



## Separation and recovery of metal values from leach liquor of waste lithium nickel cobalt manganese oxide based cathodes



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### ABSTRACT

In this study, a hydro-metallurgical process has been proposed to separate and recover valuable metals from citric acid leach solution of waste lithium nickel cobalt manganese oxide based cathodes. Nickel, cobalt, manganese and lithium were effectively separated and recycled by a combined method of selective precipitation and solvent extraction. First, about 98% of nickel was selectively precipitated by dimethylglyoxime reagent under conditions of equilibrium pH of 6 and molar ratio of Ni<sup>2+</sup> to dimethylglyoxime of 0.5, with little loss of other metals. Then about 97% of cobalt was precipitated by ammonium oxalate and recovered as CoC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O under conditions of equilibrium pH of 6, reaction temperature of 55 °C and molar ratio of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> to Co<sup>2+</sup> of 1.2. The recovery of manganese was conducted by solvent extraction method using D2EHPA with 70–75% saponification rate. About 97% of manganese was extracted under optimal experimental conditions and recovered as MnSO<sub>4</sub> after stripped with sulfuric acid solution. The McCabe–Thiele isotherm indicated that three extraction stages were needed for complete extraction of manganese at specific extraction condition. Finally, about 89% of lithium was precipitated and recovered as Li<sub>3</sub>PO<sub>4</sub> by 0.5 mol L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> solution. This combined hydro-metallurgical recovery process is a relatively simple and environment-friendly route, which all metal values in the leach liquor can be effectively separated and recovered and both dimethylglyoxime and D2EHPA can be recycled and re-used.

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### 1. Introduction

Since lithium-ion batteries (LIBs) were firstly available on the market from Sony Corp. in early 1990s, LIBs have been widely used not only in portable equipments, such as mobile devices, personal computers, and video cameras but also in hybrid- and electric-vehicles and other modern-life appliances [1,2]. Their desirable characteristics, such as modest size and weight, high cell voltage, low self-discharge rates and high energy density, may make LIBs an alternative to reduce the current dependence on fossil fuel resources [1–4]. Their extensive application in nomadic technology market and hybrid- and electric-vehicles industry has greatly stimulated the production and consumption of LIBs. However, the consequence of the expansion of LIBs usage and the reduced life of LIBs will be an increased demand for the disposal of spent LIBs in the forthcoming years [2–6]. They are usually comprised of valuable metals, organic chemicals, plastics, etc., varying from different

manufacturers and different types of batteries, and the most valuable part of spent LIBs is the cathode material which contain high valued nonferrous metals, such as cobalt, and nickel [7]. Therefore, sustainable recovery of valuable metals would be necessary towards metals recycling of spent LIBs to alleviate the depletion of nonferrous metal resources and the impact of environmental pollution [8].

Pyro-metallurgical processes are commonly used in industry for the recovery of valuable metals from spent batteries with high efficiency and high productivity [9]. These processes, however, involve some defects such as materials loss, hazardous gases and dust emission and extensive energy consumption [10–13]. Moreover, hydro-metallurgical processes are usually needed to refine the residual alloy into their purer forms (salts, hydroxides, metals). Conversely, hydro-metallurgical process may present an alternative and opportunity to turn spent batteries into pure metals or metal salts with low energy requirement and produce salts as by-products.

So far, numerous processes have been reported for the recovery of valuable metals from leach solution of spent LIBs. According to

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literature, the main technical routes investigated are listed as follows:

- the solvent extraction method [5,11–14];
- the selective precipitation method [1,15,16];
- the electrochemical method [17,18];
- the resin ion exchange method [19];
- other method [20].

Recently, several literature had reported the recovery of cobalt and lithium from lithium cobalt oxide (LiCoO<sub>2</sub>) based batteries using citric acid with reductants [21–24]. As an environment-friendly organic acid, citric acid's superior leaching performances, such as high leaching efficiency, absence of toxic gases, easy natural degradation and relatively low price, may make it a preferable candidate for the leaching reagent [21–24]. In addition, lithium nickel cobalt manganese oxides (Li[Ni<sub>x</sub>Co<sub>1–2x</sub>Mn<sub>x</sub>]O<sub>2</sub>), especially LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, shows better performances such as higher reversible capacity, improved thermal stability, lower toxicity and lower cost, over Li–M (M = Ni, Co, Mn) oxides [25].

However, as a promising cathode material, the separation and recovery of valuable metals from the citric acid leach solution of lithium nickel cobalt manganese oxides based cathodes were rarely reported. Table 1 lists the comparison of separation processes of sulfuric and citric acid system from cobalt-bearing waste studied by Ma et al. [26], in terms of separation method, product obtained and recovery percentage. In sulfuric acid media, pure Co(OH)<sub>2</sub> could be obtained with a recovery percentage of 64%. While the obtained product is a mixture of CoFe<sub>2</sub>O<sub>4</sub> and CuO in citric acid system, which further separation and purification operation may be necessary to obtain purer cobalt product. In addition, crystallization and calcination processes involved in citric acid system may discourage the recovery process due to extensive energy consumption. Hence, it is necessary to develop an effective and sustainable recovery process for the separation and recovery of valuable metals from citric acid leach liquor of waste lithium nickel cobalt manganese oxide based cathodes.

Therefore, this work is focused on the separation and recovery of metal values (nickel, cobalt, manganese and lithium) from leach liquor of waste LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode material from spent lithium nickel cobalt manganese oxide based lithium-ion batteries after pretreatment (discharging, dismantling, acid leaching, etc). In this study, a hydro-metallurgical recovery process was proposed to separate and recover metal values from the citric acid leach solution by a combined method of selective precipitation and solvent extraction. First, nickel was selectively precipitated by dimethylglyoxime reagent. The red precipitate was then dissolved with hydrochloric acid solution. Ni<sup>2+</sup> and dimethylglyoxime reagents were separated and recovered as NiCl<sub>2</sub> solution and white powder of dimethylglyoxime respectively. Then cobalt was selectively precipitated by ammonium oxalate solution and recovered as cobalt oxalate hydrate. Finally, the separation of manganese and lithium was carried out by solvent extraction method. Manganese was extracted by organic extractant (D2EHPA) and recovered as MnSO<sub>4</sub> after stripping with sulfuric acid solution. The remaining lithium could be recovered as Li<sub>3</sub>PO<sub>4</sub> by Na<sub>3</sub>PO<sub>4</sub> solution.

## 2. Experimental

### 2.1. Materials and reagents

In this study, the leach solution investigated was obtained by batch dissolving quantified waste cathode materials (5 g) in citric acid and H<sub>2</sub>O<sub>2</sub>, after pretreatment of spent LIBs and peeling off aluminum foil. A small amount of the solution (2 ml) was drawn out and analyzed the contents of Ni, Co, Mn and Li in leach liquor by inductively coupled plasma optical emission spectrometer (ICP-OES Optima 2100 DV, Perkin Elmer instruments, U.S.A.). Table 2 exhibits the metals contents in the leach solution.

The organic extraction reagent di(2-ethylhexyl) phosphoric acid (D2EHPA, 95.7% in purity) used in this study was purchased from Luoyang Aoda Chemical Co., Ltd. (Luoyang, China) with 70–75% saponification rate. All the other chemical reagents used in the experiments were of analytical grade and all the solutions at specified concentrations were prepared and diluted with deionized water.

### 2.2. Recovery of nickel and cobalt

As high valued metals, the recovery of nickel and cobalt was performed by selective precipitation method in a 250 mL three-necked bottle. There are 4930, 5837, 5269 and 1248 mg/L Ni, Co, Mn and Li in the leach liquor. And a water bath, a condenser pipe and an electromagnetic agitator were used for the control of reaction temperature, water evaporation and stirring rate respectively. Red precipitate of nickel–dimethylglyoxime was formed after adding 0.05 mol L<sup>-1</sup> dimethylglyoxime reagent (C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>) to the leach solution. Equilibrium pH and molar ratio of C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> to Ni<sup>2+</sup> were investigated under conditions of reaction time of 30 min at room temperature and stirring rate of 300 rpm. Then the precipitate was dissolved in 1 mol L<sup>-1</sup> HCl solution. C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> was regenerated and re-used as precipitant of nickel, while nickel was recycled as NiCl<sub>2</sub> in the filtrate after filtration.

The separation of cobalt from the leach solution was also conducted by selective precipitation method—through the addition of ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) solution. There are 4837, 4569 and 819 mg/L Co, Mn and Li in the leachate. Cobalt was precipitated as CoC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O after filtration and drying. Effects, such as equilibrium pH, molar ratio of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> to Co<sup>2+</sup> and reaction temperature, were investigated to obtain the appropriate precipitation conditions. The precipitation efficiency can be calculated according to Eq. (1):

$$P = \frac{C_0V_0 - C_1V_1}{C_0V_0} \times 100\% \quad (1)$$

where  $P$  is the metal precipitation efficiency;  $C_0$  and  $C_1$  are the metal ion concentrations in the solution before and after precipitation;  $V_0$  and  $V$  are the solution volumes before and after precipitation.

### 2.3. Recovery of manganese and lithium

After the recovery of nickel and cobalt, the separation of manganese from the leach solution was conducted by solvent extraction method in a 125 mL separatory funnel. About 3981 and 772 mg/L

**Table 1**  
Comparison of separation processes of sulfuric and citric acid system.

Items	Separation method	Product obtained	Recovery percentage
H <sub>2</sub> SO <sub>4</sub> system <sup>a</sup>	Solvent extraction; precipitation	Co(OH) <sub>2</sub>	About 64% Co, 8% Ni, 93% Mn
H <sub>3</sub> Cit system <sup>a</sup>	Solvent extraction; crystallization/calcination	CoFe <sub>2</sub> O <sub>4</sub> , CuO	About 81% Co, 18% Ni, 92% Mn

<sup>a</sup> Investigated by Ma et al. [26].

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