Research progress on recycling technology of waste lithium battery anode materials

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Abstract. In this paper, three kinds of recycling technologies for automotive lithium battery anode materials at home and abroad are introduced, including thermal metallurgy, hydrometallurgy and bio metallurgy. By comparison, the wet process with acid leaching precipitation extraction process has low requirements for equipment and energy consumption, and high leaching efficiency, which is an excellent technology easily introduced in industry.

1. Introduction
In recent years, the state's support for new energy vehicles has been showing a momentum of "thermal insulation". According to the first data of China Automobile Industry Association on September 11, 2018, as of August 31, 2018, the output and sales volume of new energy vehicles in China were 598000 and 594000 respectively, and the cumulative output of power pool reached 38.52gw/h. The output of power batteries increased by 22% compared with 2016. Japan and South Korea are the main producers of lithium-ion power batteries. The scale of China's lithium battery market has expanded rapidly since 2017, while the service life of power battery is only 3-5 years. It is estimated that a large number of scrapped batteries will be produced after 2022. The resource recovery of spent lithium batteries conforms to the environmental, economic and social benefits, and also helps to alleviate the global resource pressure.

2. Recyclable components and recycling processes in lithium batteries
The cell of lithium battery is composed of stainless steel shell, pole ear, positive pole piece, negative pole piece, diaphragm and electrolyte. In addition to the diaphragm and electrolyte, the recyclable component containing metal is nearly 80% [1]. Driven by the national subsidy policy for new-energy vehicles with high mileage, the market share of ternary power batteries far exceeds that of lithium iron phosphate batteries. Co and Ni have relatively high recovery value in the waste ternary battery. Co and Ni are magnetic metals, which can be used in the synthesis of magnetic materials after being recovered from the waste ternary battery. Li has the highest recycling value in waste lithium iron phosphate batteries. The contents of various metals in lithium-ion batteries are shown in Table 1 [2]. The process flow chart of positive electrode material recovery is shown in Figure 1.

Table 1. Main metal content in lithium ion batteries

| Element | Co  | Cu  | Al  | Fe  | Li  |
|---------|-----|-----|-----|-----|-----|
| Content | 15  | 14  | 4.7 | 25  | 0.1 |
3. Fire recovery and wet recovery pretreatment methods
The purpose of pretreatment is to enrich high-value metals for subsequent metal recovery. It includes three processes: discharge, disassembly and electrode material separation. Salt solution discharge is a common discharge method. The battery can be disassembled after being dried by discharge. There are two methods of disassembly: mechanical disassembly and manual disassembly. Fire recovery pretreatment only uses crushed cells. Umicore and Bartec use ultra-hot furnaces to incinerate the pulverized lithium-ion batteries to produce cobalt-nickel alloy and rare earth oxides, while graphite and organic solvents are used as fuel to release energy [3]. The pretreatment of wet recovery technology needs to screen the positive electrode materials from the mixture, soak the positive electrode materials in strong alkali or organic solvent to remove the binder, and then get the positive electrode powder after drying and grinding. With short steps and large processing capacity, the fire recovery technology is suitable for large-scale disposal of various kinds of waste lithium batteries. However, the purity of metal recovered by fire method is low, and the electrolyte is polluted greatly after calcination. Domestic lithium battery recovery technology is mainly wet method, low energy consumption, easy operation and use of reagents, low pollution, its disadvantages are low recovery efficiency, small manual operation.

4. A method for recovering valuable metals from electrode materials
The recovery methods of high price metal of positive electrode materials include fire smelting, wet leaching and biological leaching. All metals in positive active substances can be recovered by the three methods.

4.1. Method smelting
Pyrometallurgy is a process in which the mixture of broken waste lithium batteries is directly roasted to obtain metal elements and their oxides [4]. The temperature depends on the roasting method and the type of metal to be extracted. The high temperature reduction smelting method makes use of the affinity of coke for oxygen is greater than that for Ni, Co and Cu, and directly adds coke as reducing agent into the lithium battery mixture and calcinees to get the metal alloy [5]. However, this method has great defects in Co, Cu and Ni recovery, because it needs to provide high temperature of 1600°C and special
smelting equipment, and the consumables and energy consumption are large. Ammonium calcination - ammonia solution leaching combined with calcination and wet leaching technology has a good recovery effect for all metals in lithium batteries, and has a small demand for equipment and energy consumption, which can provide a new way of thinking for lithium battery recovery. Thermal metallurgy requires the provision of high temperatures and large equipment suitable for large plants.

### 4.2. Wet leaching

Hydrometallurgy has high practicability in the process of mineral decomposition and extraction, iron and steel smelting, mixture purification, metal preparation and so on. The common reagents of wet leaching are inorganic acids and organic acids. The common leaching agents are \( \text{C}_x\text{H}_y\text{O}_z \), \( \text{C}_2\text{H}_2\text{O}_4 \), \( \text{C}_6\text{H}_8\text{O}_7 \), \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \) and \( \text{HNO}_3 \). The types of leaching metals and leaching rates are shown in Table 2.

| Name          | Chemical expression | Type of cathode material | Condition                                                                 | Metal type and leaching rate |
|---------------|---------------------|--------------------------|---------------------------------------------------------------------------|-----------------------------|
| Malic acid    | \( \text{C}_4\text{H}_6\text{O}_5 \) | \( \text{LiNiCoMnO}_2 \) | Time:30min | Li, 98.9%  
Temperature:80°C | Co, 94.3%  
Acid concentration:1.2mol/L | Ni, 95.1%  
Volume ratio(liquid/liquid):1.5%  
Volume ratio(solid/liquid):40g/L | Mn, 96.4% |
| Oxalic acid   | \( \text{C}_2\text{H}_2\text{O}_4 \) | \( \text{LiCoO}_2 \) | Temperature:80°C | Li, 98%  
Acid concentration:1mol/L | Co, 98% |
| Citric acid   | \( \text{C}_6\text{H}_8\text{O}_7 \) | \( \text{LiCoO}_2 \) | Time:120min | Co, 96%  
Temperature:70°C | Acid concentration:1mol/L  
Volume ratio(solid/liquid):30g/L |
| Sulfuric acid | \( \text{H}_2\text{SO}_4 \) | \( \text{LiNiCoMnO}_2 \) | Time:120min | Li, 94.63%  
Temperature:70°C | Acid concentration percentage:10%  
Stirring rate:400r/min  
Volume ratio(solid/liquid):1:5 |
| Phosphoric acid | \( \text{H}_3\text{PO}_4 \) | \( \text{LiNiCoMnO}_2 \) | Time:60min | Li, 100%  
Temperature:60°C | Co, 96.3%  
Acid concentration:2mol/L | Ni, 98.8%  
Volume ratio(solid/liquid):50g/L  
\( \text{H}_2\text{O}_2 \) volume percentage:4% | Mn, 99.5% |
| Nitric acid   | \( \text{HNO}_2 \) | \( \text{LiFePO}_4 \) | Time:150min | Li, 91.25%  
Temperature:55°C | Acid concentration:4.5mol/L  
Volume ratio(solid/liquid):1:8 |

#### 4.2.1. Direct leaching

The direct leaching method is that the electrode material after pretreatment is directly dissolved by strong acid or by adding reductant to strong acid. Reducing agent can speed up the leaching reaction rate and prevent the production of acid gases such as \( \text{Cl}_2 \) and \( \text{SO}_2 \). The leaching rate of Co and Li in \( \text{LiCoO}_2 \) by \( \text{HCl} \) can reach 90% even without the auxiliary addition of reducing agent [6].

#### 4.2.2. Alkali dissolution - acid leaching

According to the amphoteric nature of aluminum, the recovery principle is to dissolve aluminum foil with strong alkali first, and let aluminum enter the solution in the form of \( \text{AlO}_2^- \), while \( \text{LiFePO}_4 \) is insoluble in alkali. The insoluble material was filtered out, \( \text{H}_2\text{SO}_4 \) was added to the filtrate, and \( \text{Al}^{3+} \) was precipitated to recover aluminum in the form of \( \text{Al(OH)}_3 \).
4.3. Biological leaching
MISHRA [7] et al. extracted cobalt and lithium from lithium cobaltate by inorganic autotrophic thiobacillus ferrooxidans. The bacteria use the elements sulfur and ferrous ions as energy to produce sulfuric acid, which dissolves the cobalt and lithium in lithium cobaltate, and iron trivalent ions. The results showed that after the thiobacillus ferrooxidans was inoculated to the medium containing ferrous ions and sulfur source, the cobalt and lithium in lithium cobaltate could be rapidly leached, and the cobalt dissolution rate was faster than that of lithium. Compared with the traditional wet process, biological leaching has the advantages of low consumption, high leaching rate, mild leaching conditions, environmental protection and low pollution, which is an ideal development direction for the waste lithium battery recycling industry in the future. However, the current research on bioleached bacteria is not mature, and the incubation period of leached bacteria is long and the adaptability is poor. In order to popularize the biological leaching technology, it is necessary to shorten the breeding period of the strain and domesticate the special strain with high efficiency of adsorbing metal ions.

4.4. Other methods

4.4.1. Ion exchange method. Ion exchange method is the core of ion exchange resin, adsorption, ion exchange process is essentially a process of parsing, first using the cationic exchange resin to parts of the leaching liquid metal cation adsorption onto the resin, and then rinse with corresponding solution resin, so that you can put a metal ion spun off from the leach liquor.

Ion-exchange method is widely used in industry, but ion-exchange resin is easy to pollute, expensive and difficult to regenerate, so this method needs further improvement.

4.4.2. Salting out method. Salting-out method is to add the electrolyte with high solubility to the saturated state of the leachate, and then use the solvent with low dielectric constant to reduce the dielectric constant of the mixture, so as to precipitate the metal ions in the leachate. Jin Yujian et al [8]. Used salting out method to recover cobalt salt from positive leaching solution of lithium ion battery. It was found that when the volume ratio of leaching solution, ammonium sulfate solution and anhydrous ethanol was 2:1:3, the Co²⁺ precipitation rate could reach 92%.

The metal salt products extracted by salting out method have low purity, mixed with other impurities, large defects and few related studies.

4.4.3. Electrolytic process. Electrolysis is the process by which an electric current through an electrolyte solution causes an REDOX reaction at the electrode. The electrolysis method is to apply DC voltage at both ends of the leach liquid of the positive electrode material so that the metal ions in the leach liquid can be reduced to metal elements at the cathode, so as to achieve the separation and enrichment effect. Shen Yongfeng [9] directly electrodeposited cobalt from the impurity removed leaching solution, and the cobalt obtained was in accordance with 1A # of GB 6517 -- 86 Standard, the direct recovery is more than 93%.

5. Conclusion
Compared with the three technologies of fire recovery, wet recovery and biological leaching recovery, the defects of fire recovery are too large, such as high energy consumption and equipment requirements, and low metal recovery. It is difficult to carry out the blue sky and clear water defense plan in China. On the whole, the efficiency of biological leaching recovery is low, and the living conditions of bacteria are strict, which is not easy to popularize in the current situation of relatively scarce biological metallurgy research in China. However, the wet recovery technology is mature, and the leaching rate of Li, Co and other metals is more than 95%. Low cost, low energy consumption, low equipment requirements, wide industrial introduction. The recycling of waste lithium batteries in the next few years should be dominated by wet method. For the whole recycling process of wet method, it is suggested to improve from the following two directions:
1) Improve the efficiency of pretreatment

A big reason for the long wet recovery process is the complexity of pretreatment. After the lithium battery is crushed, it is necessary to screen, sort, remove binder and grind, and the manual operation efficiency is low. If we can develop a mechanical shell-intelligent sorting integrated disassembly equipment, it will greatly improve the battery handling capacity and processing efficiency. This is the key technology point of lithium battery recovery research.

2) Reduce reagent use

The national environmental protection policy requires all industrial enterprises to make waste water treatment and solid waste disposal "harmless, reductive and recyclable". For enterprises that recycle lithium batteries by wet method, the composition of leachate waste liquid needs to be strictly controlled. Therefore, in the process of wet recovery, the types of reagents should be reduced as far as possible, the number of acid anions should be controlled, the extraction agent and acid base should be avoided at the same time, so as to reduce the difficulty of reclaiming tail liquid. At the same time, the mechanism of wet leaching should be studied in depth, and the leaching reagent with high efficiency and easy treatment should be selected.

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