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Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes

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ABSTRACT

A novel process for extracting transition metals, recovering lithium and regenerating cathode materials based on facile co-extraction and co-precipitation processes has been developed. 100% manganese, 99% cobalt and 85% nickel are co-extracted and separated from lithium by D2EHPA in kerosene. Then, Li is recovered from the raffinate as Li_2CO_3 with the purity of 99.2% by precipitation method. Finally, organic load phase is stripped with 0.5 M H_2SO_4 , and the cathode material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is directly regenerated from stripping liquor without separating metal individually by co-precipitation method. The regenerative cathode material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is micro spherical morphology without any impurities, which can meet with $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ production standard of China and exhibits good electrochemical performance. Moreover, a waste battery management model is introduced to guarantee the material supply for spent battery recycling.

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1. Introduction

Lithium ion batteries (LIBs) have been broadly applied as electrochemical power sources due to their high capacity, excellent cycle performances and high energy density (Zeng and Li, 2014). The tremendous consumption of LIBs has undoubtedly generated large amounts of spent LIBs, resulting in resource waste and environmental pollution (Zhang et al., 2014; Tanong et al., 2016).

Nowadays, the electric vehicle (EV) and plug-in hybrid electric vehicle (PHEV) have attracted extensive attention. However, LiCoO_2 cannot meet HEV and PHEV demands and current prices are too high for a broader use in electric mobility. High prices narrow down its application in electric mobility and therefore the tendency of reducing or even replacing cobalt and nickel in battery active materials is increasingly obvious (Hanisch et al., 2015b). The compositions of alternative materials are different from LiCoO_2 and thus the recycling methods for LiCoO_2 cannot be directly applied in recovering metal values from the alternative materials (e.g. $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$). Meanwhile, the mixture of two or more materials (LiMn_2O_4 , LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, LiNiO_2 and

$\text{Li}_2\text{Mn}_2\text{O}_4$, etc.) is used as cathode material (Chen et al., 2015a), which can reduce the cobalt dosage, cut cost and also enjoys advantages in safety. However, recovering valuable metals from the mixed system of spent LIBs is more difficult.

Attentions have been taken for recovering valuable metals from $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ and the mixed system of spent LIBs. The exhausted cathode materials could be extracted by HNO_3 (Meshram et al., 2016), HCl (Guo et al., 2016), H_2SO_4 (Meshram et al., 2015a) or $\text{NH}_3\text{-H}_2\text{O}$ (Zheng et al., 2016) with the help of H_2O_2 (Huang et al., 2016), NaHSO_3 (Meshram et al., 2015b). Although metal values can be leached with high leaching rate, the similar properties of these metals (such as Mn, Co and Ni) make the metal separation from the leach liquor of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ cathode material or the mixed cathode materials more complicated (Kitao et al., 2005). To recover metals (such as Mn, Co and Ni) from their mixed leaching liquor, a stepwise process involving selective precipitation (Pant and Dolker, 2016) or solvent extraction is always necessary (Provazi et al., 2011). Typically, nickel, manganese and cobalt can be recovered by dimethylglyoxime reagent, cobalt loaded D2EHPA and ammonium oxalate solution, respectively (Chen et al., 2015b).

To shorten metal separation process, we have tried to directly regenerate cathode materials from leach liquor of spent LIBs without separating nickel, cobalt and manganese individually in

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previous work (Weng et al., 2013; Yang et al., 2016a). But unfortunately, the recycling of lithium was ignored. Nowadays, the shortage of lithium resource has become a key problem restricting the development of the high-power LIBs. The demands for high-power LIBs are rapidly increasing with the development of PHEV and EV. A larger number of spent high-power LIBs will be generated and the content of lithium contained in these spent cathode material (around 7.0 wt%) is higher than the lithium grades of some salt lake brines (Li et al., 2016). Therefore, more attention should be paid to the recovery of lithium (Barik et al., 2016; Hanisch et al., 2015a). Meanwhile, if a relation between the recovery of lithium and the regeneration of high value-added products can be established with an efficient technological process, it will enjoy great significance for sustainable development, productivity enhancement and economic benefit improvement of recycling spent LIBs.

In this study, a novel process for extracting transition metals, recovering lithium and regenerating cathode materials has been proposed. The goals of lithium recover and high value-added regeneration can be achieved simultaneously through facile co-extraction and co-precipitation processes. Firstly, nickel, cobalt and manganese in leach liquor of spent LIB were co-extracted and separated from lithium. And then the lithium carbonate was prepared from the raffinate. Finally, new cathode material was directly regenerated from the mixture of nickel and cobalt manganese extract liquor.

2. Materials and methods

2.1. Materials and reagents

The extractant bis-(2-ethylhexyl) phosphoric acid (D2EHPA, P204) and diluent sulfonated kerosene were obtained from Luoyang Zhongda Chemical Co. Ltd. The organic extractants were used without further purification. All other reagents were of analytical purity and deionized water was used to prepare the solutions.

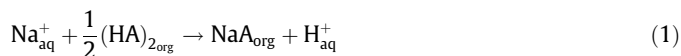
The spent LIBs were supplied by a recycling company of Brunp Recycling Technology Co., Ltd of China. All spent LIBs having poor or no electrochemical performances contain same kind cathode materials ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) (Fig. S1). The cathode collectors were obtained from spent LIBs by processes of discharging and manual dismantling (Chen et al., 2016). The spent cathode material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and Al foil were separated by thermal treatment as paper reported (Hanisch et al., 2015a; Yang et al., 2016b). The obtained spent cathode materials were leached with sulfuric acid under the condition of hydrogen peroxide. 12.5 g obtained spent cathode materials were dispersed in 100 ml mixed solution of 4 M sulfuric acid and 2 M H_2O_2 at 90 °C for 2 h to leach the metal elements. The leaching efficiencies of Ni, Co and Mn can reach 99%, 99% and 97%, respectively. Impurities such as Al, Cu, Fe and Ca were removed by precipitation and solvent extraction as reported (Joo et al., 2015): the impurities were simply removed by using 4 M NaOH at pH = 4.8, and then these impurities were deeply removed by solvent extraction under the conditions of 10% D2EHPA, 90% sulfonated kerosene, organic and aqueous phase ratio (O:A) 1:2, pH = 2, and extraction time 1.5 min. Finally, the main metal elements contained in the leach liquor were analyzed with ICP-AES, and the obtained results were listed in Table 1.

Table 1
The main metal elements contained in the leaching liquid.

Elements	Li	Ni	Co	Mn
Content (g L^{-1})	1.76	11.51	11.32	9.18

2.2. Solvent extraction

The recovery of Ni, Co and Mn was carried out by solvent extraction method using extractants D2EHPA. After adding sodium hydroxide (1 L pure D2EHPA needs 72.2 g NaOH), 60% of extractant D2EHPA was converted to the sodium salt. The neutralisation reaction equation could be described as follows (Sarangi et al., 1999):



Solvent extraction experiment started from shaking separatory funnel with required O:A at 25 °C. The experiment needs to constantly repeat until the pH value of raffinate remains the same.

The optimal extraction conditions were determined by investigating such experimental conditions as volume content of the organic, equilibrium pH, O:A and extraction time. The investigation of extraction isotherm was aimed at predicting the separation degree and the necessary extraction stages. The extraction efficiency, distribution ratio and separation factors can be calculated according to Formula (2), (3) and (4), respectively.

$$E = \frac{C_1V_1 - C_2V_2}{C_1V_1} \times 100\% \quad (2)$$

$$D = \frac{C_1V_1 - C_2V_2}{C_2V_0} \quad (3)$$

$$\beta = \frac{D_1}{D_2} \quad (4)$$

where E stands for extraction efficiency; C_1 and C_2 for metal concentrations in the aqueous before/after extraction; V_1 and V_2 for aqueous phase volume before/after extraction; D for the distribution ratio, V_0 for organic phase volume after extraction; β for the separation factor, D_1 and D_2 for the distribution ratio of metal 1 and 2.

2.3. Preparation of cathode materials and lithium carbonate

After solvent extraction, the mixed solution of MnSO_4 , CoSO_4 and NiSO_4 and the Li_2SO_4 solution were obtained. By adding pure MeSO_4 ($\text{Me} = \text{Ni, Co or Mn}$) into the obtained MnSO_4 , CoSO_4 and NiSO_4 mixed solution, the molar ratio of $\text{Co}^{2+}:\text{Mn}^{2+}:\text{Ni}^{2+}$ was adjusted to 1:1:1. The precursors $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ were synthesized from stripping liquid after composition adjustment with co-precipitation method. 2 M MeSO_4 ($\text{Me} = \text{Ni, Co or Mn}$) solution (500 ml), 4 M NaOH solution (500 ml) and 1 M $\text{NH}_3\cdot\text{H}_2\text{O}$ solution (500 ml) were added into in a stainless steel cylinder reactor ($\Phi 120 \text{ mm} \times 200 \text{ mm}$) at the same time. The reaction conditions were as follows: pH = 10.5, T = 60 °C. The 1.5 L mixed solution was constantly stirred by a mechanical agitator with the speed of 1300 rpm in the stainless steel cylinder reactor. The diameter of mixing propeller is about 60 mm. The reaction was conducted under the protection of nitrogen at normal pressure. The whole reaction device was firstly blown with nitrogen, and then the nitrogen flow rate was kept at $100 \text{ cm}^3 \text{ min}^{-1}$ to prevent air entering into reactor. Finally, dry the obtained metal hydroxides with a vacuum oven for 10 h under the constant temperature of 80 °C.

Lithium carbonate was prepared by precipitation method. The raffinate was adjusted to make the concentration of 1 M Li through evaporation. The Na_2CO_3 solution of 0.5 M was added to the raffinate with the feed rate of 2 mL/min. The reaction temperature maintained at 80 °C. The precipitated lithium carbonate was firstly filtered, then washed by distilled water to completely remove sulfate and sodium ions and finally dried with a vacuum oven for 10 h.

To regenerate $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials, the obtained precursor $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ and Li_2CO_3 was mixed

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