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A stepwise recovery of metals from hybrid cathodes of spent Li-ion batteries with leaching-flotation-precipitation process

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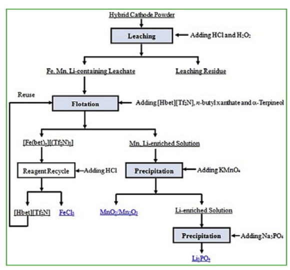
HIGHLIGHTS

- A leaching-flotation-precipitation process is adopted to recycle metals from cathode.
- Li/Fe/Mn ions are released from the cathode using HCl assisted with H_2O_2.
- Fe^{3+} ions are selectively recovered as $FeCl_3$ from the leachate in the flotation step.
- Mn^{2+}/Mn^{3+} and Li^+ ions are precipitated and separated as MnO_2/Mn_2O_3 and Li_3PO_4.
- The final products could be a source for cathode materials of Li-ion battery.

GRAPHICAL ABSTRACT



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ABSTRACT

The recovering of valuable metals in spent lithium-ion battery cathodes brings about economic and environmental benefits. A stepwise leaching-flotation-precipitation process is adopted to separate and recover Li/Fe/Mn from the mixed types of cathode materials (hybrid wastes of $LiFePO_4$ and $LiMn_2O_4$). The optimal operating conditions for the stepwise recovery process are determined and analyzed by factorial design, thermodynamics calculation, XRD and SEM characterization in this study. First, Li/Fe/Mn ions are released from the cathode using HCl assisted with H_2O_2 in the acid leaching step. The leachability of metals follows the series Li > Fe > Mn in the acidic environment. Then Fe^{3+} ions are selectively floated and recovered as $FeCl_3$ from the leachate in the flotation step. Finally, Mn^{2+}/Mn^{3+} and Li^+ ions are sequentially precipitated and separated as MnO_2/Mn_2O_3 and Li_3PO_4 using saturated $KMnO_4$ solution and hot saturated Na_3PO_4 solution, respectively. Under the optimized and advisable conditions, the total recovery of Li, Fe and Mn is respectively 80.93 ± 0.16%, 85.40 ± 0.12% and 81.02 ± 0.08%. The purity for lithium, ferrum and manganese compounds is respectively 99.32 ± 0.07%, 97.91 ± 0.05% and 98.73 ± 0.05%. This stepwise process could provide an alternative way for the effective separation and recovery of metal values from spent Li-ion battery cathodes in industry.

1. Introduction

Today lithium ion batteries are the major power supply for

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portable electronics and electric vehicles [1,2]. The annual consumption of lithium ion batteries is increased to 6 billion cells in 2015 [3]. The life span of lithium ion batteries is approximately 2–3 years depending on the usage and their quality. The increased reliance of lithium ion batteries in electronic equipment leads to a lot of spent batteries being disposed to the landfills [4]. Spent lithium ion batteries contain organic electrolytes and metals such as ferrum, titanium, aluminum, nickel, cobalt, copper, and lithium [5–8]. The improperly disposing of spent batteries particularly is easy to cause serious environmental problems, such as soil and underground water contamination [7,8]. In order to seeking an approach for recycle and utilization of spent lithium ion batteries, hence, a worldwide study is underway.

The recycling technology of spent lithium ion batteries mainly includes two categories: physical technologies and chemical technologies [9]. Physical processes as pre-treatment steps mainly involve dismantling, crushing, and sieving. Subsequently, the separated electrode powders are further treated to separate the valuable components through a series of chemical processes [9–11]. The recycling of valuable metals in spent batteries can not only save limited metal reserves, but also reduces environmental pollution. Among the components of lithium ion batteries, the active cathode materials that contain Li and other metals are the most valuable for recycling [6,10]. Some processes have been developed for recycling metals from the cathode materials. In the recycling of cathodes, metal components are generally first dissolved into the solution, followed by recovering metal ions from the leachate in different steps [12,13]. Acids such as dilute H_2SO_4, HNO_3 and HCl, are usually employed to dissolve metal ions from the cathode [14–17]. The dissolved metal ions are then separated and recovered by various processes such as chemical precipitation, solvent extraction, and electrochemical process [17–19]. Among these recovering techniques, chemical precipitation is generally used. However, it is not easy to control the target metal to be recovered from the precipitation process. The major reason is that the target metal compound is prone to co-precipitate with other metal salts [20]. This leads to a more-complicated process that is required to further separate the mixed-metal compounds.

Many techniques have already been studied to recover precious metals (including Co, Ni and Cu., et al.) from the cathode of spent lithium-ion batteries [8,19,20]. However, the main recycling routes were focused on a relatively simple spent cathode material. The preparation technologies of lithium ion batteries could change their composition elements, meaning that their electrode materials would certainly be changed continually. Nowadays, the prevalent cathode materials ($LiCoO_2$ and $LiCo_xNi_{1-x}O_2$) are being replaced by some inexpensive Fe/Mn-containing compounds such as $LiFePO_4$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $LiMn_2O_4$ [21–25]. Low-cost metals (Fe/Mn or Li) in spent cathode materials are less important than the precious metals. They can still lead to enormous waste of metal resources and serious environmental risk because of the increasing accumulation of quantity and the improper disposal with a mixing manner in China [2]. Therefore, it is very important to explore new processes to meet the requirements of metals recovering from these kinds of complicated waste cathodes in the future.

The studies of technologies for recycling spent lithium ion batteries are required to be consequently be updated with the rapid development of new kinds of cathode materials. The current recycling process developed for spent lithium ion batteries is very specific, meaning that the process may not be applicable, even if the same cathode materials, but with a different composition. In this study, a leaching-flotation-precipitation recovery process was investigated to separate and recover Fe/Mn/Li metals from the mixed types of waste cathode materials (hybrid powders of $LiFePO_4$ and $LiMn_2O_4$) after the pretreatment of spent lithium-ion batteries (including discharging, dismantling, peeling off aluminum foil and grinding of waste cathode active materials). This work is to illustrate how the stepwise recovery technique can be used to design the process and determine the optimal operating conditions of the recycling process for the cathode materials.

2. Experimental

2.1. Materials and reagents

The hybrid cathode powder was supplied by a local e-waste collection center, China. The chemical composition of the powder is given in Table 1. It shows the presence of 33.45 ± 0.15% Mn along with 4.35 ± 0.05% Li, 17.18 ± 0.12% Fe and 9.36 ± 0.07 P (analyzed by ICP-OES).

The powder was analyzed for the phase identification by XRD (Bruker D8 Discover, Germany). The XRD analysis in Fig. 1 shows the presence of $LiFePO_4$, $LiMn_2O_4$ and graphite as the major constituents in the material. The graphite was expected to be from conductive carbon black and PVDF binder (the important components in Li-ion battery) [26]. The particle size of the cathode powder was determined by the optical microscope equipped with statistical analysis software (ZEISS Axio Scope. A1, Germany). The particle size is found to be < 40 μm and 80% of size distribution being <15 μm.

Hydrochloric acid (HCl, 20 wt% concentration) and hydrogen peroxide (H_2O_2, 30.0 wt% concentration) as leaching reagents, were purchased from Tianjin Aokatet Chemical Co., Ltd., China. Betainium bis(trifluoromethylsulfonyl)imide (ionic liquid structure precipitant), *n*-butyl xanthate (collector) and α-Terpineol (frother) were used as flotation reagents, which were purchased from Sinopharm chemical reagent Co., Ltd., China. Potassium permanganate and sodium phosphate (obtained from Tianjin Aokatet Chemical Co., Ltd., China) were used as metal-precipitators. All reagents were of analytical grade and were used without further purification.

2.2. Stepwise leaching-flotation-precipitation process

The schematic diagram of stepwise recovering of valuable metals from the cathode powder is plotted in Fig. 2.

It can be seen from Fig. 2 that, the stepwise recovery of valuable metals can be divided into acid leaching, ion flotation and precipitation steps. First, ferrum, manganese and lithium are leached from the cathode powder using HCl assisted with H_2O_2. Ferrum can be selectively floated by Hbet][Tf_2N] as [Fe(*bet*)$_n$][(Tf_2N)$_3$] and *n*-butyl xanthate, respectively. The final output of ferrum is $FeCl_3$. Subsequently, manganese is precipitated by $KMnO_4$ as MnO_2/Mn_2O_3. Finally, the leaching liquor is treated with sodiumphosphate (Na_3PO_4) solution to precipitate and recover lithium as Li_3PO_4.

2.2.1. Leaching step

The leaching experiments were done to determine the optimum leaching efficiency of metals. The cathode powder was leached in a 1000 mL three-necked glass flask equipped with a magnetic stirrer, a digital controller unit and a thermostat used for controlling the reaction temperature. In addition, the reactor was provided for a reflux condenser preventing from HCl evaporation, which was

Table 1
Chemical composition of the hybrid cathode powder.

Elements	Li	Fe	Mn	P
Wt %	4.35 ± 0.05	17.18 ± 0.12	33.45 ± 0.15	9.36 ± 0.07