

Creative Method for Efficiently Leaching Ni, Co, Mn, and Li in a Mixture of  $\text{LiFePO}_4$  and  $\text{LiMO}_2$  Using Only  $\text{Fe(III)}$ 

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**ABSTRACT:** Recycling end-of-life lithium-ion batteries has attracted widespread attention due to their potential environmental hazards and the importance of key metal supplies. However, the previously reported research methods are intended only for spent Ni–Co–Mn (NCM)-based lithium-ion batteries or spent lithium iron phosphate batteries. In this letter, a new method is proposed for recovering the mixed cathode materials of  $\text{LiFePO}_4$  and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  from spent lithium-ion batteries by sole  $\text{Fe}_2(\text{SO}_4)_3$ . According to our design, ferric iron itself acts as a Lewis acid and facilitates  $\text{LiFePO}_4$  to release the reducing agent of ferrous iron to reduce  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ . Additionally, the environmentally friendly and efficient leaching process has been achieved for Ni, Co, Mn, and Li by reasonably adjusting the ratio of trivalent iron,  $\text{LiFePO}_4$ , and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ . This method of processing mixed spent lithium-ion battery cathode materials significantly reduces the amount of reducing agent or oxidant usage. Also, it is effective at reducing time, energy consumption, and water consumption. It provides a new solution to recycling used lithium-ion batteries.

**KEYWORDS:** Mixed leaching, Iron salt,  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ,  $\text{LiFePO}_4$ , Ecofriendly



## INTRODUCTION

Over the years, driven by the imperatives to improve the environment of the Earth and save energy, the production and application of electric vehicles have increased significantly.<sup>1</sup> The batteries used in electric vehicles are generally nickel–cobalt–manganese ternary lithium batteries ( $\text{LiMO}_2$ ,  $M = \text{Ni, Co, Mn, NCM}$ ) and lithium iron phosphate batteries ( $\text{LiFePO}_4$ , LFP). With the increased use of electric vehicles, a large amount of end-of-life lithium-ion batteries (LIBs) is being rapidly produced.<sup>1–4</sup> These batteries contain not only a lot of valuable metals but also various toxic organic substances, such as polyvinylidene fluoride or polyvinylidene difluoride (PVD), lithium hexafluorophosphate ( $\text{LiPF}_6$ ), and dimethyl carbonate (DMC).<sup>5,6</sup> Thus, if they cannot be handled well, the resources contained will be wasted, and the environment will cause severe pollution.<sup>7–9</sup> Therefore, there have been plenty of researches on the recycling of spent lithium-ion batteries reported over the past few years.<sup>10</sup>

At present, the main solution to recycling spent LIBs for spent ternary cathode materials is hydrometallurgical metal reclamation. The main valuable metals contained in batteries exhibit high oxidation states, such as Ni(III), Co(III), and Mn(IV), thus leading to the essential introduction of reducing agents. Carbon, glucose, sulfites, Fe(II), and so on are the commonly used reductants for the recycling of spent Ni–Co–

Mn-based lithium-ion batteries.<sup>11–16</sup> Additionally, the leaching agents can be classified into three types: inorganic acids<sup>17–19</sup> ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{HCl}$ ), organic acids<sup>8,20–22</sup> (acetic acid, oxalic acid, tartaric acid, citric acid, benzenesulfonic acid, and formic acid), and ammoniacal leaching substances.<sup>23,24</sup> Among them, when the price of organic acids is very high and it is easy for the ammonia leaching agents with cathode materials containing Mn to form a double salt,<sup>14,23,25</sup> applying inorganic acids as leaching agents is most valuable for large-scale industrial production because of their high efficiency and low cost. However, inorganic acids show a strong corrosivity but no selectivity to the impurities in spent cathode materials, which makes actual production more costly.

In general, the common solution to recovering spent LFP batteries involves the introduction of various acids and requires oxidizing agents in some cases.<sup>26–29</sup> Because of this, these methods also face the problems mentioned above. Previously, we proposed a method to efficiently leach Li from LFP by

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Table 1. Elemental Analysis of Raw Materials in Experiments

Raw material	Content (%)					
	Li	Ni	Co	Mn	Fe	P
LiFePO <sub>4</sub>	4.13	—	—	—	31.92	18.12
LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub>	5.93	26.77	10.72	15.21	—	—

adding Fe(III). In the process, Li<sup>+</sup> and Fe(II) in LFP are efficiently replaced by the added Fe(III) and leached to liquor at the same time.<sup>28</sup> Meanwhile, the generated Fe(II) serves as an efficient reducing agent for NCM. Therefore, NCM materials are applied in this process to verify whether Ni, Co, Mn, and Li can be extracted by the Fe(II) produced.

The current recycling methods are basically for NCM or LFP, but there are few proposed on how to deal with their mixture. In this letter, a salt leaching method is proposed for the simultaneous recovery of high-value metals in two spent cathode materials of NCM and LFP. The leaching reagent used in this method is only Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> without additional redox agent involved.

## EXPERIMENTAL SECTION

**Materials and Reagents.** The major elemental contents (wt %) of the cathode powders in spent LFP and NCM as obtained from Guizhou Red Star Electronic Material Co., Ltd., Guizhou, China, are listed in Table 1. All of the chemical reagents used in this study were of analytical grade and purchased from Chengdu Jinshan Chemical Reagent Co., Ltd., China. The mass fractions (wt %) of H<sub>2</sub>SO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> used in this study were 98% and 78%, respectively.

**Experimental Procedure and Analytical Method.** The experimental process was performed in a 150 mL conical flask placed in a constant-temperature water bath. Prior to magnetic stirring, 50 mL of an Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution was introduced to the flask. When the specified temperature was reached, 3 g of NCM spent cathode powders and a certain amount of LFP were added to the flask at the same time. After reaching a preset time, solid–liquid separation was performed. The leaching residues were washed several times with ultrapure water and dried at 105 °C in a vacuum drying oven. All of the samples used ICP-OES (Thermo Fisher iCAP 7400) to detect the contents of related elements in which the solid samples were dissolved in solution (HNO<sub>3</sub>:HCl = 1:3, v/v) for detection. The leaching efficiency  $X_i$  of different elements is calculated by

$$X_i = \frac{C_i V}{C_i V + w_i m} \quad (1)$$

where  $C_i$  (g/L) and  $V$  (L) represent the concentration of element  $i$  and the volume of the leachate, respectively, while  $w_i$  (%) and  $m$  (g) refer to the weight content of element  $i$  and the mass of the residue, respectively. X-ray diffraction (XRD, PANalytical, Empyrean) was used to analyze or characterize the solid samples.

## RESULTS AND DISCUSSION

**Effect of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> Concentration.** First, the effects of the ferric sulfate dosage on the leaching efficiencies of Ni, Co, Mn, and Li are shown in Figure 1. It can be seen that the leaching efficiency of all related metals showed a clear increasing trend as the amount of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> increased. When the usage of LFP was maintained at 4 g and the concentration of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was increased from 100 to 240 g/L, the leaching efficiency of Ni, Co, Mn, and Li was increased significantly from 34.51%, 34.43%, 38.22%, and 58.91% to 97.09%, 97.65%, 96.87%, and 98.22%, respectively. Previous to the leaching reaction, the pH value of the solution decreased from 1.72 to 1.53 as the level of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration increased from 100 to 240 g/L as shown in Figure 2. When the

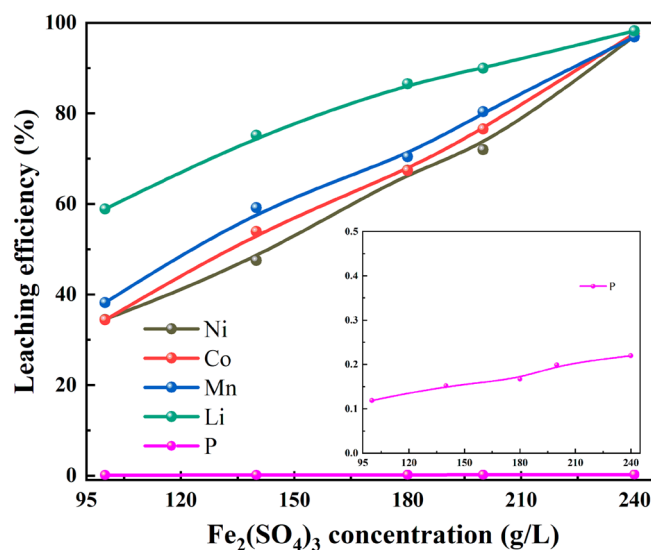


Figure 1. Effects of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration on the leaching efficiencies of Ni, Co, Mn, and Li (3 g of NCM, 4 g of LFP, 90 °C, 60 min).

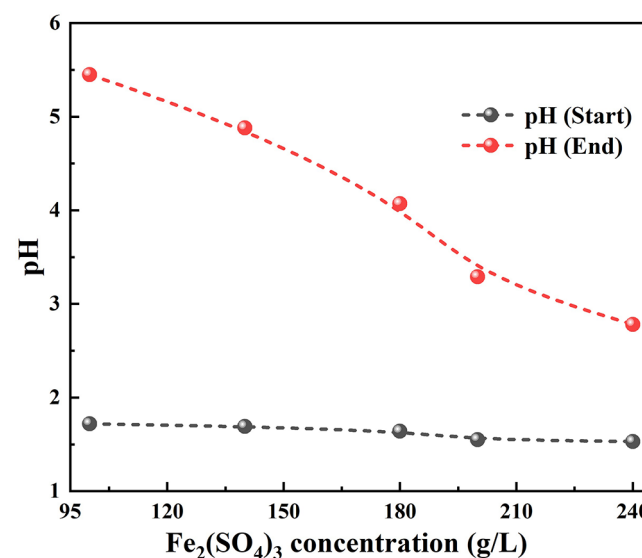
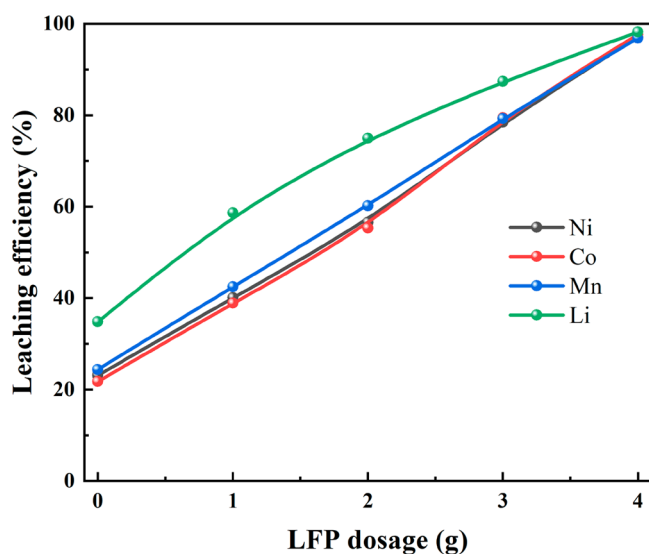


Figure 2. Solution pH changes with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration at the beginning and end of the leaching reaction (3 g of NCM, 4 g of LFP, 90 °C, 60 min).

reaction was complete, the pH value of the solution changed significantly with the change in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration. At a low Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration of 100 g/L, the pH value rose sharply from 1.72 to 5.45. When the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage was insufficient, the produced OH<sup>-</sup> was depleted by Fe(III) and even combined with M<sup>2+</sup> to generate M(OH)<sub>2</sub>, thus preventing the continued progress of the reaction. The leaching efficiency of P at different Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentrations was lower than

0.3%, indicating the combination of  $\text{PO}_4^{3-}$  with Fe(III) to form  $\text{FePO}_4$ .

**Effect of LFP Dosage.** LFP was used for the first time as a reducing agent to leach NCM, and its dosage made a significant difference to the leaching efficiency of nickel, cobalt, and manganese, as shown in Figure 3. In the absence of

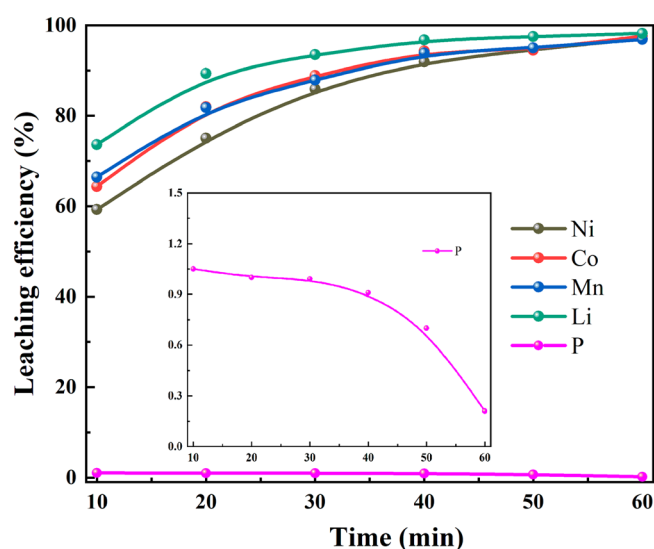


**Figure 3.** Effects of LFP dosage (0–4 g) on the leaching efficiencies of Ni, Co, Mn, and Li (3 g of NCM, 90 °C, 240 g/L of  $\text{Fe}_2(\text{SO}_4)_3$ , 60 min).

lithium iron phosphate, about 20% of Ni, Co, and Mn and 35% Li could be leached, suggesting that some metals do not exist in the form of a high oxidation state in spent  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ , and Fe(III) does have enough acidity to participate in the leaching process. As the amount of lithium iron phosphate increased, the leaching efficiency of nickel, cobalt, and manganese improved, suggesting that with the addition of LFP reacting with Fe(III), Fe(II) was released and further participated in the reduction reaction process of NCM, thus causing Ni, Co, Mn, and Li to be leached out on a continued basis. When the dosage of lithium iron phosphate was increased to 4 g, the leaching efficiency of nickel, cobalt, and manganese reached 97.09%, 97.65%, and 96.88%, respectively.

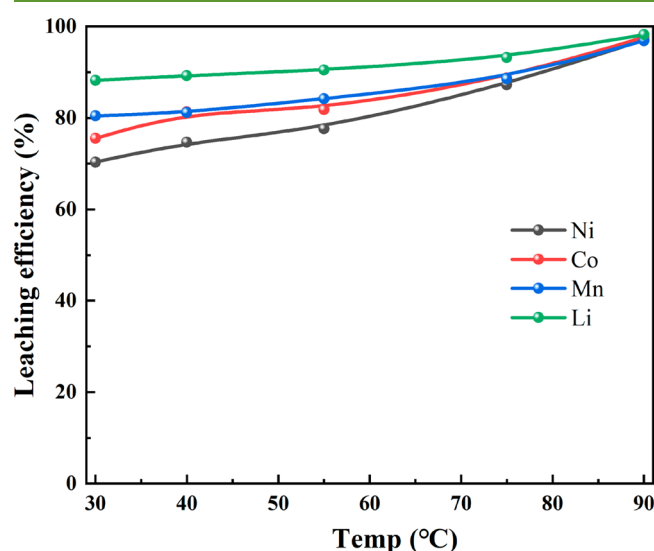
**Effect of Reaction Time.** Extending the reaction time is obviously conducive to the leaching reaction. Figure 4 shows the leaching efficiency of the metal depending on reaction time. The leaching efficiencies of Ni, Co, Mn, and Li increased rapidly during the first 10 min, indicating the fast reaction rate for that leaching process. Then, the improvement of the leaching efficiencies for all metals slowed progressively after 60 min. For example, Ni leaching efficiency was increased from 59.28% to 97.09% as the time was extended from 10 to 60 min. It is worth mentioning that there was an anomaly in which the leaching efficiency of P decreased gradually over time. When the reaction time was extended from 10 to 60 min, the leaching efficiency of P decreased from 1.06% to 0.21%. This is because when the reaction time was extended, the  $\text{OH}^-$  produced by the reduction of NCM caused the pH value to increase, as a result of which  $\text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$  at the beginning was transformed gradually into  $\text{PO}_4^{3-}$  precipitated with Fe(III).

**Effect of Temperature.** Reaction temperature is an important factor and has a significant effect on the leaching



**Figure 4.** Effects of leaching time (0–60 min) on the leaching efficiencies of Ni, Co, Mn, and Li (3 g of NCM, 4 g of LFP, 240 g/L of  $\text{Fe}_2(\text{SO}_4)_3$ , 90 °C).

process. Practically, the leaching reaction of most metals is endothermic, indicating that high temperatures will be more conducive. Figure 5 shows the dependence of the metal



**Figure 5.** Effects of leaching temperature (30–90 °C) on the leaching efficiencies of Ni, Co, Mn, and Li (3 g NCM, 4 g LFP, 240 g/L  $\text{Fe}_2(\text{SO}_4)_3$ , 60 min).

leaching efficiency on the temperature. The leaching efficiencies improved with the temperature increasing from 30 to 90 °C under the same conditions of 60 min. At 30 °C, the leaching efficiencies of Ni, Co, Mn, and Li reached 70.35%, 75.54%, 80.44%, and 88.32%, respectively. When the temperature rose to 90 °C, their leaching efficiency exceeded 96%, respectively.

**Characterization of Cathodic Materials and Leaching Residues.** The XRD patterns of the raw materials and the leaching residues obtained under the optimum conditions are exhibited in Figure 6. The sample of spent NCM cathode material could be indexed on the basis of a hexagonal  $\alpha$ - $\text{NaFeO}_2$  structure with the major diffraction peaks for the

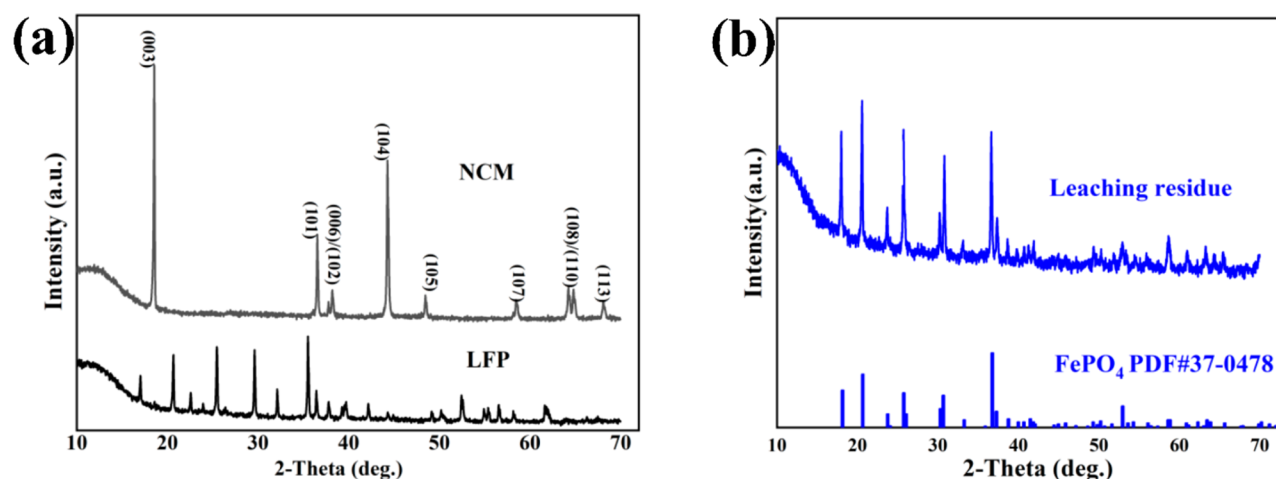


Figure 6. XRD characterization of raw material (a) and leaching residue (b)

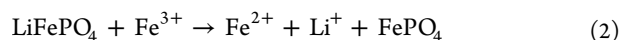
Table 2. Leaching Efficiencies of Related Elements and pH Change Using Four Reagents

Leaching reagent	concentration(g/L)	Leaching efficiencies (%)						pH (start)	pH (end)
		Ni	Co	Mn	Li	Fe	P		
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	240	97.09	97.65	96.88	98.32	–	0.21	1.52	2.78
H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	60	15.44	14.76	16.29	46.87	59.63	58.20	<0.50	1.98
H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	180	99.56	99.55	99.57	99.76	86.69	87.13	<0.50	1.48
CuSO <sub>4</sub> ·5H <sub>2</sub> O <sup>a</sup>	300	46.95	44.42	48.54	76.71	–	–	4.31	5.79
MgSO <sub>4</sub> ·7H <sub>2</sub> O <sup>a</sup>	295	0.21	0.01	0.21	4.81	–	–	7.96	7.81

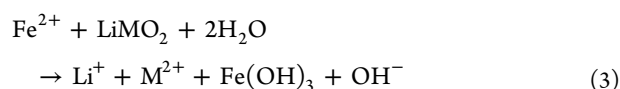
<sup>a</sup>Other reaction conditions are the same in the four systems (3 g of NCM, 4 g of LFP, 95 °C, 60 min).

(003), (101), (006), (102), (104), (015), (107), (108), (110), and (113) planes.<sup>18</sup> The diffraction peaks of spent LFP match well with the standard pattern of orthorhombic olivine-structured LiFePO<sub>4</sub>.<sup>30</sup> With the addition of ferric sulfate, all the diffraction peaks of NCM disappeared, and the leaching residues were transformed into FePO<sub>4</sub>, indicating that the spent LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> powder was completely dissolved by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

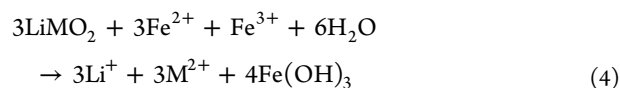
**Leaching Mechanism of Fe(III).** According to our previous work,<sup>28</sup> in this reaction process, Fe(III) can quickly replace Fe(II) and Li from LFP, and the related reaction equation is expressed as follows



According to a previous reported study,<sup>29</sup> the Fe(II) replaced by Fe(III) can be used as an effective reducing agent to react with NCM as follows



Obviously, the pH value of the system in this process will rise due to the generation of OH<sup>-</sup>. In fact, the pH value of the solution did increase to varying degrees as shown in Figure 2. In traditional methods, however, to consume the generated OH<sup>-</sup>, the acids that can provide H<sup>+</sup>, such as sulfuric acids, are often added to the system. In this study, Fe(III) taken as a Lewis acid achieved the same purpose

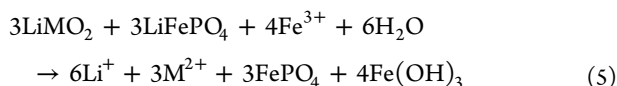


As expected, when the concentration of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was increased to 240 g/L, the end pH dropped sharply, although the initial pH was not significantly different from 100 g/L, but the leaching efficiencies of Ni, Co, Mn, and Li improved substantially. It is suggested that the addition of Fe(III) can be effective consuming OH<sup>-</sup> produced during the reaction, thus ensuring that reaction 3 can effectively proceed to the right. In order to further prove the correctness of the mechanism, a series of verification experiments were conducted with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> replaced by other Lewis acids added, such as H<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O, and MgSO<sub>4</sub>·7H<sub>2</sub>O, so as to study the leaching efficiencies of Ni, Co, Mn, and Li under other conditions. The experimental results are summarized in Table 2. It can be seen from the table that the leaching efficiencies of Ni, Co, and Mn were lower than 20%, but the P leaching efficiency was close to 55% when the same concentration of H<sup>+</sup> as Fe(III) was used. When the concentration of H<sup>+</sup> was increased to three times the concentration of Fe(III), the leaching efficiencies of Ni, Co, Mn, and Li were close to Fe(III), but the leaching efficiencies of Fe and P increased to nearly 90%, suggesting a large amount of HPO<sub>4</sub><sup>2-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup> present in the system. In contrast, the P leaching efficiency in the Fe(III) system was only 0.21%. When the system was added with the same molar amount of weaker Lewis acid, Cu<sup>2+</sup> that could prove the comparison of the solubility product constant in Table 3, the end pH reached 5.79, and the leaching efficiencies of Ni, Co, and Mn were lower than 50%. Furthermore, with the addition of Mg<sup>2+</sup>, reaction 3 can hardly occur, and the Ni, Co, and Mn leaching efficiencies were close to 0%. Obviously, the weaker the acidity of the added Lewis acid is, the weaker the ability of the combination with OH<sup>-</sup>. Then, the tendency of reaction 2 to proceed to the right would be weakened, and the final leaching efficiencies of Ni, Co, and

Table 3. Solubility Product Constant of Species<sup>28</sup>

Species	
Fe(OH) <sub>3</sub>	$2.79 \times 10^{-39}$
Cu(OH) <sub>2</sub>	$2.20 \times 10^{-20}$
Mg(OH) <sub>2</sub>	$5.61 \times 10^{-12}$

Mn would be reduced. As a result, the total reaction can be written as



## CONCLUSIONS

In this letter, a creative hydrometallurgical process, Fe(III) leaching, was proposed for recovering the metals contained in a mixture of cathode materials of NCM and LFP. Under the optimal extraction conditions: 3 g of NCM, 4 g of LFP, 240 g/L of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and a reaction at 90 °C for 60 min, the leaching efficiencies for Ni, Co, Mn, Li, and P could be achieved at 97.09%, 97.65%, 96.88%, 98.32%, and 0.21%, respectively. To the best of our knowledge, this kind of mixed leaching method has yet to be reported, and it can significantly reduce the amount of reducing agent used or oxidant usage, energy consumption, labor costs, and water consumption, which is consistent with the principles of ecofriendly chemistry. It is expected that this method of Fe(III) leaching may provide a new solution to recycling end-of-life lithium-ion batteries and other types of metal minerals.

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### Notes

The authors declare no competing financial interest.

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