様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　６ 年　 ６ 月　 ６ 日現在

機関番号：１１３０１
研究種目：基盤研究(C)（一般）
研究期間：2021～2023
課題番号：２１Ｋ１２３０２

研究課題名（和文）Low/no-corrosion leaching of spent lithium-ion battery cathode materials in hydrothermal water using amino acid or mixed organic acids as the leachant

研究課題名（英文）Low/no-corrosion leaching of spent lithium-ion battery cathode materials in hydrothermal water using amino acid or mixed organic acids as the leachant

研究代表者

鄭　慶新（ZHENG, QINGXIN）

東北大学・工学研究科・特任助教

研究者番号：３０８３５５０９

交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：このプロジェクトでは、研究代表者が使用済みリチウムイオン電池（LIB）正極材料の水熱浸出に対して、高い浸出効率を達成し、酸腐食の問題を解決できる有機酸を探求することを目指しました。文献調査と初期実験に基づいて、グリシンとクエン酸/グリシン混合酸が候補浸出剤として選ばれました。最終的に、さまざまなLIB正極材料の酸浸出が、約100%の浸出率と低/無酸腐食のグリーンプロセスを通じて初めて達成されました。研究期間中に、トップジャーナルに4本の査読付き英語論文が発表され、特許が出願され、国際および国内会議で2つの招待講演を含む6つの口頭発表と1つのポスター発表が行われました。

研究成果の学術的意義や社会的意義
This research effectively eliminated the acid corrosion problem during the leaching process, significantly improving current LIB recycling methods. The results will help conserve natural resources, reduce environmental problems, ensure resource stability and security, and bring economic benefits.

研究成果の概要（英文）：In this project, the Principal Investigator aimed to explore a kind of organic acids for the hydrothermal leaching of spent lithium-ion battery (LIB) cathode materials, which can achieve high leaching efficiency and resolve the problem of acid corrosion. Based on a literature investigation and initial experiments, glycine and citric acid/glycine mixture were selected as candidate leaching agents. Finally, it was the first time to achieve the acid leaching of different types of LIB cathode materials including LiCoO2, LiNiO2, and LiMn2O4, and LiNixMnyCo1-x-yO2 (NCM), through a green process with high efficiency of about 100% and low/no acid corrosion.
During the research period, 4 peer-reviewed English papers were published in top journals such as ACS Sustainable Chemistry and Engineering, a patent was submitted, and six oral presentations and one poster presentation were delivered, including two invited presentations, at international and domestic conferences.

研究分野：化学工学

キーワード：Recycling　Lithium-ion batteries　Hydrothermal leaching　Metal recovery　Acid corrosion　Glycine　Citric acid　Mixed organic acid

様　式　Ｃ－１９、Ｆ－１９－１（共通）

１．研究開始当初の背景

Recovering valuable metal components (e.g., Li, Co, Ni, and Mn) from spent lithium-ion battery (LIB) cathode materials, such as $LiCoO_2$ (LCO), $LiNiO_2$ (LNO), $LiMn_2O_4$ (LMO), $LiFePO_4$ (LFPO), $LiCo_xNi_yMn_zO_2$ (NCM), and their mixtures, is beneficial to conserve natural resources, reduce environmental pollution, keep resource stability and security, and has economic benefits.

Hydrometallurgy is the most common and industrially adopted method of metal recovery and consists of two steps: acid leaching and metal separation. The traditional acid leaching process is performed in non-pressurized hot water using various acids as the leachant in the presence of reductants (e.g., H_2O_2, $NaHSO_3$, or $Na_2S_2O_3$). In the traditional leaching process, high-concentration acids and reductants are largely consumed, and long reaction time is required for complete leaching, which causes environmental pollution and acid corrosion, greatly increases the cost, and makes it difficult to achieve continuous leaching.

To resolve these problems, a method of 'hydrothermal leaching' regarding pressurized hot water as the medium and using citric acid as the leachant was proposed. Compared to the traditional leaching method, hydrothermal leaching shows many advantages, such as the use of low-concentration acid, no consumption of reductant, controlled reaction rate, and continuous leaching. However, the acid corrosion is still an obstacle that cannot be resolved, because no matter in any leaching process, the protons provided by the acids are regarded to be indispensable for leaching metal ions, which are also the source of acid corrosion.

２．研究の目的

In this study, the researcher aims to explore suitable organic acids for the hydrothermal leaching of spent LIB cathode materials, which can achieve high leaching efficiency and resolve the problem of acid corrosion.

３．研究の方法

(1) Initial screening of possible organic acids (referred to as 'acid X') to achieve high leaching efficiency with low or no acid corrosion by literature investigation.
(2) Execution and parameter optimization of hydrothermal leaching of LIB cathode materials with acid X.
(3) Realization of continuous hydrothermal leaching of LIB cathode materials to confirm the leaching efficiency and evaluate the acid corrosion.
(4) Kinetic study of hydrothermal leaching of LIB cathode materials with acid X.
(5) Separating metal components from metal ion solution obtained by hydrothermal leaching of spent LIBs with acid X.
(6) Evaluation of the whole metal recovery process including hydrothermal leaching and separation processes.

４．研究成果

(1) To achieve high leaching efficiency and avoid acid corrosion during hydrothermal leaching of spent LIB cathode materials, a screening of new acid leachant was executed. Based on a literature investigation and initial experiments, a kind of amino acid, glycine, was chosen tentatively.

(2) With glycine, hydrothermal leaching of LIB cathode materials including commercial LCO, LNO, and LMO, and spent NCM cathode material, was performed at 90-200°C for 5-90 min. The leaching efficiencies of all metals with glycine were lower than those using citric acid under the same conditions, especially for Mn. The aqueous solution during the hydrothermal leaching with glycine exhibited a pH value of 5.8-9.0, close to neutral. The above results indicated that the use of glycine can decrease acid corrosion, although its leaching performance is lower than citric acid.

To combine the advantages of citric acid on leaching performance and glycine on low acid corrosion, a citric acid/glycine mixture was proposed and applied to be the acid leachant for the hydrothermal leaching of spent NCM cathode material at 200°C for 5 min. After a parameter optimization, the best leaching performance was found at the ratio of citric acid/glycine of 10%/90%; the leaching efficiency of each metal achieved >90%, and the pH value during the leaching process changed from 3.6 to 7.0. This was the first time to achieve the acid leaching of spent LIB cathode materials through a green process with high efficiency of about 100% and low/no acid corrosion. Until here, the mixture of citric acid and glycine with a specifical ratio was regarded as 'acid X' in this research.

(3) Continuous hydrothermal leaching of spent NCM cathode materials was successfully achieved by employing a flow system and using acid X as the leaching agent. After feeding the slurry of raw materials for 50 mins, the leaching efficiencies of Li, Co, Ni, and Mn achieved >90% and the pH value of the obtained leachate was kept at around 6.5. That was the first time to realize the continuous acid leaching of spent NCM cathode materials through a green process with high efficiency and low/no acid corrosion.

(4) A kinetic study for the hydrothermal leaching of spent NCM cathode materials with acid X was conducted using a shrinking unreacted core model. Diffusion within the product layer was found to be the rate-limiting step for leaching Li, Co, Ni, and Mn. According to the determined reaction rates and Arrhenius equations, the activation energies for leaching Li, Co, Ni, and Mn were calculated.

(5) Furthermore, hydrothermal leaching of LCO/LNO cathode materials with citric acid was performed and the metal components in the obtained leachate were separated in order using a series of precipitants. Finally, the recovery rates of Ni, Co, and Li were 97.2, 96.1, and 94.1%, respectively, with the purities of Ni, Co, and Li in the corresponding precipitate being 96.3, 96.2, and 99.9%, respectively.

(6) With the above success, an upgraded hydrometallurgical method, composed of hydrothermal leaching and precipitation separation steps, was officially launched for LIB recycling and is subject to further development.

(7) In addition, the initial experiments about hydrothermal leaching of LFPO cathode materials with different organic acids have performed and some achievements have been obtained.

During the research period, 4 peer-reviewed English papers were published in top journals such as *ACS Sustainable Chemistry and Engineering* and *Advanced Sustainable Systems*, a patent was submitted, three oral presentations were delivered at international conferences, and three oral presentations (Two were invited presentations) and one poster presentation were delivered at domestic conferences. This research effectively eliminated the problem of acid corrosion during the hydrothermal leaching process, significantly improved the current leaching process, and further promoted the practical application of hydrometallurgy recycling method. The results will help conserve natural resources, reduce environmental problems, ensure resource stability and security, and bring economic benefits.

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　4件／うち国際共著　0件／うちオープンアクセス　1件）

１．著者名 Zheng Qingxin、Hirama Seiya、Nakajima Akitoshi、Ogawa Tetsufumi、Nakayasu Yuta、Li Zixian、Watanabe Masaru	４．巻 11
２．論文標題 Excellent Performance of Glycine in Isolating Mn during Hydrothermal Leaching of LiMn2O4 Cathode Materials	５．発行年 2023年
３．雑誌名 ACS Sustainable Chemistry & Engineering	６．最初と最後の頁 13033～13042
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acssuschemeng.3c02854	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Li Zixian、Zheng Qingxin、Nakajima Akitoshi、Zhang Zhengyang、Watanabe Masaru	４．巻 8
２．論文標題 Organic Acid‐Based Hydrothermal Leaching of LiFePO4 Cathode Materials	５．発行年 2023年
３．雑誌名 Advanced Sustainable Systems	６．最初と最後の頁 2300421
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adsu.202300421	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Nakajima Akitoshi、Zheng Qingxin、Ogawa Tetsufumi、Hirama Seiya、Watanabe Masaru	４．巻 10
２．論文標題 Metal Recovery of LiCoO2/LiNiO2 Cathode Materials by Hydrothermal Leaching and Precipitation Separation	５．発行年 2022年
３．雑誌名 ACS Sustainable Chemistry & Engineering	６．最初と最後の頁 12852～12863
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acssuschemeng.2c04259	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Zheng Qingxin、Shibazaki Kensuke、Ogawa Tetsufumi、Watanabe Masaru	４．巻 9
２．論文標題 Single-Step Recovery of Divalent Mn Component from LiMn2O4 Cathode Material at Hydrothermal Conditions as an Mn-Citrate Complex	５．発行年 2021年
３．雑誌名 ACS Sustainable Chemistry & Engineering	６．最初と最後の頁 10970～10976
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acssuschemeng.1c03459	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計7件（うち招待講演　2件／うち国際学会　3件）

1．発表者名
Masaru Watanabe、Qingxin Zheng、Akitoshi Nakajima

2．発表標題
Metal recovery of LiMn2O4-based spent lithium-ion battery cathode material using hydrothermal leaching with organic acids and precipitation separation

3．学会等名
19th European Meeting on Supercritical fluids（国際学会）

4．発表年
2023年

1．発表者名
Zixian Li、Qingxin Zheng、Masaru Watanabe

2．発表標題
Application of hydrothermal leaching process with organic acids on LiFePO4 cathode materials

3．学会等名
化学系学協会東北大会

4．発表年
2023年

1．発表者名
李 子賢、鄭 慶新、渡邉 賢

2．発表標題
Hydrothermal leaching of LiFePO4 using organic acids

3．学会等名
化学工学会第54回秋季大会

4．発表年
2023年

1．発表者名
Qingxin Zheng, Masaru Watanabe

2．発表標題
Development of Hydrothermal Leaching Technology for Recycling of Spent Lithium-ion Batteries

3．学会等名
SCEJ 89th Annual Meeting（招待講演）

4．発表年
2023年

１．発表者名
NAKAJIMA Akitoshi, ZHENG Qingxin, OGAWA Tetsufumi, NAKAYASU Yuta, WATANEBE Masaru

２．発表標題
METAL RECOVERY OF THE LEACHATE OBTAINED FROM COMMERCIAL CATHODE MATERIALS BY HYDROTHERMAL LEACHING

３．学会等名
9th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng2022)（国際学会）

４．発表年
2022年

１．発表者名
ZHENG Qingxin, OGAWA Tetsufumi, NAKAJIMA Akitoshi, WATANABE Masaru

２．発表標題
LOW/NO-CORROSION LEACHING OF SPENT LITHIUM-ION BATTERY CATHODE MATERIALS BY HYDROTHERMAL METHOD USING AMINO ACID ORMIXED ORGANIC ACIDS AS THE LEACHANT

３．学会等名
9th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng2022)（国際学会）

４．発表年
2022年

１．発表者名
Masaru Watanabe, Qingxin Zheng, Kensuke Shibazaki, Tetsufumi Ogawa, Atsushi Kishita, Yuya Hiraga

２．発表標題
Application of Hydrothermal Leaching Technology to Spent LIB Cathode Materials withCitric Acid Using Batch-type Device and Flow System

３．学会等名
化学工学会 第53回秋季大会（招待講演）

４．発表年
2022年

〔図書〕　計0件

〔出願〕　計1件

産業財産権の名称	発明者	権利者
クエン酸マンガンの製造方法	渡邉 賢，鄭 慶新，宮崎 秀喜	国立大学法人東北大学，恵和興業株式会社
産業財産権の種類、番号	出願年	国内・外国の別
特許、特開2022-169401	2021年	国内

〔取得〕　計0件

〔その他〕

―

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関