



Acid-Free Leaching Nickel, Cobalt, Manganese, and Lithium from Spent Lithium-Ion Batteries Using Fe(II) and Fe(III) Solution

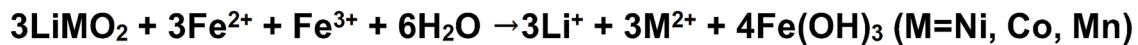
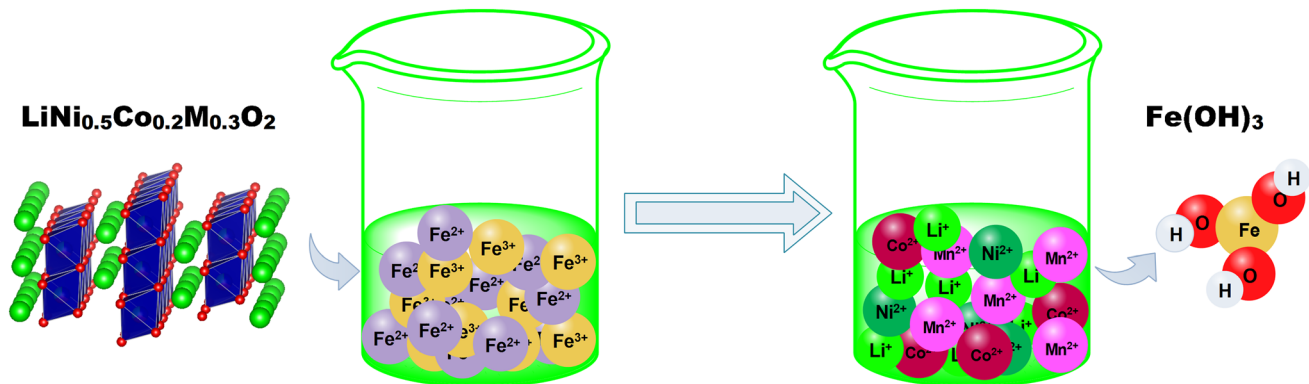
Yang Dai^{1,2} · Ning Wang¹ · Zhaodong Xu² · Hannian Gu^{1,4} · Mengjun Chen³ · Dong Hua²

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Abstract

End-of-life lithium-ion batteries (LIBs) have received unprecedented consideration because of their potential environmental pollution and the value of decisive metal supplies. The dosage of over-stoichiometric amounts of acids, including all kinds of organic or inorganic acids, may result in corrosion of the equipment or production of toxic and harmful gases. Herein, an unconventional acid-free method—salt leaching to extract Ni, Co, Mn, and Li from a spent $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material using Fe(II) (reductant reagent) and Fe(III) (precipitation) is proposed. Under the condition with 0.2 mol/L $\text{Fe}_2(\text{SO}_4)_3$, 0.36 mol/L FeSO_4 , 40 min, and 90 °C, the leaching efficiencies of Ni, Co, Mn, and Li are all higher than 96%. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) characterizations are applied for revealing the phase changes in leaching process. This new type of acid-free salt-leaching method provides a new idea for the recycling of spent LIBs containing metals such as nickel, cobalt, and manganese.

Graphical Abstract



Keywords Spent lithium-ion batteries · Acid-free · Recyclable · $\text{Fe}_2(\text{SO}_4)_3$ · FeSO_4

Introduction

With the increase of greenhouse gas emissions and the over-exploitation of non-renewable resources, governments around the world are vigorously advocating the use of electric vehicles [1]. This has led to a large increase in the production and use of electric vehicles in recent years [2].

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✉ Hannian Gu
guhannian@vip.gyig.ac.cn

Extended author information available on the last page of the article

As more and more people choose to use electric vehicles, a mass of spent lithium-ion batteries (LIBs) in them are being rapidly produced [3]. These end-of-life electric vehicles generate a lot of waste disposal problems, the most prominent of which is the disposal of spent LIBs [4, 5]. These batteries are rich in metal resources, e.g., nickel, cobalt, manganese, and lithium in cathode materials, and contain toxic organic substances in electrolyte [6, 7], such as PVDF [poly(1, 1-difluoroethylene)], LiPF₆, and DMC (dimethyl carbonate) [8, 9]. If they are not handled properly, a lot of valuable resources cannot be recycled, and the environment may be polluted at the same time [10–12]. Therefore, both research institutes and manufacturing companies are working on the recycling of spent LIBs [13] especially that of cathode materials containing nickel, cobalt, and manganese [14].

At present, the recycling methods of spent LIBs for ternary (Ni–Co–Mn, NCM) cathode materials can be divided into pyrometallurgical recovery [15, 16], physical material separation [17, 18], hydrometallurgical metal reclamation [19], direct recycling [20], and biological metal reclamation [21–23]. Due to the long time, most of the bio-recovery methods are not used into large-scale industrial application. Hydrometallurgy and combinations of hydrometallurgy and other methods, such as pyrometallurgy, mechanical activation and flotation, are the most studied methods for recycling spent LIBs containing Ni, Co, Mn, etc.

Additionally, the leaching agents of hydrometallurgy can be grouped into three types: (1) inorganic acids (H₂SO₄ [24], H₃PO₄ [25], HCl [26, 27], etc.), (2) organic acids (acetic acid [28], oxalic acid [29], tartaric acid [30], citric acid [31, 32], benzene sulfonic acid [33], formic acid [34], etc.), and (3) ammoniacal leaching substances [35]. Using inorganic acids as leaching agents is efficient and inexpensive, but they have a strong corrosivity and require high-quality and corrosion-resistant equipment, which also increases the costs of production to a certain extent. Compared with inorganic acids, organic acids have the advantage of being easily biodegradable and not producing toxic gases during the leaching process. However, the disadvantages of organic acid are that the regeneration and recycling are difficult to achieve. Ammoniacal leaching reagents are suitable for spent LIBs containing cobalt but not for Mn. This is because manganese in a solution of ammonium sulfate or ammonium sulfite can easily form double salts such as (NH₄)₂Mn(SO₃)₂·H₂O and (NH₄)₂Mn(SO₄)₂·6H₂O [36–38], which can cause the leaching efficiency to be low. Therefore, it is particularly important to find a low-cost leaching reagent that is nontoxic and easy recycle, and can simultaneously leach nickel, cobalt, and manganese from spent NCM system LIBs.

Most metals in the NCM cathode materials, such as Ni, Co, and Mn, are in high valence states. In the recycling process, the introduction of a reducing agent is essential. H₂O₂ [39–42], C [43–45], glucose [46], citric acid [47], sulfites

[36, 38], Fe²⁺ [23, 48], etc. are common reductants used for the leaching process.

In this paper, we propose a salt leaching method using a mixture of ferric sulfate [Fe₂(SO₄)₃] and ferrous sulfate (FeSO₄) as a leaching reagent to extract and recover valuable metals from spent NCM Li-ion batteries. During the salt leaching process, the leaching efficiency of the valuable metals, the phase composition, and structure changes of the materials were systematically investigated. Ferric sulfate was innovatively selected as the leachate because of its abundance, low price, and nontoxicity [49, 50]. Moreover, the Fe³⁺ in ferric sulfate and the product of Fe²⁺ oxidized in ferrous sulfate can combine with OH[−] to generate Fe(OH)₃ without generating toxic gas. The purpose of this study was (1) to explore the factors affecting the leaching of the metals, (2) to determine the changes in the crystal structure and material composition of the spent LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode powders, and (3) to evaluate the economic and environmental benefits of the salt leachant combination of ferrous and ferric sulfate for recycling the metals in end-of-life LIBs.

Materials and Experimental Methods

Materials

The spent LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode material used in this study was obtained from Guizhou Red Star Electronic Material Co., Ltd., Guizhou, China. The major elemental contents (wt%) of the cathode powders were 5.83% Li, 26.73% Ni, 10.69% Co, and 15.17% Mn. In the leaching process, the effects of various parameters such as Fe₂(SO₄)₃ dosage, FeSO₄ dosage, temperature, and time were investigated. All chemicals used in this research were analytical grade and purchased from Chengdu Jinshan Chemical Reagent Co., Ltd., China, and all solutions were prepared with ultrapure water.

Experimental Procedures

The leaching experiment was carried out in a 150 mL conical flask placed in a constant-temperature water bath. Before leaching, 50 mL ultrapure water was introduced to the flask, and then magnetic stirring started. When a given temperature was arrived, 2 g (solid–liquid ratio 40 g/L) spent LIB cathode powder and amounts of Fe₂(SO₄)₃ and FeSO₄·7H₂O were added to the flask under continuous stirring. After reacting for a preset time, the suspensions were solid–liquid separated. The leached residue was washed with ultrapure water for several times and then dried in a 105 °C vacuum drying oven. The above leaching experiments were carried

out triplicate in order to effectively reduce the experimental error.

Analysis Methods

In this paper, the leaching efficiency X_i of the related elements is studied by Eq. (1):

$$X_i = \frac{C_i V}{C_i V + \omega_i m}, \tag{1}$$

where C_i (g/L) is the concentration of element i , V (L) is the volume of the leachate, ω_i (%) is the weight content of element i in leaching residue, and m (g) is the mass of the residue.

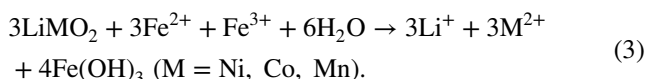
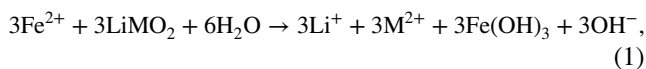
The contents of cathode powders and leaching residues were completely dissolved in Aqua Regia solution ($\text{HNO}_3:\text{HCl}=1:3$, v/v) for detection by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher iCAP 7400). X-ray diffraction (XRD, PANalytical, Empyrean), X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi), Fourier transform infrared spectroscopy (FTIR, Bruker, VERTEX 70), and scanning electron microscopy (SEM, Scios, FEI) were used to characterize the solid samples.

Results and Discussion

Effect of Leaching Reagent Compositions

$\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 are cheap, common, nontoxic, and nonpolluting chemical materials. Ferric iron is a Lewis acid, so ferric sulfate solution becomes acidic. Divalent iron is reducible, and FeSO_4 can be used as a reductant. Due to the influence of charge–discharge in the early stage, Ni, Co, and Mn in spent LIBs are oxidized to high valence, in Fig. 1. Therefore, some reducing agents are needed to recover the

nickel, cobalt, and manganese from spent LIBs. The electrode reactions of nickel, cobalt, manganese, and iron are listed in Table 1, which shows that divalent iron can reduce tetravalent manganese, trivalent manganese, trivalent nickel, and trivalent cobalt. Therefore, Fe^{3+} and Fe^{2+} can be used for the recovery of nickel, cobalt, manganese, and lithium from spent LIBs. The reaction equations about NCM and Fe(II)/Fe(III) are as the following Reactions (1)–(3):



It can be seen from the Reaction (1) that H_2O provides H^+ , which enables the reaction to proceed. If Fe(II) and Fe(III) are not added, the liquid phase is alkaline with only H_2O , implying that at least a part of the H_2O has undergone obvious dissociation. In the case of the enhanced alkalinity, the reaction will no longer occur. Because of the presence of Fe(III), the OH^- generated in the process of NCM oxidation of Fe(II) is consumed by it in Reaction (2), so that the concentration of ferric iron in the solution does not increase,

Table 1 Standard electrode potentials of Fe, Mn, Co, and Ni in acid conditions 298.15 K [51]

	Electrode reaction	E^θ (V)
$\text{Fe}^{3+}/\text{Fe}^{2+}$	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.771
$\text{Mn}^{3+}/\text{Mn}^{2+}$	$\text{Mn}^{3+} + \text{e}^- = \text{Mn}^{2+}$	1.488
$\text{MnO}_2/\text{Mn}^{2+}$	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O} + \text{Mn}^{2+}$	1.230
$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{Co}^{3+} + \text{e}^- = \text{Co}^{2+}$	1.800
$\text{Ni}(\text{OH})_3/\text{Ni}^{2+}$	$\text{Ni}(\text{OH})_3 + 3\text{H}^+ + \text{e}^- = 3\text{H}_2\text{O} + \text{Ni}^{2+}$	2.080

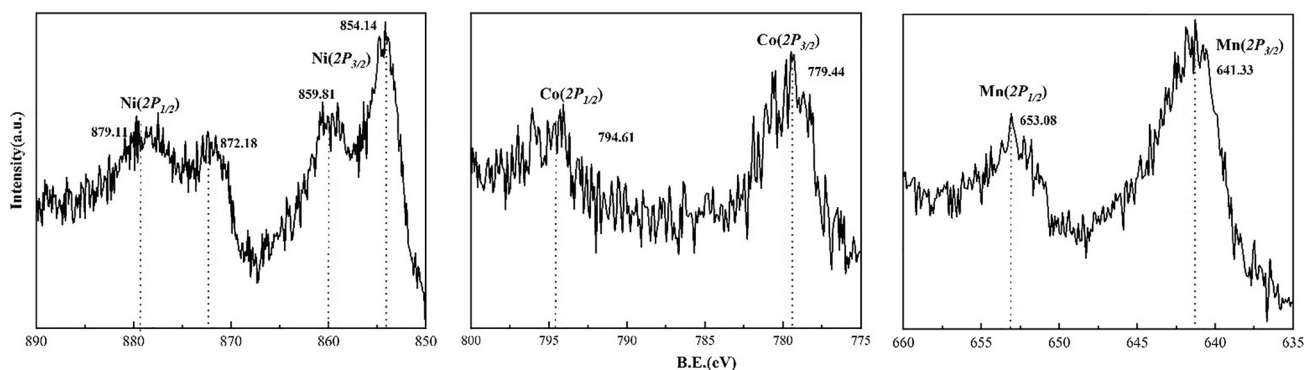


Fig. 1 XPS analysis of Ni, Co, and Mn in spent cathode materials

and the acidity of the system can be maintained, facilitating the Reaction (1). Therefore, the role of Fe(II) and Fe(III) is reductant and precipitant, respectively.

The effect of the amount of ferric sulfate and ferrous sulfate used was investigated. First, the effects of the ferric sulfate dosage on the leaching efficiencies of Ni, Co, Mn, and Li are shown in Fig. 2a. A comparison of the leaching efficiencies of each metal in a certain amount of ferrous sulfate with different concentrations of ferric sulfate shows that the leaching efficiencies of all related metals had clear trends of change. The leaching efficiencies of Ni, Co, and Mn increased to 96.98%, 96.83%, and 96.01%, respectively, upon the addition of ferric sulfate. The leaching efficiency of Li increased further to 99.12% with 0.2 mol/L ferric sulfate. With only Fe(II), the leaching efficiencies of nickel, cobalt, and manganese reached 35.14%, 36.12%, 42.06%, and 48.21%, respectively. The experimental results can be explained by the following reasons: the spent cathode materials contained small amounts of Ni^{2+} , Co^{2+} , and Mn^{2+} ; the Reaction (1) could happen in the beginning, and Fe^{2+} was easily oxidized in hot water. The optimum usage of ferric sulfate occurred for 0.2 mol/L $\text{Fe}_2(\text{SO}_4)_3$.

Second, the ferrous sulfate concentration was changed with the amount of ferric sulfate fixed. There were large amounts of high-valent metals in the spent ternary cathode powder after the repeated charge–discharge process. Reductants such as hydrogen peroxide [52, 53], sulfite [37], sucrose [54], and citric acid [47] were used in previous studies. Fe^{2+} could reduce the oxidation numbers of Ni, Co, and Mn, resulting in an increased dissolution rate. The leaching efficiency of each metal depending on the ferrous sulfate dosage is illustrated in Fig. 2b. Due to the acidic of Fe(III) stronger than Fe(II), the leaching efficiencies of nickel, cobalt, and manganese with only Fe(III) are higher than in only existent of Fe(II). It is obvious that all

the metals have similar trends. For example, the leaching efficiency of nickel increases from 29.12% without ferrous sulfate to 96.98% with a 0.36 mol/L ferrous sulfate. Co and Mn exhibit parallel leaching behavior. In addition, the Li leaching efficiency varies from 45.40 to 99.19%. Therefore, the necessary concentration of FeSO_4 is 0.36 mol/L that of the spent cathode powder.

Effects of Leaching Time and Temperature

Reaction temperatures and time are important factors and have significant effects on the leaching process. Figure 3 shows the time and temperature dependencies of the leaching efficiencies of the metals. In essence, the leaching process of most metal elements is an endothermic reaction. Thus, a high reaction temperature is conducive to a favorable thermodynamic environment [55]. Increasing reaction time is obviously beneficial for the leaching reactions. Metals of Ni, Co, Mn, and Li show relatively quick leaching kinetics, and their leaching efficiencies reach a maximum after 40 min. In addition, their leaching efficiencies increase with temperatures increasing from 40 to 90 °C. For leaching conditions of 40 °C for 40 min, the leaching efficiencies of Ni, Co, Mn, and Li are 63.33, 66.02, 70.85, and 69.17%, respectively. All the metals have leaching efficiencies greater than 96% at 90 °C. It is obvious that the leaching efficiencies of Ni, Co, and Mn obtained with Fe(II)/Fe(II) solution are higher than those of the other leaching methods (ammonia leaching and bioleaching) listed in Table 2. This can be ascribed to the faster hydrolysis rate of trivalent iron ions at high temperatures, leading to ferric sulfate solution with a lower pH. To improve the leaching efficiency of the metals, 90 °C and 40 min are selected as the optimal reaction temperature and time.

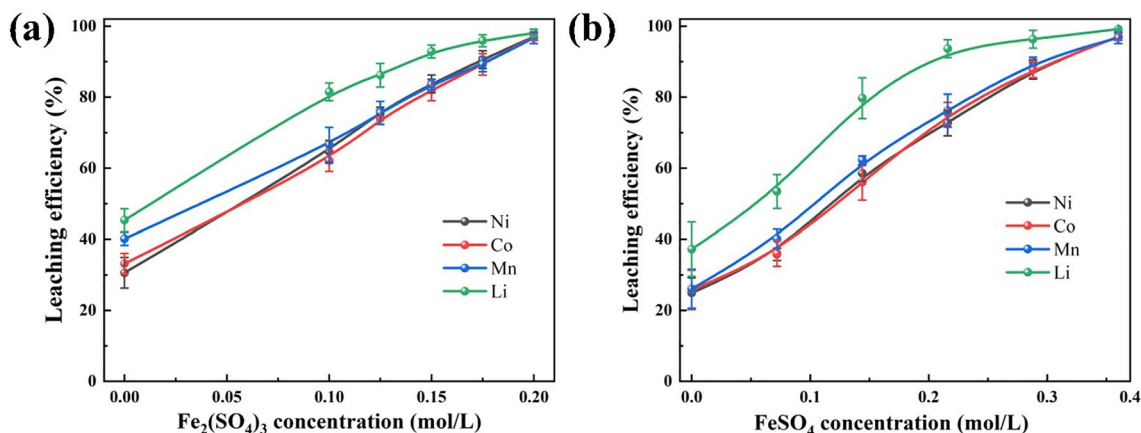


Fig. 2 Effects of $\text{Fe}_2(\text{SO}_4)_3$ (a) and FeSO_4 (b) dosages on the leaching efficiencies of Ni, Co, Mn, and Li with 0.36 mol/L FeSO_4 for a and 0.20 mol/L $\text{Fe}_2(\text{SO}_4)_3$ for b, 90 °C, 60 min

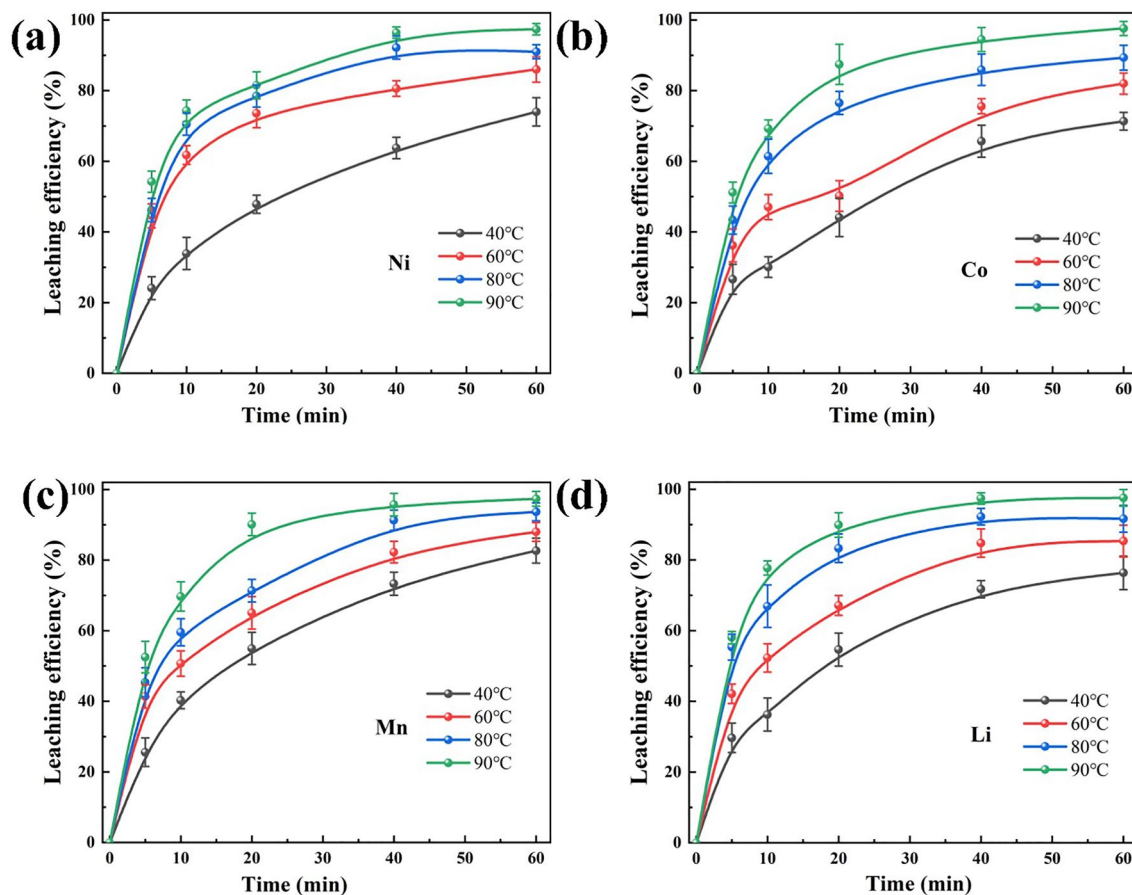


Fig. 3 Effects of leaching time (0–40 min) and leaching temperature (40–90 °C) on the leaching efficiencies of **a** Ni, **b** Co, **c** Mn, and **d** Li with 0.36 mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.20 mol/L $\text{Fe}_2(\text{SO}_4)_3$

Table 2 The leaching efficiencies of Li, Ni, Co, and Mn in different systems

Materials	Leaching reagents	Leaching efficiencies	References
1 LiCoO ₂ , LiO ₂ , LiNi _{0.5} Mn _{1.1} Ti _{0.4} O ₄	<i>Aspergillus niger</i> , sucrose	100% Li, 45% Ni, 38% Co, 74% Mn	Bahaloo-Horeh et al. [22]
2 LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	NH ₃ ·H ₂ O, Na ₂ SO ₃ (NH ₄) ₂ SO ₄	95% Li, 90% Ni, 81% Co, 4% Mn	Zheng et al. [37]
3 LiCoO ₂ , LiMn ₂ O ₄ , Li _{0.9} Ni _{0.5} Co _{0.5} O _{2-x}	(NH ₄) ₂ SO ₃ , (NH ₄) ₂ SO ₄	98% Li, 98% Ni, 81% Co, 92% Mn	Chen et al. [38]
4 LiCoO ₂ , LiNiO ₂ , Li ₄ Mn ₅ O ₁₂ , Li _{0.9} MnO ₂	Fe(II), thermophilic bacteria	84% Li, 99% Ni, 99% Co	Ghassa et al. [56]
5 LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	(NH ₄) ₂ SO ₄ roasting and water leaching	Over 98.5% of Li, Ni, Co, and Mn	Tang et al. [57]
6 LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂	Fe(II)/Fe(III)	99% Li, 97% Ni, 97% Co, 96% Mn	This paper

Characterization of Cathode Powders and Leaching Residues

The XRD patterns of the spent LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode powders and the leaching residues obtained under the optimum conditions are exhibited in Fig. 4a. The sample of cathode material could be indexed on the basis of a hexagonal

a-NaFeO₂ structure with the major diffraction peaks for the (003), (101), (006), (102), (104), (015), (107), (108), (110), and (113) planes, which are the same results as those of previous studies [58–60]. With the addition of ferrous sulfate and ferric sulfate, all the diffraction peaks disappear, and the leaching residues become amorphous materials. This makes it clear that the spent LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ powder

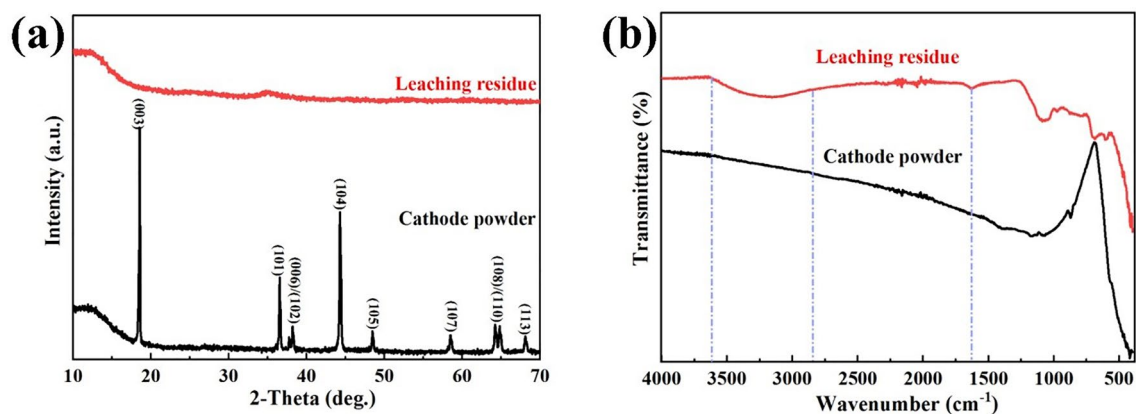


Fig. 4 Characterization of cathode powders and residues in **a** XRD and **b** FTIR

is completely dissolved by $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 and forms ferric hydroxide precipitates.

Figure 4b shows the FTIR analysis of the cathode powders and the leaching residues. The comparison in the figure shows that the two materials do not have the same absorption peaks. There are more obvious weak peaks at $3600\text{--}2970$ and $1700\text{--}1500\text{ cm}^{-1}$ in the leaching residues, showing that when ferric and ferrous sulfates are added, a large amount of OH^- can be produced [47]. The cathode materials do not have these absorption peaks, indicating that the composition of the spent cathode materials has changed.

Furthermore, to clearly observe the micromorphology of solid samples before and after the leaching reaction, SEM analyses are displayed in Fig. 5. The spherical microscopic morphology of the cathode material has undergone obvious changes, and the residues do not reveal a specific shape. EDS

analysis of several points in the residues find that the main components are Fe and O and do not contain Ni, Co, Mn, and Li (Fig. 5d). This result indicates that the ferric sulfate and ferrous sulfate have fully reacted with the cathode materials, and the value metals have dissolved into liquid phase.

Conclusions

In this paper, a novel hydrometallurgical process—salt leaching—was proposed for recovering the metals in spent $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode materials of spent LIBs using mixed iron salts composed of $\text{Fe}_2(\text{SO}_4)_3$ (precipitant) and FeSO_4 (reducing agent). Under the optimal extraction conditions: $0.2\text{ mol/L Fe}_2(\text{SO}_4)_3$, $0.36\text{ mol/L FeSO}_4 \cdot 7\text{H}_2\text{O}$, a reaction time of 40 min, a reaction temperature of $90\text{ }^\circ\text{C}$,

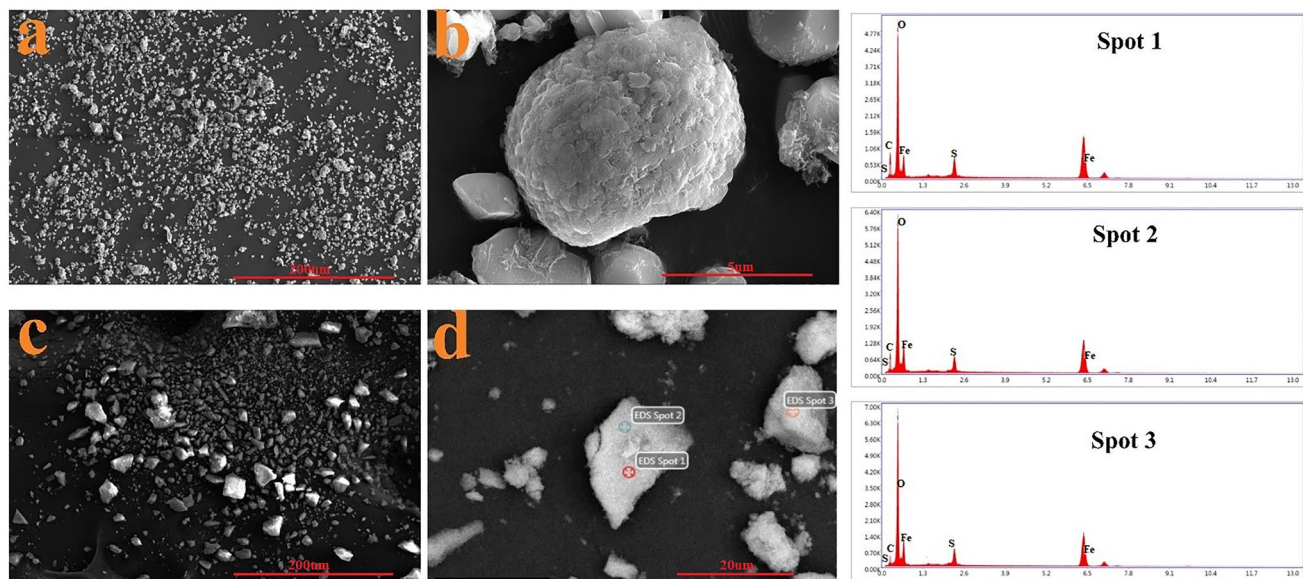


Fig. 5 SEM analysis of cathode powders (**a** and **b**) and residues (**c** and **d**) using mixed iron salts for leaching

leaching efficiencies for Ni, Co, Mn, and Li of 96.98, 96.83, 96.01, and 99.91%, respectively, were achieved. The introduced ferric and ferrous iron were transformed into iron hydroxides which can be separated with the leaching solution including valuable metals. The method of salt leaching is considered to be environmentally friendly and provides a new idea for the recycling of ternary cathode material of spent LIBs.

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Declarations

Conflict of interest There are no conflicts to declare.

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Authors and Affiliations

Yang Dai^{1,2} · Ning Wang¹ · Zhaodong Xu² · Hannian Gu^{1,4}  · Mengjun Chen³ · Dong Hua²

¹ Key Laboratory of High-Temperature and High-Pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, Guizhou, China

² Qingdao Red Star Chemical Refco Co., Ltd, Qingdao 266011, Shandong, China

³ Key Laboratory of Solid Waste Treatment and Resource Recycle, Southwest University of Science and Technology, Ministry of Education, Mianyang 621010, China

⁴ University of Chinese Academy of Sciences, Beijing 100049, China