



Separation and recovery of nickel cobalt manganese lithium from waste ternary lithium-ion batteries

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ABSTRACT

In this paper, a combination of precipitation and solvent extraction was used to study the separation and recovery of nickel, cobalt, manganese and lithium from the acid leach solution of wasted ternary lithium-ion battery cathode materials. The effects of sulfuric acid concentration, hydrogen peroxide addition, liquid-to-solid ratio, time and temperature on the metal leaching rate were optimized, and the leaching kinetic analysis showed that the metal leaching was controlled by both the diffusion of the solid-phase product layer and the chemical reaction, but the diffusion of the solid-phase product layer was dominant. Dimethylglyoxime (DMG) was first used to remove nickel as Ni-(C₄H₈N₂O₂)₂, and P2O4 and C272 were used to extract manganese and cobalt ions from the post-nickel removal solution step by step. The effects of volume fraction of organic solvent, O/A, pH of the aqueous phase and extraction time on the extraction rate were optimized, and the extraction mechanism was analyzed by FT-IR and slope method as a cation exchange reaction, specifically the ionic exchange of metal ions with H⁺ in the P—OH of the organic solvent, and also the coordination of trace metal ions with the P=O. Finally, the metals in loaded organic phase were stripped to the solution by dilute sulfuric acid which were recovered as MnO₂, CoC₂O₄ and Li₂CO₃, respectively. The recovery rates for nickel, cobalt, manganese and lithium in the whole process were 96.84 %, 81.46 %, 92.65 % and 91.39 % respectively, a technical route to recover nickel, cobalt, manganese and lithium from ternary LIBs was optimized, and extractants and DMG in the process could be recycled and reused.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in the automotive industry to power vehicles in terms of small volume, high energy density, low self-discharge rate, and long service life [8,18,22,39]. The cathode materials of commercial power lithium batteries are generally lithium cobaltate (LCO), lithium iron phosphate (LFP), lithium nickel cobalt manganese (NCM), etc. In recent years, NCM has become the mainstream cathode materials for new energy vehicles due to their good overall performance, especially in the passenger car sector [14,32]. It is estimated that the number of battery-powered passenger cars is expected to exceed 0.1 billion by 2050 [38]. The use of a large number of LIBs will certainly produce a large amount of battery waste, they contain a large number of valuable metals, such as nickel, cobalt, manganese and lithium, and the content of metals of waste LIBs is much higher than the

content of metals in ore, which has a very high recycling value and is of great significance to alleviate the shortage of resources [44]. In addition, waste LIBs also contain many harmful chemicals, which will pose a serious threat to the ecological environment and human health [50]. Therefore, recycling waste LIBs can effectively alleviate resource shortages and protect the environment.

Due to the high metal recovery value of ternary lithium-ion batteries, many studies have focused on the separation and recovery of metals in waste ternary lithium-ion batteries, mainly including pyrometallurgy and hydrometallurgy. Pyrometallurgy requires a lot of energy and releases harmful gases, which will cause serious air pollution [29,51]. Hydrometallurgy has the advantages of mild reaction conditions, environmental friendliness and high recovery efficiency, and is currently the mainstream method for laboratory and industrial production [7,36].

Hydrometallurgy mainly includes the pretreatment of waste lithium

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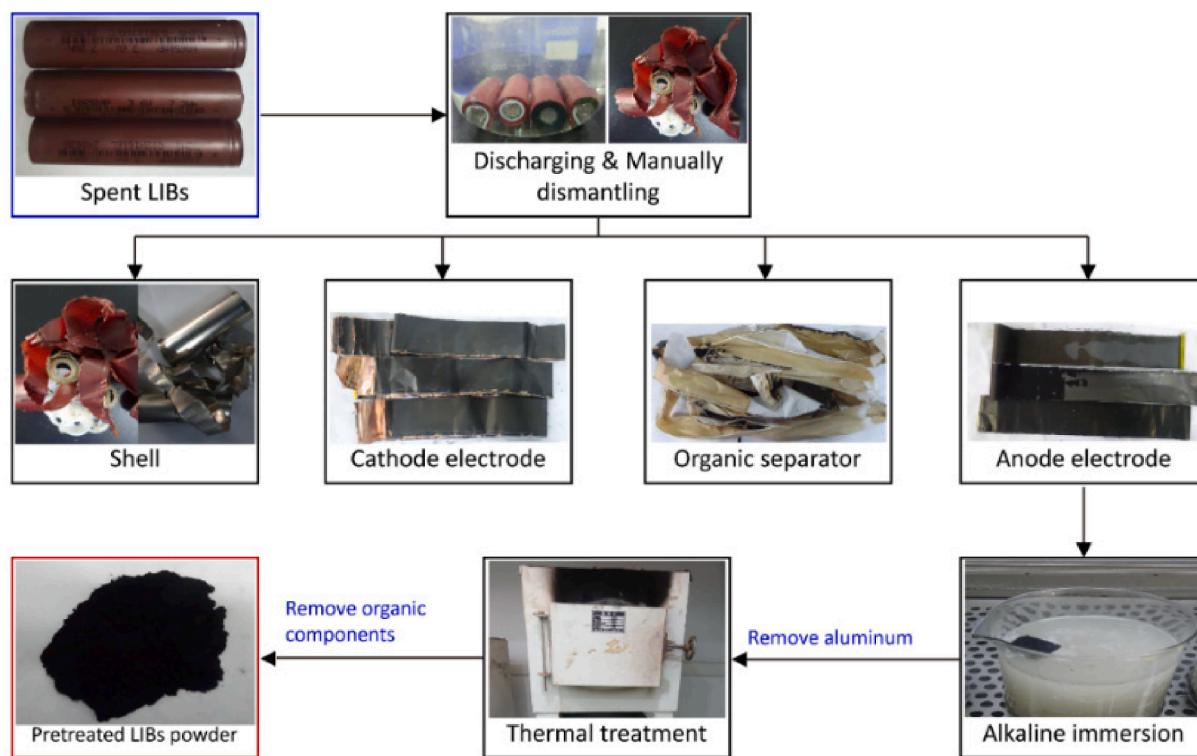


Fig. 1. Cathode powder preparation process.

batteries, the leaching of valuable metals, and the separation and recovery of leached metals [5,47]. The purpose of pretreatment is to obtain valuable cathode powder, which generally includes the steps of discharge, dismantling, crushing, and impurity sorting [46], and then the valuable metals in the cathode powder are leached into the solution by H_2SO_4 [50], HNO_3 [48], HCl [41], citric acid [34], tartaric acid [3], etc. The addition of reducing agents can greatly improve the metal leaching efficiency by oxidizing the high-valent metals to low-valent, such as H_2O_2 , $NaHSO_4$, methanol, $C_6H_{12}O_6$ [10,21,45]. There are also some new studies using solid-state chlorination [37], deep eutectic solvents (DESs) [28] or Ferro-chemistry [17] to leaching metals from waste LIBs, which can avoid the production of waste acid or the use of a large amount of reducing agents during the leaching process, but the leaching efficiency is lower than that of the traditional leaching method, leaching cost and the complexity of the leaching process has increased.

The metals are leached into the solution, and the subsequent separation and recovery is an important step related recycling process during hydrometallurgy. There are many kinds of metals in the leaching solution of waste ternary LIBs, which are challenging to be separated and recycled efficiently and environmentally friendly from the complex solutions one by one, therefore most studies have focused on the regeneration of cathode materials by co-precipitation [5,9,24], solid-state sintering [11,31] and sol-gel [25,49]. However, the process of regenerating cathode materials is also relatively complicated, including metal leaching, and the process of removing impurities also involves the consumption of many chemicals, it is difficult to guarantee secondary pollution control, and the products may also have some defects of electrochemical performance [4], hence, it is necessary to study the gradual separation and recovery of metals from wasted ternary LIBs, which will help to recover metals and mitigate the risk of metal supply.

There are some relevant studies on the gradual separation and recovery of metals from spent ternary LIBs by solvent extraction [43,47], chemical precipitation [15,26] and electrochemical deposition [33], etc. However, gradual recovery of metals by precipitation requires good control of impurities, and the energy consumption of electrochemical

deposition is relatively high, therefore, solvent extraction has become a preferred method in the hydrometallurgical process with the advantages of easy operation, low energy consumption and good separation effect [1,39]. P204 and C272 are widely used to extract and separate metals from spent ternary LIBs, but some new studies use ionic liquids [19] or add lactic acid to organic systems for extraction, which is more environmentally friendly but the cost of extraction is high and not conducive to industrial applications. However, it is difficult to effectively separate multiple metals only by a single extraction and a combination of several methods is required. Recently, some studies have combined solvent extraction with precipitation process to separate and recover the metals in the spent ternary LIBs. Zhang [49] first used phosphate to separate the aluminum in the acid leach solution, and after that, Mn, Co and Ni were co-extracted with 1 mol/L of P507 with 60 % saponification and 1.4:1O/A, while Li was left in the solution, and finally the mixed metal solution obtained by stripping could be used to regenerate the precursor of the cathode material. Wang [42] used deep eutectic solvents (DESs) to extract valuable metals from the cathode material, and prepared regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by co-extraction and co-precipitation method. However, these studies mainly focused on the co-extraction of metals in the leaching solution, and did not realize the separation of metals one by one. Only few studies have been conducted to recover nickel, cobalt, manganese and lithium in the form of metal salts one by one by a combination of selective precipitation and solvent extraction [6,36], and the main separation methods of these studies have focused on selective precipitation, which can reduce the interference of metal ions on extraction, but too many precipitation steps will lead to more loss of other metal ions and affect the purity of precipitation products, therefore, further research is needed for the separation and recovery of metals from spent ternary LIBs.

In this study, H_2SO_4 and H_2O_2 are used to leach valuable metals in cathode powder, then DMG is used to precipitate and separate nickel, and organic solvent is used to extract manganese and cobalt ions step by step to achieve efficient separation of nickel, cobalt, manganese and lithium. Finally, manganese, cobalt and lithium metal ions are recovered

in the form of precipitates, and the complex-precipitation of nickel and DMG can be dissolved in sulfuric acid and recrystallization to recycle DMG and NiSO₄ respectively. The technical route of acid leaching, selective precipitation, solvent extraction and precipitation recovery was optimized by adding steps to the extraction to decrease the loss of metal ions, and extractants in the process could be recycled and reused to reduce the cost.

2. Experiments

2.1. Materials

The waste 18,650 ternary LIBs used in this research are purchased from a second-hand recycling plant. H₂SO₄, H₂O₂, NaOH, dimethylglyoxime (DMG) and other reagents used are analytical pure purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification. Bis-2-ethylhexylphosphoric acid (P204), bis(2,4,4-trimethylpentyl) phosphinic acid (C272), tributylphosphate (TBP) and sulfonated kerosene are all purchased from Guangdong Wengjiang Chemical Reagent Co., Ltd, the purity grade is industrial grade. All solutions were prepared in distilled water.

2.2. Pretreatment of waste ternary LIBs

The cathodes and anodes were manually separated after being soaked in a 5 % NaCl solution for 24–48 h for discharge, and the cathodes were cut into small pieces of 20 mm × 20 mm and dissolved in a 20 g/L NaOH solution at 50 °C for 60 min with a solid–liquid ratio of 100 g/L, and the cathode material after aluminum removal was filtered, and the aluminum removal rate reached 99.21 %. By TGA-DSC analysis and SEM characterization, it was determined that acetylene black and polyvinylidene fluoride (PVDF) were removed from the cathode material by pyrolysis at a high temperature of 500 °C × 5 h, and cathode powder was obtained after cooling and grinding, the pretreatment flow chart is shown in Fig. 1:

2.3. Reductive acid leaching of valuable metals

The cathode powder obtained from the 2.2 treatment was put into a conical bottle with a certain concentration of H₂SO₄ and H₂O₂. The bottle mouth was sealed with plastic film to prevent liquid splashing. The conical bottle was placed in a constant temperature water bath oscillator at a fixed speed of 200r/min to carry out valuable metal leaching. To investigate the effects of sulphuric acid concentration, liquid to solid ratio, temperature, hydrogen peroxide addition and time on the leaching rate of valuable metals from anode materials, under optimal conditions, 10 g of cathode powder was taken to leach the metal and the leachate was set aside. Metal leaching rates are calculated as shown in (1):

$$\eta_{Me} = \frac{c_1 V_1}{c_1 V_1 + c_2 V_2} \times 100\% \quad (1)$$

Where, η_{Me} represents the leaching rate of nickel, cobalt, manganese and lithium, %; c_1 and c_2 represent the concentrations of nickel, cobalt, manganese and lithium in the leaching solution and filter residue solution, mg/L; V_1 and V_2 represents the volume of leaching solution and filter residue solution, L. All experiments were designed with three parallel experiments to avoid chance errors.

2.4. Separation and recovery of metals in leaching solution

According to Section 2.3, the content of each metal in the leachate, NiSO₄·6H₂O, MnSO₄·H₂O, CoSO₄·7H₂O and Li₂SO₄·H₂O are used to prepare a simulated solution of equal concentration. 50 ml simulated solution was taken, and nickel was precipitated by DMG, the speed of the constant temperature magnetic stirrer was controlled at 200r/min, and

the reaction temperature was 60 °C for 40 min. The solution was filtered and separated to obtain the nickel removal solution. According to the content of metal in the solution after nickel removal, the same concentration of the simulated solution is configured, 50 ml simulated solution is taken as the extraction solution and mixed P204, C272 according to a certain oil-aqueous ratio, poured into a separatory funnel and extracted in steps of Mn²⁺ and Co²⁺ at room temperature using an HSP-6 reciprocating horizontal extraction oscillator. To investigate the effect of organic solvent volume fraction, oil-aqueous ratio, pH, and shaking time on the extraction and separation of manganese and lithium cobalt. Under the oil-aqueous ratio of 1:1 and a shaking time of 5 min, the above organic phase was stripped with dilute sulfuric acid at room temperature to explore the effect of sulfuric acid concentration on the metal stripping rate. The separation and recovery of Mn²⁺, Co²⁺ and Li⁺ were carried out with the leaching solution of 2.3 according to the above optimum experimental parameters. The metals in the organic phase are reversely extracted to the aqueous phase with dilute H₂SO₄ and the manganese, cobalt and lithium are recovered as precipitates of MnO₂, Co₂O₄ and Li₂CO₃, the experimental conditions for manganese recovery by precipitation were: pH 2, reaction temperature 80 °C, reaction time 60 min, the molar ratio of potassium permanganate to manganese 1.8:1; The experimental conditions for the recovery of cobalt were: pH 2, reaction temperature 60 °C, reaction time 60 min, the molar ratio of oxalic acid to cobalt: 1.5:1; The experimental conditions for the recovery of lithium were: pH 12, reaction temperature 95 °C, reaction time 60 min, the molar ratio of sodium carbonate to lithium 1.5:1, all of precipitates are recovered after repeated washing to ensure the removal of impurities.

The preparation of the organic phase is as follows: fully mix a certain volume of P204, C272 and sulfonated kerosene, saponify 60 % and 50 % respectively with NaOH, and mix them with 10 %TBP to prevent emulsification.

The calculation of extraction rate (E) is as follows:

$$E_{Me} = \frac{c_0 V_0}{c_0 V_0 + c_a V_a} \times 100\% \quad (2)$$

Where, c_0 is the concentration of metal ions in organic phase, mg/L; c_a is the concentration of metal ions in aqueous phase, mg/L; V_0 is the volume of the organic phase, L; V_a is the volume of aqueous phase, L.

The precipitation rate is calculated by the following equation:

$$P_{Me} = \frac{c_B - c_A}{c_A} \times 100\% \quad (3)$$

Where c_B indicates the metal content of the solution before precipitation, mg/L; c_A indicates the metal content of the filtrate after precipitation, mg/L; and P_{Me} indicates the precipitation rate of the metals, %.

2.5. Analysis methods

The optimum temperature and time for pyrolysis of the cathode materials were determined with a thermogravimetric differential scanning calorimeter (TGA-DSC, NETZSCH, STA449F5, Germany), the experiment was carried out in air at a heating rate of 5 °C/min from 30 °C to 800 °C. Metal content in solid powder and solution was determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Symerfield, 7900I, USA). Characterization and analysis of the crystal structure of the cathode material and metal precipitates by X-ray diffractometer (XRD, Bruker, D8 Advance, Germany) with Cu target, Ka radiation, a sampling interval of 0.02° and experiment angle 2θ of 5°–70°. The apparent morphology of the cathode material was observed using a scanning electron microscope (SEM, Tesken, VEGA, Czech Republic); the molecular structure of the organic phase before and after extraction was characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker, VERTEX80V, Germany).

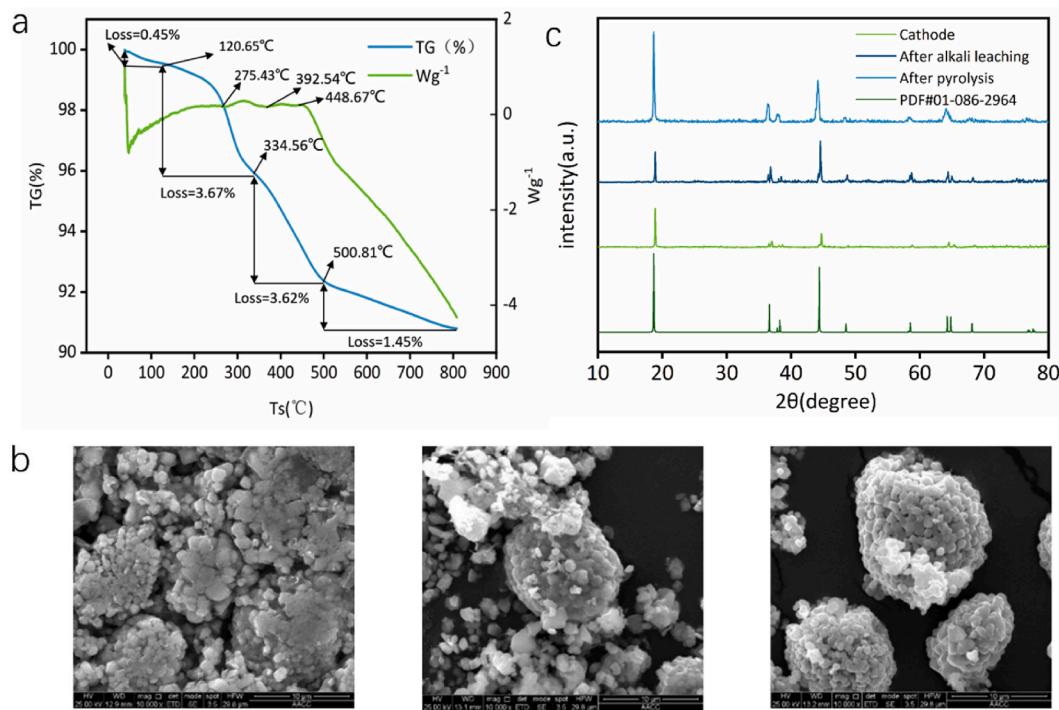


Fig. 2. A, TGA-DSC curve of cathode power; b, SEM of cathode material: from left to right, these are cathode material before alkali leaching, cathode material after alkali leaching, cathode material after calcination respectively; XRD characterization of anode materials at various stages of pretreatment.

Table 1
Metal content in powder samples.

Element	Ni	Co	Mn	Li	Al	Fe	Cu
Wt.%	19.41	9.19	17.87	3.44	<0.01	<0.01	<0.01

3. Results and discussion

3.1. Characterization of cathode materials

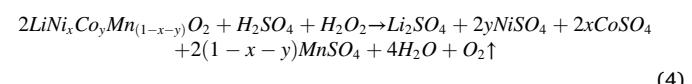
In order to obtain a high purity cathode powder for subsequent metal leaching and separation experiments, characterization is an indispensable step in the pretreatment process, TGA-DSC and SEM characterization were used to confirm the optimal temperature and time for the removal of acetylene black and PVDF, and the XRD and ICP-OES characterization can confirm the removal of impurities from the powder and provide basic data for the subsequent leaching and recovery experiments. TGA-DSC results are shown in Fig. 2-a, it can be seen that the weight loss of the cathode powder is mainly concentrated in the range 120.65–334.56 °C (3.67 %) and 334.56–500.81 °C (3.62 %), with significant exothermic peaks at 275.43 °C, 392.54 °C and 448.67 °C respectively, corresponding to the thermal decomposition of acetylene black and PVDF [13]. Above 500 °C, a loss of 1.45 % was observed, which may be due to the high temperature, resulting in some loss and phase change of the metals in the sample [27]. Therefore, the optimum pyrolysis temperature and time for the removal of organic carbon is 500 °C for 5 h. The morphological changes of the pretreated powder samples were observed by SEM and magnified 10,000 times, the results are shown in Fig. 2-b, after pyrolysis, the agglomeration of the cathode material increases significantly, the surface of the spherical sample is relatively smooth and the impurity particles almost disappear. It indicates that the carbon-containing materials such as PVDF and acetylene black are basically decomposed after hydrolysis at 500 °C for 5 h. The XRD characterization of the cathode material during pretreatment is shown in Fig. 2-c, the XRD characterization of cathode material did not change much before and after pretreatment and is completely consistent

with the characteristic peak of the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ standard spectrum (PDF#01-086-2964) without any impurity peaks. This indicates that the crystal structure of the sample is intact and that the cathode powder is of high purity. The metal content of the powder samples measured by ICP-OES is shown in Table 1, and the impurity content is <0.01 %, indicating that the impurities in the pretreatment process are well controlled. The contents of nickel, cobalt, manganese, and lithium are 19.41 %, 9.19 %, 17.87 %, and 3.44 %, respectively.

3.2. Reducing acid leaching of valuable metals

3.2.1. Effect of different experiment parameters on metal leaching rate

The specific reaction of H₂SO₄ and H₂O₂ leaching valuable metals from cathode powder is as follows:



Hydrogen peroxide is involved in a disproportionation reaction where O[−] loses electrons to give electrons to another O[−], but in a strongly acidic solution, the structure of LiNiMnCoO₂ is destroyed by H⁺ and the ability to gain electrons is much stronger than O[−], so the metals of LiNiMnCoO₂ get electrons and are reduced to low-valent ions, while SO₄^{2−} preferentially combines with low-valent metal ions, making the structure of LiNiMnCoO₂ accelerate the destruction and the low-valent metal ions precipitate out of the surface and rapidly dissolve in the sulphuric acid solution, and the dissolution process is accelerated [23].

The effects of different experiment parameters on metal leaching rate are shown in Fig. 3.

The effect of leaching time on metal leaching rate is shown in Fig. 3-a, with the increase of leaching time, the leaching rate of metal increases significantly. When the leaching time exceeds 60 min, the leaching rate of metal tends to be stable, indicating that the reaction basically reaches the upper limit at 60 min, and the relatively low leaching rate of nickel is probably because nickel has the lowest metal activity and also the highest nickel content, which takes longer to leach completely.

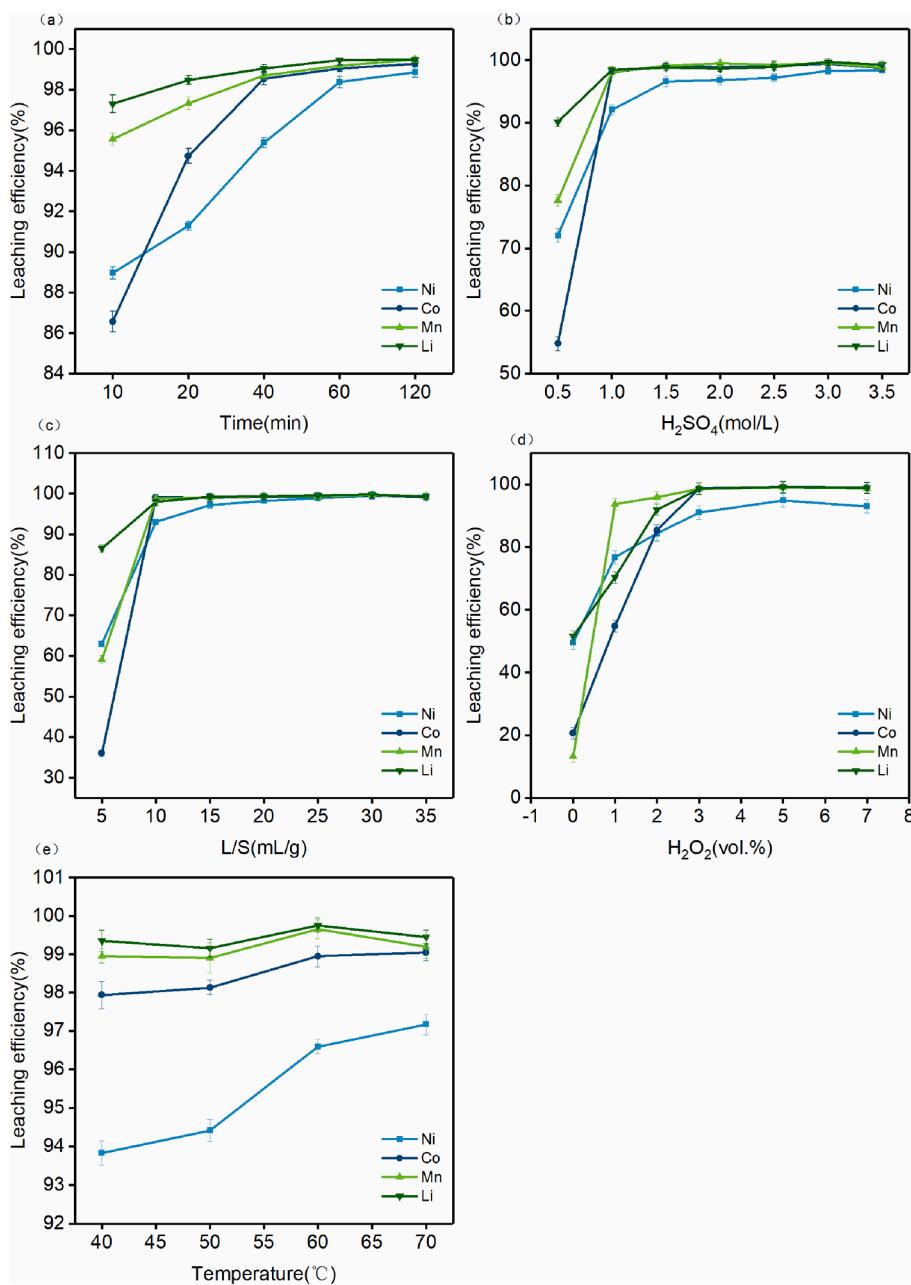


Fig. 3. The effect of experiment variables on the leaching rate of valuable metals: a, time (H_2SO_4 2.5 mol/L, H_2O_2 5 vol%, L/S 25 ml/g, temperature 60 °C); b, sulfuric acid concentration (H_2O_2 5 vol%, L/S 25 ml/g, temperature 60 °C, time 60 min); c, liquid solid ratio (H_2SO_4 2.5 mol/L, H_2O_2 5 vol%, temperature 60 °C, time 60 min); d, hydrogen peroxide addition (H_2SO_4 2.5 mol/L, L/S 25 ml/g, temperature 60 °C, time 60 min); e, temperature (H_2SO_4 2.5 mol/L, L/S 25 ml/g, time 60 min, H_2O_2 5 vol%).

Therefore, 60 min is the best leaching time. It can be seen from Fig. 3-b that the leaching rates of nickel, cobalt, manganese and lithium show a significant rise with the increase of H_2SO_4 concentration, the leaching rate rises fastest from 0.5 mol/L to 1 mol/L, and when the H_2SO_4 concentration is 1 mol/L, the metal leaching rate all rise to more than 90 %, which due to the increase of H^+ in the solution and increases the collision probability of reactants and speeds up the chemical reaction rate, when the concentration of H_2SO_4 continues to increase, the change of metal leaching rate gradually slows down, when it reaches 2.5 mol/L, the leaching rate of metals basically completely leaching, so 2.5 mol/L is the best acid leaching concentration. Fig. 3-c shows that when the liquid-solid ratio rises from 5 ml/g to 10 ml/g, the leaching rate rises rapidly. This is because the liquid-solid ratio increases and the volume of the solution increases, which is conducive to the diffusion of metals in the powder. At the same time, the contact area between the powder particles and the liquid increases, which is conducive to accelerating the leaching reaction. With the continuous increase of the liquid-solid ratio,

the leaching rate of nickel increases significantly, comprehensively considered, 25 ml/g is selected as the optimum liquid-solid ratio. Fig. 3-d shows that the effect of adding H_2O_2 on the metal leaching rate is very obvious, because hydrogen peroxide can effectively reduce the metal in the cathode material and make it easy to leach; After adding hydrogen peroxide to 3 %, the growth of metal leaching rate slows down relatively, when increasing the hydrogen peroxide to 7 vol%, a slight decrease in the metal leaching rate of all four metals was observed. Considering comprehensively, the optimum hydrogen peroxide addition is 5 vol%. Fig. 3-e shows the effect of temperature on the metal leaching rate, it can be seen that the metal leaching rate increases gradually with the increase of temperature, that's because with the increase of temperature, the activation energy required for chemical reaction decreases, therefore, the reaction rate increases, when the temperature rise from 60 °C to 70 °C, the leaching rates of manganese and lithium decreased slightly, that's because the temperature is too high, H_2O_2 will decompose rapidly, and the metal was not completely reduced, which is not

Table 2
Leaching rate of each metal in the sulfuric acid system.

Elements	Ni	Co	Mn	Li
Leaching rate (%)	97.20	99.12	99.23	99.54

conducive to metal leaching [6]. Therefore, the optimized reaction temperature should be 60 °C.

Comprehensive consideration of leaching efficiency and energy consumption, the optimal reduction acid leaching experimental conditions are as follows: H₂SO₄ concentration of 2.5 mol/L, H₂O₂ dosage of 5 vol%, liquid-solid ratio of 25 ml/g, time of 60 min, temperature of 60 °C, the optimum leaching rates of metals are shown in Table 2.

Due to the leaching of other impurities metal content are very low, so it can be ignored. 10 g of cathode powder was taken to leach under the optimal acid leaching conditions for standby, and the metal content in

the leaching solution was as follows: Ni 20.150 g/L, Co 8.644 g/L, Mn 11.610 g/L, Li 2.736 g/L. Although the sulfuric acid leaches most of the metals, there are still a small amount of heavy metals remaining in the filter residue. Heavy metals cannot be degraded in the environment, and will accumulate in organisms or the environment with time migration, causing serious harm to human health and the natural environment. According to the National List of Hazardous Wastes (2021 Edition), in the field of battery manufacturing, leaching residues containing heavy metals are hazardous wastes, which need to be collected and handed over to qualified hazardous waste disposal units for disposal.

3.2.2. Acid leaching kinetics

The rate of the leaching reaction is determined by the step with the slowest reaction and the great experiment reaction resistance. During solid-liquid leaching reactions, the reaction rate is mainly controlled by diffusion outside the liquid-phase boundary layer (5), diffusion inside

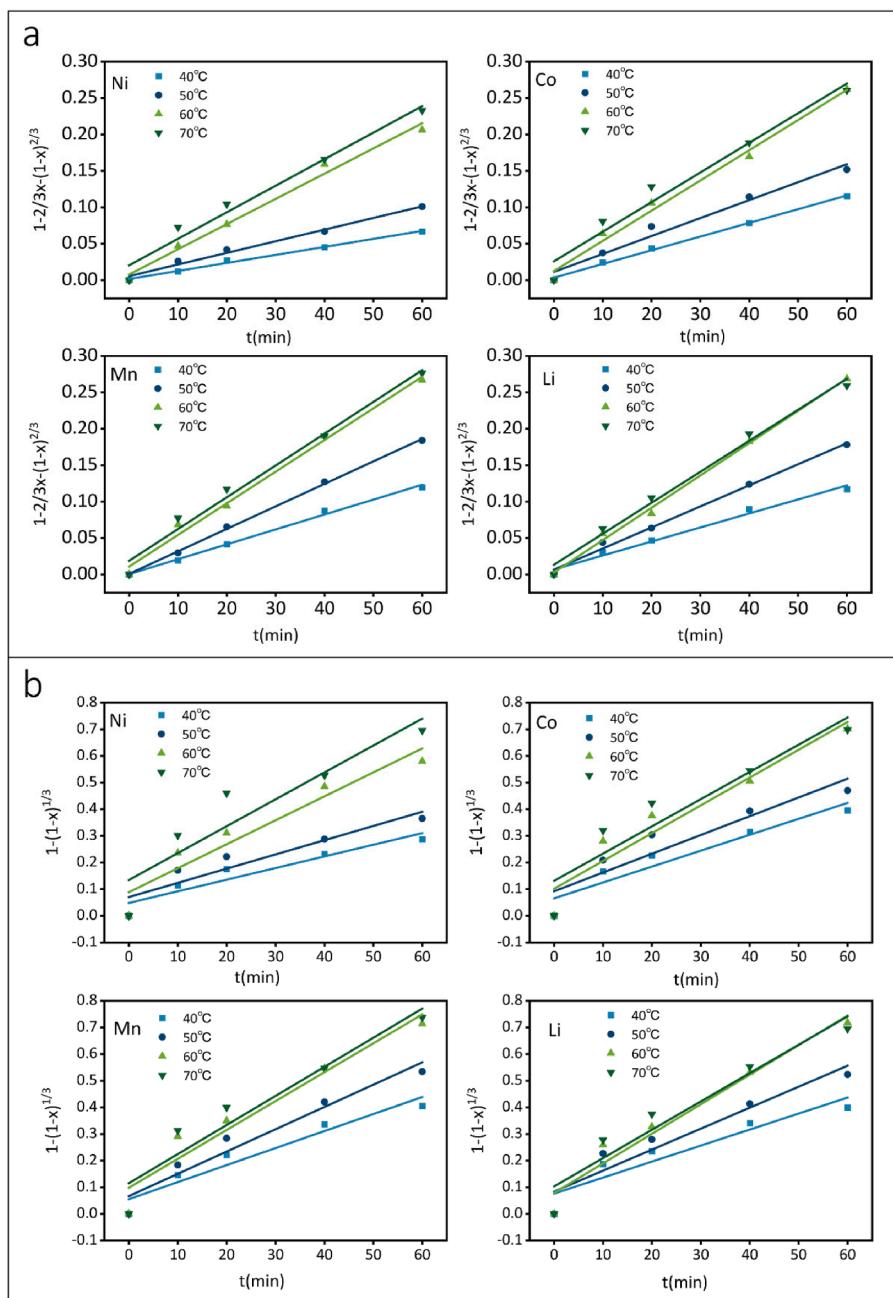


Fig. 4. $1 - 2/3x - (1 - x)^{2/3} = k_2 t$, $1 - (1 - x)^{1/3} = k_3 t$ fitting relationship of nickel, cobalt, manganese and lithium at different temperatures.

Table 3

$1 - 2/3x - (1 - x)^{2/3} = k_2t$, $1 - (1 - x)/3 = k_3t$ fitting parameters of nickel, cobalt, manganese and lithium at different temperatures.

Fitting equation	Metals	Fitting parameters	40 °C	50 °C	60 °C	70 °C
$1 - 2/3x - (1 - x)^{2/3} = k_2t$	Ni	k_2	0.00110	0.00160	0.00346	0.00364
		R^2	0.99205	0.98317	0.98419	0.96509
	Co	k_2	0.00188	0.00246	0.00415	0.00407
		R^2	0.99603	0.96561	0.98523	0.95328
$1 - (1 - x)^{1/3} = k_3t$	Mn	k_3	0.01188	0.01325	0.01347	0.01318
		R^2	0.9801	0.99181	0.99568	0.98593
	Li	k_3	0.00192	0.00289	0.00444	0.00426
		R^2	0.98010	0.99181	0.99568	0.98593
	Ni	k_3	0.00110	0.00160	0.00346	0.00364
		R^2	0.99205	0.98317	0.98419	0.96509
	Co	k_3	0.00597	0.00704	0.01043	0.01021
		R^2	0.87437	0.81939	0.89712	0.83395
	Mn	k_3	0.00639	0.00836	0.01084	0.01092
		R^2	0.90833	0.92568	0.91107	0.88330
	Li	k_3	0.00192	0.00289	0.00444	0.00426
		R^2	0.98010	0.99181	0.99568	0.98593

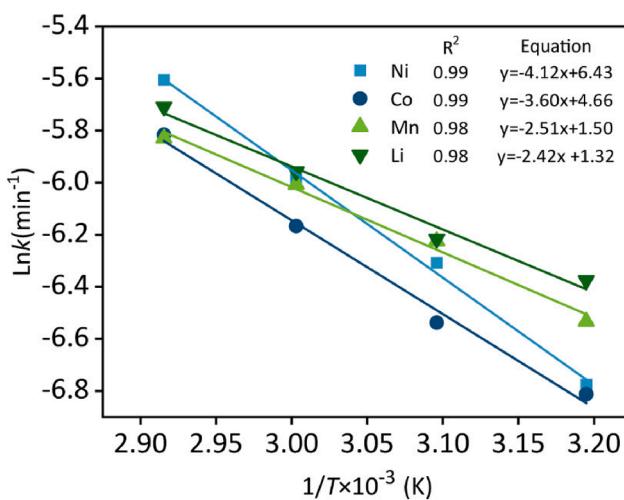


Fig. 5. Arrhenius fitting curve of nickel, cobalt, manganese and lithium at different temperatures.

the solid-phase product layer (6), and interfacial chemical reactions (7) [16]:

$$x = k_1 t \quad (5)$$

$$1 - 2/3x - (1 - x)^{2/3} = k_2 t \quad (6)$$

$$1 - (1 - x)^{1/3} = k_3 t \quad (7)$$

Where k_1 , k_2 and k_3 are the apparent rate constants of chemical reaction in different models, min^{-1} , t is the leaching time, min and x is the leaching rate of metals, %.

If the reaction is controlled by diffusion outside the liquid-phase boundary layer, it is greatly affected by stirring, but this situation did not occur in this experiment. Therefore, so only a linear fit of the leaching rate of the valuable metal from the cathode material at different temperatures with time was carried out for (6) and (7), and a fitted graph of the leaching kinetics was obtained as shown in Fig. 4, and the fitted parameters for each model are shown in Table 3. In general, R^2 of $1 - 2/3x - (1 - x)^{2/3} = k_2 t$ is more than 95 %, R^2 of $1 - (1 - x)^{1/3} = k_3 t$ is more than 83 %. The fitting effect of $1 - 2/3x - (1 - x)^{2/3} = k_2 t$ is better, indicating that the leaching of valuable metals from the cathode material with sulfuric acid and hydrogen peroxide is controlled by the diffusion inside the solid-phase product layer.

The metal leaching rate constants at different temperatures are substituted into the following Arrhenius equation for linear fitting. The

Arrhenius equation is as follows:

$$\ln k = \frac{Ea}{RT} + C \quad (8)$$

Where, k is the reaction rate constant, min^{-1} , Ea is the apparent activation energy, $\text{kJ} \cdot \text{mol}^{-1}$, R is the ideal gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, T is the leaching temperature, K, C is independent constants.

The fitting results are shown in Fig. 5, which shows a good linear relationship. According to the Arrhenius formula calculation, the leaching activation energies of nickel, cobalt, manganese and lithium are $34.32 \text{ kJ} \cdot \text{mol}^{-1}$, $29.94 \text{ kJ} \cdot \text{mol}^{-1}$, $20.84 \text{ kJ} \cdot \text{mol}^{-1}$, $20.12 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. According to the principle that the lower the activation energy is, the more likely the reaction is to occur, the leaching reaction of manganese and lithium is easier, and the leaching of nickel is the slowest, and when $Ea < 20 \text{ kJ} \cdot \text{mol}^{-1}$, leaching is controlled by diffusion, when $20 \text{ kJ} \cdot \text{mol}^{-1} < Ea < 40 \text{ kJ} \cdot \text{mol}^{-1}$, leaching is controlled by the mixture of interface diffusion and chemical reaction, when $Ea > 40 \text{ kJ} \cdot \text{mol}^{-1}$, leaching is controlled by chemical reaction [12]. In summary, the Ea obtained in this paper is in the range of $20 \text{ kJ} \cdot \text{mol}^{-1}$ – $40 \text{ kJ} \cdot \text{mol}^{-1}$, indicating that the leaching reaction is mainly controlled by the mixture of a surface chemical reaction and the diffusion inside the solid-phase product layer, with the diffusion inside the solid-phase product layer being the dominant control.

3.3. Separation and recovery of valuable metals

Considering the results of the preliminary pre-experiment, P204 and C272 are selected for the extraction and separation of manganese and cobalt in the acid leaching solution. Due to the variety of metals, the separation effect of the four metals was not obvious in the early pre-experiment, because the high content of nickel in the leaching solution would interfere the extraction of manganese, therefore, dimethylglyoxime (DMG) was used to remove nickel by precipitation first, and then P204 and C272 were used to separate manganese, cobalt and lithium in the solution step by step.

3.3.1. Separation of metals by precipitation extraction method

Usually, in order to separate cobalt and nickel, the solvent extraction method is mainly used, but this method is only suitable for the low concentration of nickel in the leaching solution, otherwise it is difficult to achieve the required separation factor ($\beta_{\text{Co}/\text{Ni}}$), and the ion concentration of nickel in this study is larger than that of cobalt, the extraction method is difficult to achieve the desired effect, so use DMG to recover nickel.

Nickel can be precipitated by DMG ($\text{C}_4\text{H}_8\text{N}_2\text{O}_2$). The specific reaction is as follows:

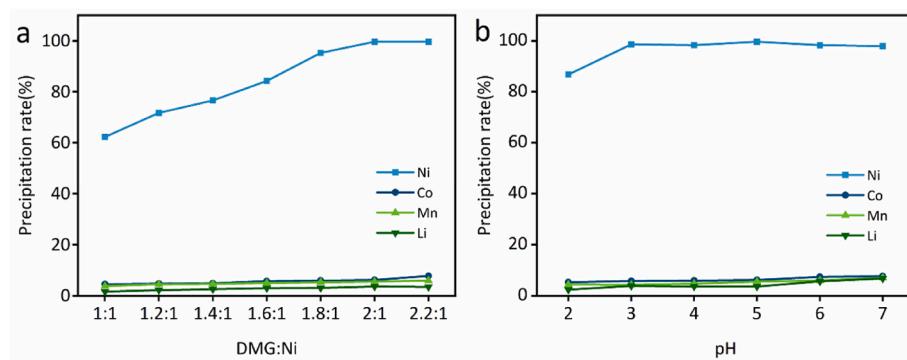


Fig. 6. The effect of pH, molar ratio of DMG to nickel on nickel precipitation rate: a, molar ratio of DMG to nickel (pH 5, speed 200 r/min, temperature 60 °C, time 40 min); b, pH (molar ratio of DMG to nickel 2:1, speed 200r/min, temperature 60 °C, time 40 min).

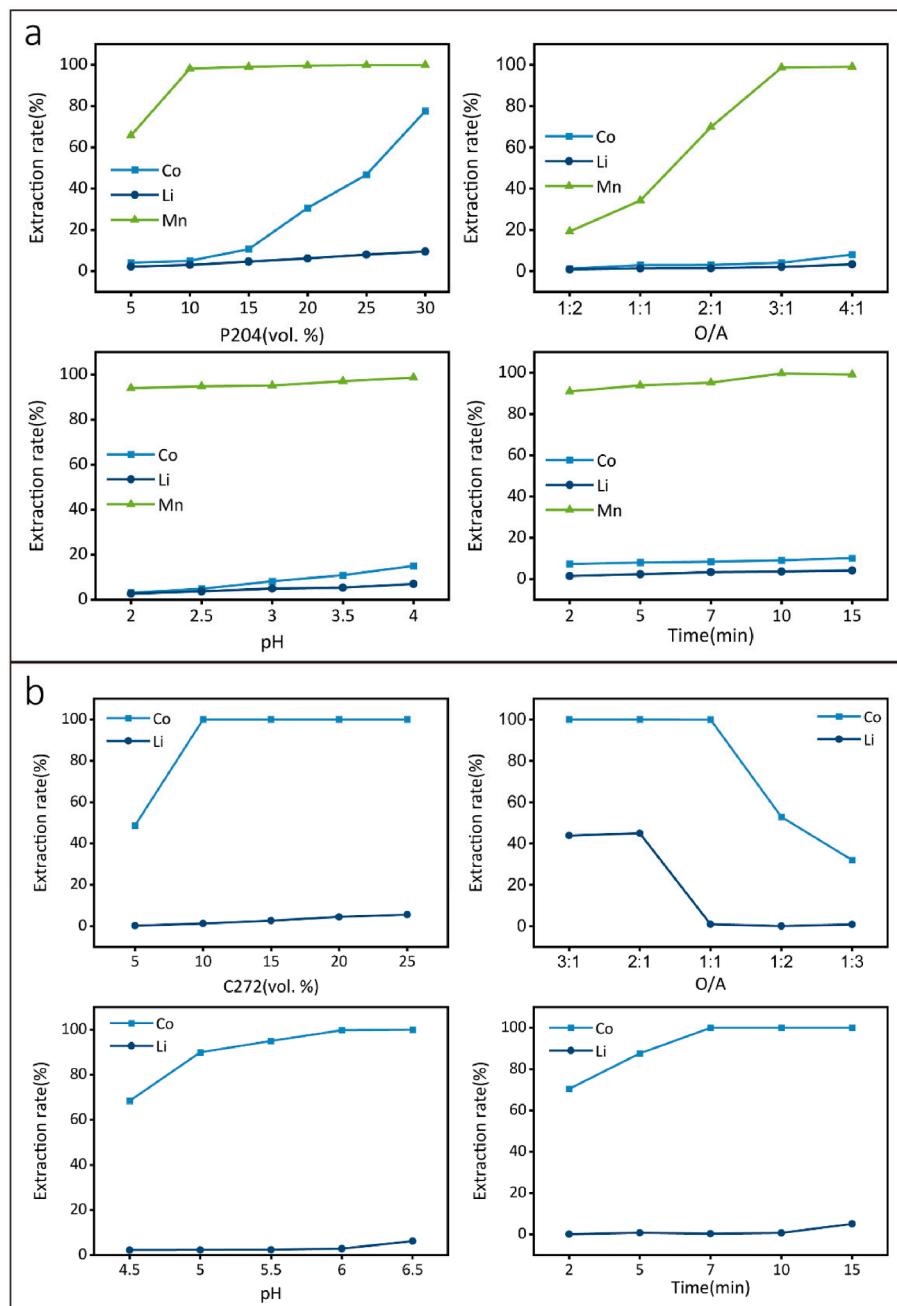
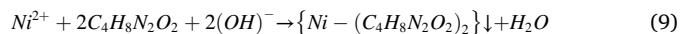


Fig. 7. The effect of experiment parameters on manganese extraction rate: a, P204 extract manganese, the volume fraction of P204 (O/A = 3:1, pH = 3.5, time 10 min), the O/A (10vol.%P204, pH = 3.5, time 10 min), the pH (10vol.%P204, O/A = 3:1, time 10 min), Time (10 vol.%P204, pH = 3.5, O/A = 3:1); b, C272 extract cobalt, the volume fraction of C272 (O/A = 1:1, pH = 6, time 7 min), the O/A (10 vol.%C272, pH = 6, time 7 min), the pH (10 vol.%C272, O/A = 1:1, time 7 min), Time (10 vol.%C272, pH = 6, O/A = 1:1).



The effects of pH at the reaction endpoint of precipitation and the molar ratio of DMG to Ni on the precipitation effect are explored. The results are shown in Fig. 6 of support materials:

As can be seen from Fig. 6-a, the precipitation rate of nickel rises continuously with the molar ratio of DMG to Ni. When the molar ratio of DMG to Ni is 2:1, the precipitation rate of nickel rises to 99.63 %, and there is no significant change in the precipitation rate of nickel when the molar ratio of DMG to Ni continues to increase, and the loss rate of the other three metals increases slightly, mainly because the more precipitate there is, the more other metal ions are entrained. Therefore, the optimum molar ratio of DMG to Ni is 2:1, this is also in consistent with the theoretical proportions of the complex compound, with almost no dimethylglyoxime residues, in order to save cost, DMG and NiSO₄ can be recovered by acid leaching and recrystallization of the precipitate [35]. The influence of pH on nickel precipitation rate is shown in Fig. 6-b, it can be seen from Fig. 6-b that the precipitation rate of nickel increases significantly with the increase of pH, mainly because as the pH increased, it facilitated the ionization of H⁺ on the hydroxyl group and increased the basicity and coordination ability of the nitrogen atom, which in turn increased its complexation ability with nickel. When pH = 5, the precipitation rate exceeds 99 %, and the precipitation rate changes little when the pH continues to increase, so the optimal pH of precipitated nickel is 5.

3.3.2. Effect of different experiment parameters on metal extraction rate

The effects of volume fraction of P204 and C272, oil-aqueous ratio (O/A), pH of aqueous phase and shaking time on metal extraction rate are explored. The results are shown in Fig. 7:

It can be seen from Fig. 7-a that an increase in the volume fraction of P204 and O/A contributed to the extraction of manganese, which indicated that the extraction rate was influenced by the volume fraction of P204 and O/A. After the volume fraction of P204 increased to 10 vol% and O/A increased to 3:1, the extraction rates of manganese are 98.13 % and 98.63 % respectively, almost completely extracted, while extraction rates of cobalt and lithium are relatively low, which is conducive to the separation of manganese and cobalt/lithium. The continuous increase in the volume fraction of P204 and O/A led to the co-extraction of cobalt into the organic phase, which made it difficult to separate manganese from lithium/cobalt, while the system became viscous and the phase separation time was prolonged. The effects of aqueous pH and shaking time on the P204 extraction of manganese were relatively small, indicating that manganese was preferentially extracted in this P204 system and the reaction tended to be complete within a short period of time. Lithium was not easily co-extracted into the organic phase in the P204 system, indicating that the divalent metal was preferentially extracted over lithium, which is consistent with the previous study [2]. Considering comprehensively, the optimal extraction conditions for the separation of manganese and lithium/cobalt metals with P204 are as follows: P204 of 10 vol%, O/A of 3:1, aqueous phase pH of 3.5 and shaking time of 10 min, the optimum extraction rate of manganese was 99.35 %.

As can be seen from Fig. 7-b that an increase in the volume fraction of C272, O/A, pH and shaking time all contributed to the extraction of cobalt. When the volume fraction of C272 was increased to 10 vol%, O/A to 1:1, pH to 6 and time to 7 min, the extraction of cobalt tended to be complete, and there was no significant change in the extraction rate of cobalt when the variable values were continuously increased; lithium was not easily co-extracted into the organic phase in the C272 system, but the lithium extraction was greatly influenced by O/A, when O/A exceeded 1:1, the extraction rate of lithium gradually increased, which was not conducive to the separation of cobalt and lithium. Therefore, the optimum experimental conditions for cobalt extraction with C272 are as follows: C272 of 10 vol%, O/A of 1:1, aqueous phase pH of 6 and shaking time of 7 min, the extraction rate of cobalt was 99.95 %.

For the leachate in 3.2, the above operation was carried out under

Table 4
Changes of metals content in each treatment stage.

Treatment	Metals			
	Ni	Co	Mn	Li
Leachate (g/L)	20.150	8.645	11.610	2.736
Metal content after nickel removal (g/L)	0.075	8.109	10.971	2.639
Metal content after manganese extraction (g/L)	/	7.439	0.071	2.550
Metal content after cobalt extraction (g/L)	/	0.004	/	2.516

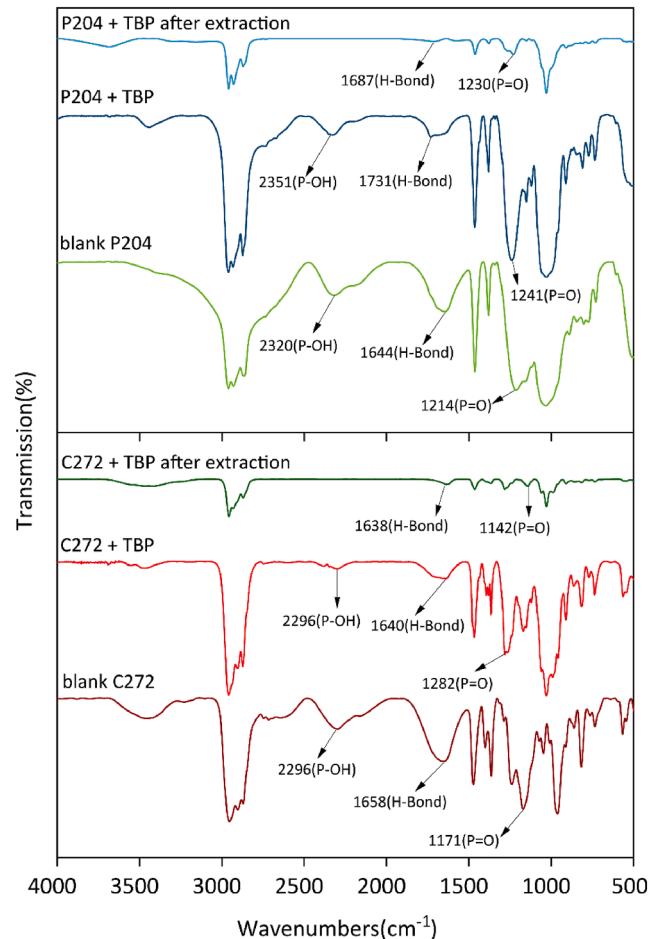


Fig. 8. Infrared spectra of the extraction process of P204 and C272.

optimum conditions and the variation in metal content at each treatment stage is shown in Table 4:

3.3.3. Extraction mechanism

Fourier transform infrared spectrometer is used to analyze the changes of chemical bonds of organic phase before and after extraction, and determine the reaction mechanism of extraction process, as shown in Fig. 8:

It can be seen from Fig. 8 that the characteristic peaks' positions of blank P204 and blank P204 + TBP are slightly different. After the addition of TBP, P=O, P—OH and dimer hydrogen bonds all move to the high wave and the peak intensity weakens, which may be caused by the pairing between P204 and TBP, so the symmetry of P204 changes and the formation of hydrogen bond of P204 dimer is impeded. The apparent disappearance of the P—OH bond after extraction was due to the cation exchange reaction between P—OH and manganese ions, which was converted to P—O—Mn, which fully confirmed the above extraction mechanism. After extraction, the P=O bond moved from 1241 cm⁻¹ to

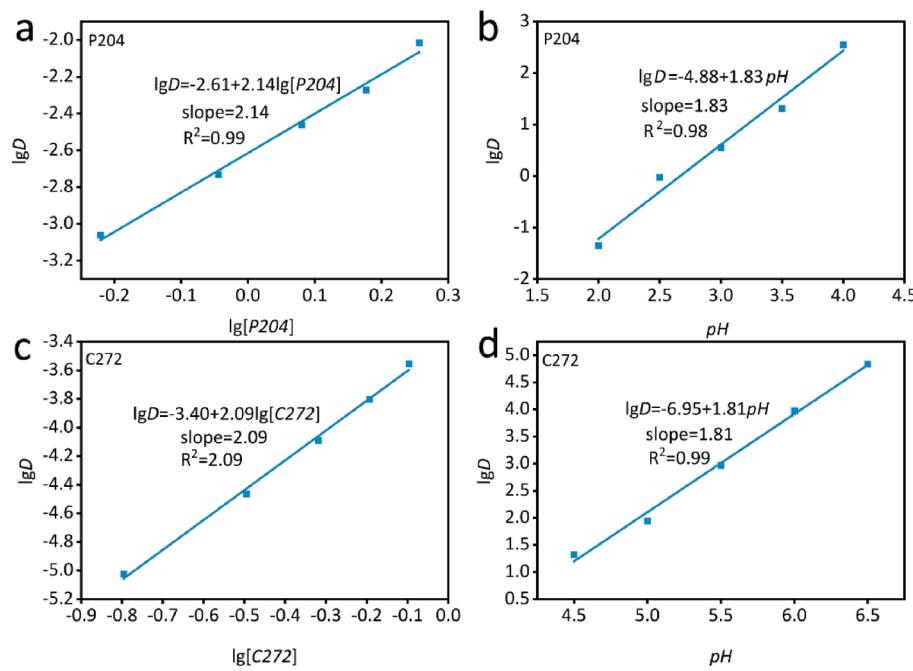


Fig. 9. The slope analysis P204 and C272 extraction.

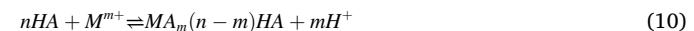
1230 cm⁻¹, and the peak strength decreased significantly, which indicates after extraction, the manganese ion reacts with P=O to generate P=O—Mn, which reduces electron cloud density and vibration frequency of P=O, and is beneficial to extraction. Moreover, P=O appears shoulder peak at the low wave, which fully demonstrates that P=O and Mn²⁺ exist a coordination reaction.

Infrared spectra of cobalt extracted by C272 are shown in Fig. 8. The stretching vibration of P=O of blank C272 at 1171 cm⁻¹, after TBP is added, the stretching vibration at 1282 cm⁻¹, obviously moving towards higher wave, and the peak intensity is significantly reduced, which is due to the coordination of TBP, the symmetry of C272 is changed and P=O dipole moment is changed; The hydrogen bond formed by C272 dimer was significantly shifted from 1658 cm⁻¹ to 1640 cm⁻¹ after the addition of TBP, and the peak strength weakened, indicating that the addition of TBP hindered the formation of C272 dimer hydrogen bond. At 2296 cm⁻¹, the characteristic peak of P—OH appeared, after mixing with TBP, the peak position remained unchanged and the peak intensity decreased significantly, because C272 paired with TBP resulted in the reduction of C272 free molecules and the decrease of P—OH intensity. After extraction, the position of P=O changed from 1282 cm⁻¹ to 1142 cm⁻¹, obviously moving towards the lower wave, indicating that after extraction, Co²⁺ coordinated with P=O to generate P=O—Co, which reduced the electron cloud density of P=O and made the vibration frequency of P=O decreased, that's conducive to extraction; The characteristic peak of P—OH did not appear in the infrared spectrograph after extraction, because P—OH reacted with Co²⁺ and became P—O—Co, which fully confirmed extraction of cobalt by C272 is a cation exchange reaction.

The slope method (also known as Slope Analysis) is widely used and is particularly suitable for the study of complex extraction systems. The essence of the slope analysis is to treat the extraction process as a single chemical reaction and to determine the constant ratio of the chemical reaction by applying the mass action principles. D and the concentration of [HA_(org)]_J, D and pH under different equilibrium conditions can be determined by an isothermal extraction distribution equilibrium experiment. The values of m and n can be determined by plotting lgD against lg[HA_(org)]_J, lgD against pH for the isothermal extraction equilibrium reaction and performing a linear fit. The resulting m and n are then brought into the equation to determine the constant ratio

relationship for the extraction reaction, and the extraction mechanism is further confirmed [30].

According to the result of experiment, TBP, as a modifier, did not participate in the extraction reaction. Therefore, the reaction of P204, C272 extract manganese and cobalt is as follows [20]:



Where M is the metal ion, m is the valence state of the metal ion, HA is the organic extractant, and n is the molecular number of the organic extractant participating in the reaction.

According to the calculation formula of the chemical equilibrium constant, the chemical equilibrium constant K and partition ratio D can be calculated from (10):

$$K = \frac{MA_m(n-m)HA + [H^+]^m}{[HA]^n \times [M^{m+}]} \quad (11)$$

$$D = \frac{MA_m(n-m)HA}{[M^{m+}]} \quad (12)$$

It can be obtained from equations (11) and (12):

$$K = D \frac{[H^+]^m}{[HA]^n} \quad (13)$$

Take logarithms on both sides of formula (13) to obtain:

$$\lg D = \lg K + n \lg [HA] + m \lg H^+ \quad (14)$$

According to Equimolar method, lgD-lg[HA], lgD-pH are made, as shown in Fig. 9:

As can be seen from Fig. 9-a, the slope of lgD-lg[HA] is close to 2, which means that 2 P204 molecules are required to extract one manganese ion, so n is 2; Fig. 9-b shows that the slope of lgD-pH is approximately 2, which means that extracting one manganese ion releases 2H⁺, so m is 2. Therefore, it shows that the mechanism of P204 extracting manganese is a cation exchange reaction. Similarly, the slopes of lgD-lg [C272] and lgD-pH are also approximately 2, which means that extracting cobalt requires 2 C272 molecules and releases 2H⁺, indicating that extracting cobalt with C272 is also a cation exchange reaction.

In conclusion, the mechanism of extraction of manganese and cobalt

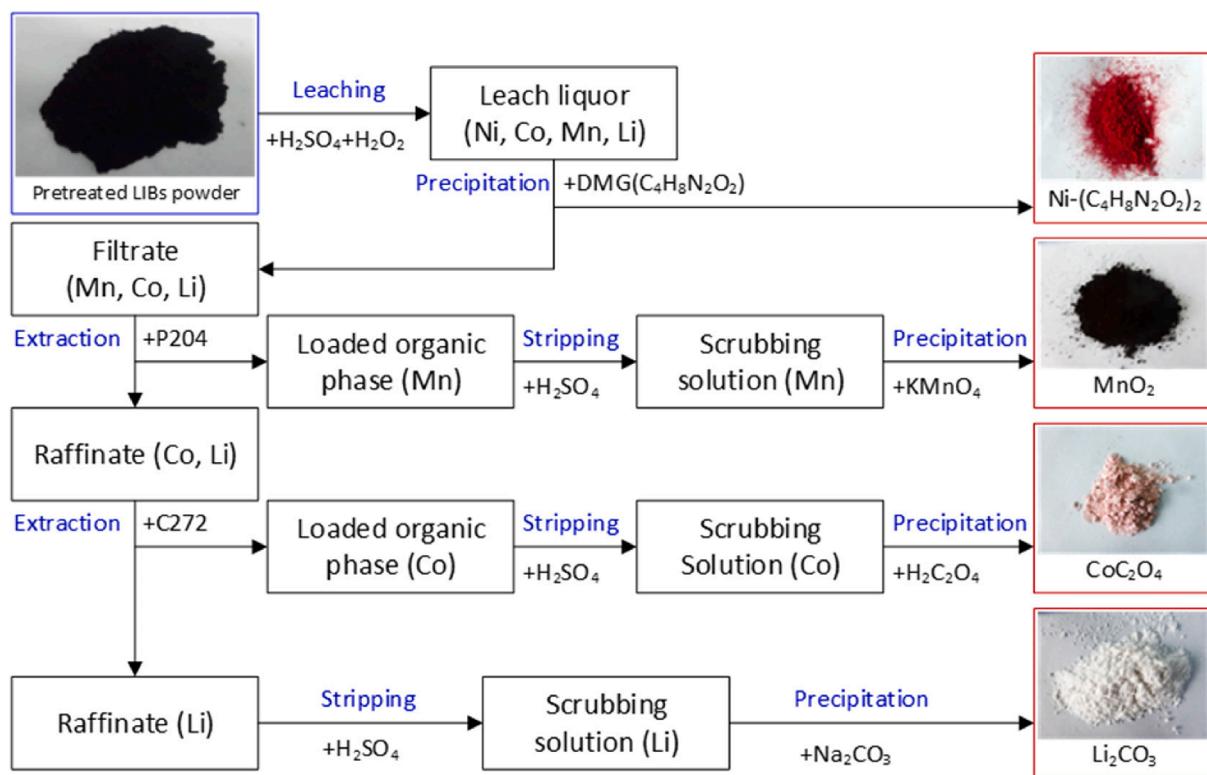


Fig. 10. The flow chart of metal recovery.

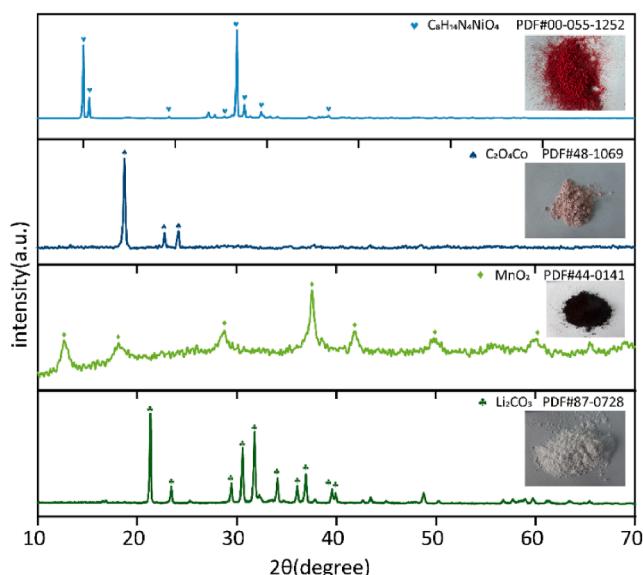
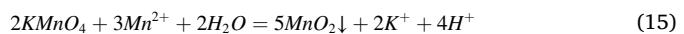


Fig. 11. XRD characterization of precipitation products.

by P204 and C272 is a cation exchange reaction. The metal ions are exchanged with H^+ in P-OH, the characteristic functional group of the organic solvent. There is also a coordination reaction between trace metal ions and the P=O of the organic solvent. The blank organic phase after stripping can be reused by saponification.

3.3.4. Metals recovery

The manganese and cobalt ions loaded with organic phase are washed and stripped with dilute sulfuric acid, and then the manganese, cobalt and lithium are recovered in the form of potassium permanganate, oxalic acid and sodium carbonate. The reactions are as follows:



The flow chart of metal recovery is shown in Fig. 10.

The XRD characterization of the recovered products is shown in Fig. 11. The XRD characteristic peaks of precipitated products of the three metals are consistent with the standard card, indicating that the crystallization of the precipitated products is relatively complete and the purity is high, in addition, as shown in Table 5, ICP quantitative analysis also indicates that the metal contents of the sample are close to that of the standard sample, and the product purity is high. The precipitation rates of manganese, cobalt and lithium are 99.87 %, 95.83 % and 99.83

Table 5
Content of precipitated products.

Precipitate	Element								
	Ni	Co	Mn	Li	Al	Fe	Cu	Na	K
CoC_2O_4	0.003	31.74	0.001	0.002	0.001	0.003	0.002	0.004	0.001
Li_2CO_3	0.003	0.006	0.001	97.64	0.002	0.001	0.001	0.02	0.002
MnO_2 (Grade 4)	0.005	0.002	55.83	0.003	0.001	0.002	0.001	0.01	0.03

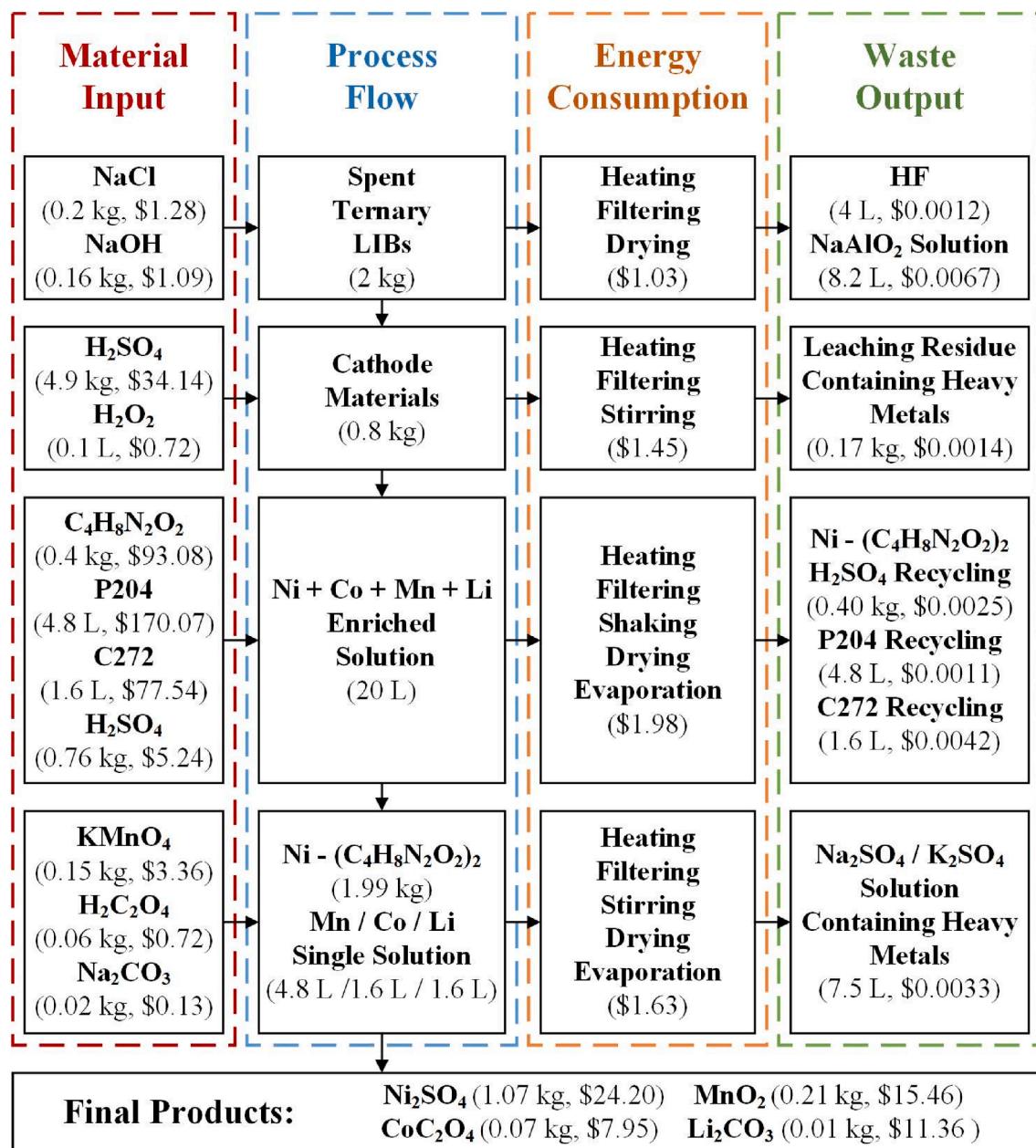


Fig. 12. Economic analysis of the whole process.

% respectively. The wastewater after metals precipitation is mainly sulfuric acid waste liquid containing a small amount of heavy metal ions, which can be treated by the lime neutralization method [40], through the traditional lime neutralization method, the heavy metals can be precipitated to form hydroxides and removed, and the filtrate can be reused after treatment.

After acid leaching - selective precipitation - solvent extraction - precipitation recovery, the nickel, cobalt, manganese and lithium in the wasted ternary lithium batteries are separated and recovered one by one, a technical route for the separation and recovery of lithium nickel cobalt manganese from wasted lithium-ion battery cathode materials is proposed. Compared with a single method, the combined use of several methods can achieve efficient separation and recovery of metals from spent ternary LIBs, in addition, the process of combined selective precipitation-solvent extraction method to separate and recover metals from spent ternary LIBs was optimized to minimize the loss of metal ions, and organic solvents and DMG in the process can be recovered and

reused, which is beneficial to the environment and can reduce cost. The recovery rates of nickel cobalt manganese lithium for the whole process were calculated as 96.84 %, 81.46 %, 92.65 % and 91.39 % respectively.

3.4. Economic analysis

Fig. 12 shows the flow chart of nickel, cobalt, manganese and lithium recovery from spent ternary LIBs, as well as the material input, energy consumption and waste output involved in the whole process. The largest proportion of material cost used in the whole process is DMG (\$93.08), P204 (\$170.07) and C272 (\$77.54), but the complex formed by DMG and nickel can be regenerated in the form of DMG and nickel sulfate by acid leaching, dissolution and recrystallization, and the used P204 and C272 can also be re-saponified and reused, therefore, the costs of the three materials is basically negligible, the overall material cost is \$46.68. In addition, the energy consumption and waste treatment of the process are \$6.09 and \$0.02 respectively, the cost of waste treatment is

relatively low because most of waste was reused as much as possible to reduce the environmental impact, and the remaining acidic wastewater was to be neutralized with conventional lime, with the full cost calculated at \$52.79. Based on the market price, the total selling price of the recycled products is \$58.97, therefore, the net profit of recycling 2 kg of spent ternary LIBs is \$6.18.

4. Conclusion

In this study, nickel, cobalt, manganese and lithium in the cathode power of wasted ternary lithium-ion battery were leached by $H_2SO_4 + H_2O_2$, the reaction was carried out for 60 min at 2.5 mol/L H_2SO_4 , 5 vol % H_2O_2 , 25 ml/g liquid to solid ratio and a temperature of 50 °C, and the optimum leaching rates are 97.20 % Ni, 99.12 % Co, 99.23 % Mn and 99.54 % Li, respectively. The leaching kinetics analysis shows that the leaching reaction is mainly controlled by the surface chemical reaction and diffusion of solid-phase product layer, and the diffusion of solid-phase product layer is dominant. The optimum precipitation rate of nickel precipitated by DMG is 99.63 %. Manganese and cobalt were extracted in steps with P204 and C272 respectively, the optimum extraction conditions for the extraction of manganese are 10 vol% P204, O/A3:1, pH 3.5 and the time of 10 min, and the optimum extraction rate of manganese was 99.35 %; The optimum experimental conditions for the extraction of cobalt by C272 are as follows: the 10 vol% C272, O/A 1:1, pH 6 and the time of 7 min, and the extraction rate of cobalt was 99.95 %. The slope method and FT-IR analysis of the extraction mechanism is cation exchange reaction between metal ions and H^+ in $P-OH$ of organic solvent occurs, and also occurs the coordination between $P=O$ and metal ions. Finally, dilute H_2SO_4 was used to strip the loaded organic phase, and Mn^{2+} , Co^{2+} , Li^+ were recovered by precipitation with $KMnO_4$, $H_2C_2O_4$ and Na_2CO_3 . The recovery rates of metals for the whole process were calculated as 96.84 %, 81.46 %, 92.65 % and 91.39 % respectively, and a technical route for separation and recovery of nickel, cobalt, manganese and lithium from waste ternary lithium-ion batteries was optimized, the DMG and extractants can be recycled and reused which is beneficial to the environment and cost.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

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