



A closed-loop process for recycling $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the cathode scraps of lithium-ion batteries: Process optimization and kinetics analysis



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ABSTRACT

A closed-loop process for recycling $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the cathode scraps for lithium-ion batteries (LIBs) is preliminarily established in this research. Biodegradable trichloroacetic acid (TCA) with hydrogen peroxide (H_2O_2) is innovatively developed to dissolve $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the cathode scraps. Operational parameters are optimized to obtain a lower Al dissolution rate, but not at the expense of sacrificing other metals. Under the optimal leaching condition of 3.0 M TCA, 4 vol.% H_2O_2 , a solid to liquid (S/L) ratio of 50 g/L at 60 °C for 30 min, the leaching rates of Ni, Co, Mn and Li are 93.0%, 91.8%, 89.8% and 99.7%, respectively. In this optimum condition, only 7.0% of Al is leached, and this could be further controlled according to the subsequent utilization of the leachate. Avrami equation is introduced to describe the leaching kinetics of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the cathode scraps. The apparent activation energies for leaching of Ni, Co, Mn and Li are determined as 44.51, 44.79, 43.81 and 28.00 kJ/mol, respectively, indicating that the surface chemical reaction is the rate-controlling step during this leaching process.

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1. Introduction

The production and demand of lithium-ion batteries (LIBs) have significantly increased due to the wide applications in communication, consumer electronics, transportation, power grid and portable appliances [1–3]. The annual production of LIBs increased by 800% throughout the world from 2000 to 2010 [2], which would be further stimulated by the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) [2,3]. Large quantities of spent LIBs along with scraps will be generated due to their limited life spans and rapid updating of electronic products. Moreover, the metals, especially the toxic heavy metals, contained in these spent LIBs may cause serious environmental problems, such as soil and underground water contamination, which might affect the health of human beings and animals [4,5]. A substantial number of critical metals, such as Co and Li [6], are also contained in these wastes.

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Therefore, by recycling metals from these wastes, not only the risks to environmental and public health could be avoided, but also the shortage of some metals used as the raw materials during the production of LIBs could be fulfilled.

Previous reviews [2,3,7] indicated that hydrometallurgical processes were preferred in metal recycling due to the complete recovery of metals with higher purity, lower energy consumption [8] and lower gas emission [9]. In these processes, LiCoO_2 -based cathode materials are mainly focused, but studies on other cathode chemistries such as LiMn_2O_4 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ were scarce. Acidic leaching plays an important role in these processes, thus a substantial number of the reported leaching processes [10–14] mostly concentrate on extracting as many metal values as possible or even complete recovery from spent LIBs by optimizing the leaching parameters. However, these processes seldom dealt with the treatment and utilization of the obtained leachate. In order to separate the cathode materials from other materials (Fe, Al, Cu and plastics), various pretreatment procedures, including mechanical methods [10–18], thermal methods [10–13,18,19], selective precipitation [20], N-methylpyrrolidone (NMP) dissolution [10–13,18], vacuum pyrolysis [14] and

ultrasonic processes [12,13,17] were employed in the developed recycling processes. Since the single pretreatment method can hardly separate the cathode materials completely, the combination of two or even more methods is typically used in most cases. Nevertheless, this will make the recycling process complicated and increase the processing cost accordingly [21]. Additionally, an obvious tendency is emerging from the transition of inorganic acids (i.e., hydrochloric acid (HCl), sulfuric acid (H₂SO₄) and nitric acid (HNO₃)) to some degradable organic acids owing to the environmental considerations [2,3].

In our previous research [22], we developed a compact and environment-friendly recycling process, in which the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode scraps were directly immersed in trifluoroacetic acid (TFA) solution. When we tried to synthesize precursors for LIBs from the leachate by co-precipitation method, it was necessary to remove Al³⁺ in the leachate, but part of Ni²⁺, Co²⁺ and Mn²⁺ would be lost during this process [23]. Taking account of the requirement on the Al concentration during utilizing the leachate, developing a compact, economic and flexible leaching process is in high demand. Leaching kinetics is also an important factor in industrial application as it is closely related to the treatment capacity and cost. However, only a few studies investigated the leaching kinetics of spent LIBs [19,24–26]. In these studies, various kinetic models were employed. To the best of our knowledge, the determination of the rate-controlling step, applicability and verification of these models during these leaching processes are not discussed sufficiently.

As there are a substantial number of researches [27–32] emphasizing on the separation processes for the recovery of different metals from spent LIBs, we intend to develop a relatively simple and flexible process to recycling LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ from the cathode scraps for LIBs. By selective leaching in the biodegradable trichloroacetic acid (TCA), most of the Al was separated from the leachate, and the dissolution of Al could be controlled further according to the usage of the leachate in this work. The influences of different parameters including leachant concentration, solid to liquid (S/L) ratio, reductant dosage, leaching temperature and time were investigated systematically to determine the optimal leaching condition. The leaching kinetics was also investigated, and the corresponding apparent activation energies for metals dissolution were determined.

2. Experimental

2.1. Materials and analysis

The cathode scraps were collected from a recycling company of spent power LIBs in China. They were cut into small pieces with the size of approximate 10 × 10 mm, and dried at 60 °C for 24 h. The dried sample was completely dissolved in the aqua regia solution (HNO₃: HCl = 1:3, v/v) to determine the contents of metals by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 6300 Radial, Thermo Scientific). It was also submitted to a scanning electron microscope (SEM, Quanta 250) associated with an energy dispersive spectrometer (EDS, EDAX Genesis-SiLi) to observe the morphology and confirm the elemental composition of the sample. All chemical reagents used in this work were analytical grade and all solutions were prepared with ultrapure water (Milli-Q, Millipore).

2.2. Experimental procedure

The leaching experiments were performed in a series of 100 mL conical flasks placed in a constant-temperature shaker (THZ-82, Changzhou Guohua). The accuracy of temperature control was

±0.5 °C. All the experiments were conducted in batch mode. For each run, 50 mL acidic solution with 1.0–7.0 M leachants (i.e., H₂SO₄, acetic acid (HAc), TFA and TCA) and 0–12 vol.% reductants (i.e., 30 wt.% hydrogen peroxide (H₂O₂), 1.5 M sodium sulfite (Na₂SO₃) and 2.0 M sodium thiosulfate (Na₂S₂O₃)) was added into the flask and heated to the pre-determined temperature in the range of 25–80 °C under constant shaking speed. Then a certain amount of the cathode scraps were added into the flask under continuous shaking. After a certain time, the flask was taken out and filtered immediately under vacuum. The residues were washed several times with ultrapure water until the pH of the filtrate reached 7.0 and dried at 60 °C for 24 h. Then they were subjected to SEM analysis. The concentrations of metals in the leachate were determined by ICP-OES. The leaching rate of each metal can be calculated by the ratio of mass dissolved into the solution and the total mass in the cathode scraps.

3. Results and discussion

3.1. Analysis of the cathode scraps

Table 1 presents the ICP result of the cathode scraps. The main metals identified in the cathode scraps are nickel, cobalt, manganese, lithium and aluminum. The impurities of copper and iron were both less than 0.02%. The mole ratio of Li, Ni, Co and Mn is determined as approximate 3:1:1:1. Thus, we can infer that the active material in the cathode scraps can be LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

The SEM and EDS patterns of the cathode scraps are provided in Fig. 1. We observe that the fine particles of cathode materials constitute these agglomerates with different sizes. Lithium cannot be detected by the EDS probe analysis [33], but the other metals in the cathode scraps are in accordance with the ICP result (Table 1). Carbon and fluorine are also determined due to the addition of conductive additives and organic binders such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) during the cathode fabrication process [7,22,34]. From the XRD pattern of the cathode scraps [22], the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ phase is undoubtedly confirmed.

3.2. Effect of leaching parameters on metal recovery

3.2.1. Effect of various leachants

Three types of organic acids (HAc, TFA and TCA) and a commonly used inorganic acid (H₂SO₄) were employed as the leachants. The leaching rates of different metals using these acids are presented in Fig. 2.

As shown in Fig. 2a, the leaching rates of Ni, Co, Mn and Li increase from 11.5%, 29.8%, 38.5% and 45.7% to 40.9%, 39.5%, 39.3%, and 50.5%, respectively, when the concentration of HAc increases from 1.0 M to 2.0 M. The leaching rates begin to decrease when the concentration exceeds 2.0 M. The same tendency can be observed for Ni, Co and Mn leaching as the TCA concentration higher than 3.0 M (Fig. 2c). It could be attributed to the increase of H⁺ ions with the increase of acid concentration, the rate of chemical reaction is accelerated initially and the dissociated H⁺ ions and the transfer rate of ions might begin to decrease when the acid concentration increases to a certain value [10,35]. However, the leaching rates of Ni, Co and Mn approximately increase with the increase of the concentration of TFA and H₂SO₄, respectively

Table 1
Main elemental composition of the cathode scraps.

Metal	Ni	Co	Mn	Li	Al	Cu	Fe
Composition (wt.%)	18.32	18.65	17.57	6.15	7.86	0.01	0.01

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