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Separation and recovery of valuable metals from spent lithium ion batteries: Simultaneous recovery of Li and Co in a single step

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ABSTRACT

Sustainable recovery of metals from spent lithium-ion batteries (LIBs) may be of great significance regarding the conservation of metal resources and alleviation of potential risk towards eco-system. Herein an environmentally benign process was proposed for the recovery of high value-added metals (Co and Li) from typical waste cathode materials ($LiCoO_2$) of spent LIBs using mild tartaric acid as both leaching and precipitating reagent. Leaching results indicate that Co and Li can be effectively separated under experimental conditions of reaction temperature- 80 °C, retention time- 30 min, pulp density- 30 mL/g, reducatant dosage- 3 vol% H_2O_2 and acid concentration- 0.6 mol/L. After leaching, 98% Co and 97% Li can be recovered as precipitate and Li^+ enriched solution, respectively. And the leaching of Co and Li fits well to logarithmic rate model, with apparent activation energy of 34.5 and 29.7 KJ/mol, respectively. In addition, characterization results (i.e. FT-IR, SEM-EDS and TGA-DSC) suggest that Co can be directly recovered as relatively pure cobalt tartrate ($C_4H_4O_6Co$, with a purity of 96.4%) in leaching residues. This whole process can be a sustainable alternative for the simultaneous recovery of Li and Co from waste cathode materials of spent LIBs.

1. Introduction

Since their commercial application in 1990s, lithium-ion batteries (LIBs) have been considered as one of the most promising energy storage device due to their electrochemical superiorities in terms of long service life, high voltage and energy density, wide operating temperature range etc. [1–4]. Meanwhile, LIBs have been witnessing increasing applications in EV/HV vehicles, electronic/electrical and portable equipment (e.g. cellphones, laptops, cameras) [5]. It was estimated that the number of LIBs market will sharply increase from 700 million in 2004 to 10 billion in 2020 [6,7]. However, the service life for a typical LIB is 2–3 years and it is inevitable that a large amount of spent LIBs will be generated with their end-of-life. Besides, noxious substances (e.g. electrolyte, heavy metals) contained in exhausted LIBs may present severe impact on eco-system and human-being [8]. On the other hand, spent LIBs always contain a considerable amount of valuable metals (e.g. Co, Li) and the sustainable recovery of value-added metals from spent LIBs may not only alleviate potentially risk towards environment and human-being, but also alleviate the current severe depletion of critical metals (e.g. Co and Li) in China [9–11]. Therefore, the sustainable recycling of high value-added metals from spent LIBs will be beneficial for the security of critical metal resources and protection of the environment.

Recently, an increasing attention has been paid on the recycling of valuable metals from spent LIBs and the main recycling techniques for the separation and recovery of valuable metals from spent LIBs can be divided into mechanical, pyro-metallurgical and hydro-metallurgical (include bioleaching and electrochemical process) method. Mechanical method is a relatively simple route for metals recovery from spent LIBs with high yields (e.g. recovery efficiencies of 77.15%, 91.25%, 100% and 99.9% for Li, Co, Mn and Ni can be attained via a mechanochemical reduction process with iron powders as reported by Guan et al. [12]). Pyro-metallurgical method is a conventional process involved with high-temperature treatment to recover metals from minerals. Vacuum pyrolysis method was adopted by Sun and Qiu [13] to peel off Al foils from cathode materials and high efficiency of 99% can be obtained under optimized conditions of temperature- 600 °C, vacuum evaporation time- 30 min and residual gas pressure- 1.0 kPa. Hydro-metallurgical method, involved with leaching (including bioleaching) [14–16], solvent extraction [17,18], chemical precipitating [19], electrochemical process [20,21] etc., has been attracting an increasing attention due to its obvious advantages in terms of high recovery

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Table 1
A Brief summary of the different leaching systems for the recovery of metals from spent LIBs.

Ref.	Sample	Leaching reagent	Experimental condition	Yield
[5]	NCM	4 mol/L HCl	80 °C, 1 h, L/S- 20 g/L	97% Li, 98% Mn, 97% Co, 97% Ni
[30]	LCO	2 mol/L H_2SO_4	60 °C, 2 h, S/L- 33 g/L	96% Co, 88% Li
[31]	LCO	1 mol/L HNO_3	75 °C, S/L- 10–20 g/L	95% Co and Li
[32]	LCO	0.7 mol/L H_3PO_4	40 °C, 1 h, L/S- 50 g/L	99% Co, 99% Li
[33]	NCM	2 mol/L FA + 6 vol% H_2O_2	60 °C, 10 min, L/S- 50 g/L	98% Li, 100% Co 100% Ni, 100%Mn
[26]	LCO	1.5 mol/L MA + 2 vol% H_2O_2	40 min, 90 °C, S/L- 20 g/L	90% Co, 100% Li
[34]	LCO	3 mol/L OA	90 min, 80 °C, S/L- 50 g/L	99%Co, 99% Li
[35]	LCO	1.5 mol/L SA	70 °C, 0.67 h, S/L- 15 g/L	96% Co, 100% Li
[36]	NCM	3 mol/L TCA	60 °C, 0.5 h, S/L- 50 g/L	100% Li, 90% Mn, 92% Co, 93% Ni
[37]	LCO	1.25 mol/L CA	90 °C, 0.5 h, S/L- 20 g/L	100% Li, 90% Co
[38]	LCO	1 mol/L IA + 0.02 mol/L AA	80 °C, 360 min	99% Li, 91% Co
[39]	LCO	0.4 mol/L TA + 0.02 mol/L AA	80 °C, 5 h	95% Co, 95% Li

LCO: $LiCoO_2$; NCM: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; FA: formic acid; MA: malic acid; OA: oxalic acid; SA: Succinic acid; TCA: biodegradable trichloroacetic acid; CA: citric acid; TA: tartaric acid; AA: ascorbic acid. IA: Iminodiacetic acid.

efficiency, less hazardous substances, purified products etc. over other recycling methods. For example, electrochemical cathode-reduction method was innovatively adopted for the recovery of Co and Li, with yields about 90% for Co and 94% for Li using 1.25 mol/L of malic acid and a working voltage of 8 V for 180 min at 70 °C. In our previous studies, reductive leaching, selective precipitation and solvent extraction methods were adopted to separate and recover valuable metals from spent LIBs [22,23]. In addition, recycling processes combined with different techniques (e.g. combination of mechanical pretreatment and hydrometallurgical method) are becoming increasingly welcomed for metals recycling from already complicated wastes [24].

Currently, increasing interests were concentrated on the application of different acids for the effective leaching and recovery of valuable metals from spent LIBs. As shown in Table 1, both mineral and organic acids were widely adopted during leaching process and it can be also discovered that organic acids, including oxalic acid [25], DL-malic acid [26], ascorbic acid [27,28] and citric acid [37] illustrate similar leaching ability with mineral acids, which indicates that these environmentally-benign leaching agents can be efficient candidates for the recovery of metals from spent LIBs. According to He et al. [29], for example, valuable metals can be effectively recovered from waste cathode materials of spent LIBs, with leaching efficiencies of 99.31% Mn, 99.07% Li, 98.64% Co and 99.31% Ni. However, almost all of these organic acids are solely used as leaching agents and higher acid concentrations are always required to completely dissolve the waste cathode materials [34,36]. And subsequent separation or recovery processes will be still needed for the effective recycling of different metals from spent LIBs, which may frustrate the whole recycling process due to the tedious recycling processes. Furthermore, it was discovered in our previous studies that it is difficult to extract different metals from organic acidic medium due to the strong chelation of metal ions with organic acid [40]. Therefore, selective recovery of valuable metals from waste cathode materials of spent LIBs in mild organic acidic medium may address above issues involved with high acid consumption and metal separation from leaching solution.

Herein, L-(+)-tartaric acid ($C_4H_6O_6$, called as tartaric acid) was innovatively used as leaching and precipitating reagent for selective separation and recovery of high value-added metal- Co from waste cathode materials of spent LIBs in this study. Optimization of leaching conditions, leaching kinetics and corresponding characterization were conducted to explore leaching behaviors of Co and Li in mild tartaric acidic medium. It is expected that Co and Li can be selectively separated and recovered in a single leaching step under optimized leaching conditions. The whole recovery process may be an alternative to simultaneously recover Co and Li from waste cathode materials of spent LIBs with an environmentally benign, high efficiency and short-cut way, which may also improve the traditional "Leaching + Separation + Recycling" model for metal recycling from spent LIBs.

2. Materials and methods

2.1. Materials and reagents

Spent LIBs (Different types of spent cell phone batteries, 3.7–4.2 V) were collected from a local recycling center and waste cathode materials were obtained after pretreatment including manual dismantling, peeling off Al foils, calcination and ball-milling [40,41]. Chemical reagents of tartaric acid (99.5% $C_4H_6O_6$, A.R.), hydrogen peroxide (30 vol % H_2O_2, A.R.), hydrochloric acid (36% HCl, A.R.), nitric acid (65% HNO_3, A.R.) and sodium sulfate (99% Na_2SO_4, A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. Other chemical reagents used were of analytical purity and all solutions were prepared or diluted with deionized water.

2.2. Pretreatment process

Pretreatment of spent LIBs mainly includes discharging, manual dismantling, ultrasonic cleaning, calcining and grinding [42,43]. Firstly, spent LIBs were immersed in sodium sulfate solution for 24 h and then dried at 60 °C to completely discharge residual electricity [44]. Then, these exhausted batteries were manually disassembled into plastic packages, metallic shells, anodes, cathodes and separators. Cathodes were subsequently cut into small pieces (~10 × 20 mm) and immersed in ultrasonic cleaner under conditions of temperature-70 °C, ultrasonic power- 240 W and retention time- 90 min, and Al foils and waste cathode materials can be effectively separated. Then the waste cathode materials (a mixture of cathode materials and graphite) were then calcined in a muffle furnace (700 °C for 120 min) [45] to remove graphite. Finally, waste cathode materials of $LiCoO_2$ with fine particle size can be obtained after ball-milling for 60 min. Waste $LiCoO_2$ was used as raw materials during the following leaching step. The whole pretreatment procedures and main metal contents in waste $LiCoO_2$ can be found in Fig. S1 and Table 2, respectively.

2.3. Reductive leaching

All leaching experiments were carried out in a 250 mL three-necked

Table 2
Contents of different metals in waste $LiCoO_2$.

Metal element	Li	Co	Ni	Mn	Others
Mass content (wt.%)	6.69	58.11	0.39	0.14	0.12