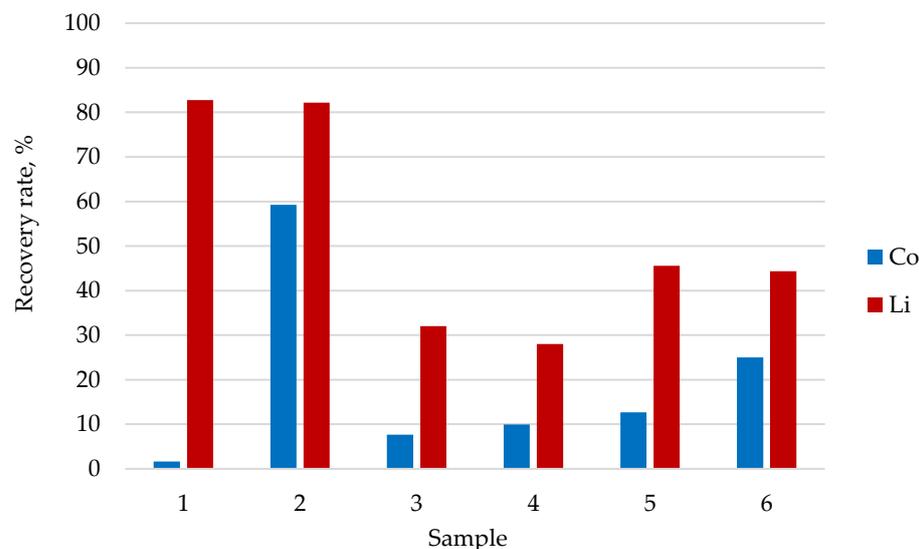


Figure 1. Recovery rates of Li and Co obtained as a result of acid leaching of electrode powder from spent Li-ion batteries.

The results of the Co and Li recovery rates indicate that the highest leaching of these two metals was simultaneously obtained in sample 2, where the sulfuric acid was used as leaching agent and the reducing agents were H₂O₂, and glutaric acid (59% and 82%, respectively). In turn, the lowest rate of cobalt recovery was obtained in sample 1 (1.5 M H₂SO₄ + H₂O₂), despite the use of hydrogen peroxide as a reducing agent, which is often indicated in the literature as a compound that significantly improves the leaching of this metal [6]. The low cobalt recovery rate in the present experiments, despite the use of H₂O₂, can probably be explained by the application of too small of a dose of this factor. The preparation of the powder material for testing may also have had an impact—the entire electrode powder was used (i.e., anodic and cathodic mass) without additional thermal or chemical treatment, which is often practiced in literature sources to eliminate potential contamination, at the same time representing a more complicated material preparation process than the one presented in this paper. The use of organic acids as leaching agents affected the Li recovery rates—these results were much lower than for the sulfuric acid leach tests, while higher rates of this metal recovery were obtained for samples 5 and 6 leached with formic acid (47% and 45%, respectively). In the case of cobalt recovery, for samples 3–6, the rates were higher than for sample 1, but also lower than for sample 2. Among the experiments with organic acids, the best results for both tested metals were received for sample 6 (5 M CH₂O₂ + H₂O₂ + C₅H₈O₄)—Co: 26%, Li: 45%. Nevertheless, they are significantly lower than for a similar blend of reducing agents but combined with an inorganic leaching agent in the form of H₂SO₄ (sample 2).

4. Conclusions

The obtained results of the conducted experiments on the acidic leaching of the electrode powder from spent Li-ion batteries indicate that it is possible to effectively recover the Li and Co metals contained in this type of waste material. The best results were received for the sample leached with inorganic sulfuric acid with the simultaneous use of two reducing agents: hydrogen peroxide and glutaric acid, which indicates the synergism of these two compounds in the acidic reaction environment. An alternative to the use of inorganic acids as leaching agents may be organic acids (e.g., lactic or formic acid), but the processes with their use require appropriate modeling and preliminary preparation of the research material to maximize the efficiency of the recovery of metals contained in the battery powder. The proposed method of obtaining metallic raw materials from spent batteries is in line with modern ideas of the circular economy model. It is also focused on the sustainable development and rational management of raw materials from natural resources, because after the selective separation process, the Co and Li from solutions gained following acidic leaching (e.g., in precipitation or solvent extraction processes) can be reused to produce, inter alia, new lithium-ion batteries.

Author Contributions: W.U. and M.O. conceived and designed the experiments; W.U., M.O. and S.W. performed the experiments; W.U., M.O. and S.W. analyzed the data; W.U., M.O. and S.W. contributed reagents/materials/analysis tools; W.U., M.O. and S.W. wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yao, Y.; Zhu, M.; Zhao, Z.; Tong, B.; Fan, Y.; Hua, Z. Hydrometallurgical Processes for Recycling Spent Lithium-Ion Batteries: A Critical Review. *ACS Sustain. Chem. Eng.* **2018**, *6*, 13611–13627. [[CrossRef](#)]

2. Lv, W.; Wang, Z.; Cao, H.; Sun, Y.; Zhang, Y.; Zhi, S. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2018**, *6*, 1504–1521. [[CrossRef](#)]
3. Majid Alipanah, M.; Saha, A.K.; Vahidi, E.; Jin, H. Value recovery from spent lithium-ion batteries: A review on technologies, environmental impacts, economics, and supply chain. *Clean Technol. Recycl.* **2021**, *1*, 152–184. [[CrossRef](#)]
4. Urbańska, W. Recovery of Co, Li, and Ni from Spent Li-Ion Batteries by the Inorganic and/or Organic Reducer Assisted Leaching Method. *Minerals* **2020**, *10*, 555. [[CrossRef](#)]
5. Urbańska, W.; Osial, M. Investigation of the Physico-Chemical Properties of the Products Obtained after Mixed Organic-Inorganic Leaching of Spent Li-Ion Batteries. *Energies* **2020**, *13*, 6732. [[CrossRef](#)]
6. Cheng, X.; Guo, G.; Cheng, Y.; Liu, M.; Ji, J. Effect of Hydrogen Peroxide on the Recovery of Valuable Metals from Spent $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ Batteries. *Energy Technol.* **2022**, *10*, 2200039. [[CrossRef](#)]
7. Fan, E.; Yang, J.; Huang, Y.; Lin, J.; Arshad, F.; Wu, F.; Li, L.; Chen, R. Leaching Mechanisms of Recycling Valuable Metals from Spent Lithium-Ion Batteries by a Malonic Acid-Based Leaching System. *ACS Appl. Energy Mater.* **2020**, *3*, 8532–8542. [[CrossRef](#)]
8. Li, P.; Luo, S.; Su, F.; Zhang, L.; Yan, S.; Lei, X.; Mu, W.; Wang, Q.; Zhang, Y.; Liu, X.; et al. Optimization of Synergistic Leaching of Valuable Metals from Spent Lithium-Ion Batteries by the Sulfuric Acid-Malonic Acid System Using Response Surface Methodology. *ACS Appl. Mater. Interfaces* **2022**, *14*, 11359–11374. [[CrossRef](#)] [[PubMed](#)]
9. Zeba, G.T.C.; Paulino, J.F.; Afonso, J.C. Recovery of metals from electroactive components of spent Li-ion batteries after leaching with formic acid. *Braz. J. Chem. Eng.* **2022**, *39*, 147–158. [[CrossRef](#)]
10. Chabhadiya, K.; Srivastava, R.R.; Pathak, P. Two-step leaching process and kinetics for an eco-friendly recycling of critical metals from spent Li-ion batteries. *J. Environ. Chem. Eng.* **2021**, *9*, 105232. [[CrossRef](#)]
11. Santhosh, G.; Nayaka, G.P. Cobalt recovery from spent Li-ion batteries using lactic acid as dissolution agent. *Clean. Eng. Technol.* **2021**, *3*, 100122. [[CrossRef](#)]
12. Song, D.; Wang, T.; Liu, Z.; Zhao, S.; Quan, J.; Li, G.; Zhu, H.; Huang, J.; He, W. Characteristic comparison of leaching valuable metals from spent power Li-ion batteries for vehicles using the inorganic and organic acid system. *J. Environ. Chem. Eng.* **2022**, *10*, 107102. [[CrossRef](#)]