Hydrometallurgy of Lithium Batteries

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Spent lithium batteries can cause pollution to the soil and seriously threaten the safety and property of people. They contain valuable metals, such as cobalt and lithium, which are nonrenewable resources, and their recycling and treatment have important economic, strategic, and environmental benefits. The hydrometallurgy process uses reagents such as hydrochloric acid (HCl), nitric acid (HNO3), sulfuric acid (H2SO4), phosphoric acid (H3PO4), organic acids, and hydrogen peroxide (H2O2) to extract and separate the cathode metals, usually operating below 100 °C, and can recover lithium in addition to the other transition metals.

Keywords: spent cathode material ; lithium-ion battery ; recycling

1. Introduction

The hydrometallurgy process uses reagents such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), organic acids, and hydrogen peroxide (H_2O_2) to extract and separate the cathode metals, usually operating below 100 °C, and can recover lithium in addition to the other transition metals.

This paper reviewed various hydrometallurgy methods developed in the last decade for the recovery of cathode materials for lithium-ion batteries from various battery chemicals, such as LCO, LMO, NCM, and LFP, for the recovery of cobalt, nickel, manganese, and lithium.

As shown in **Figure 1**, hydrometallurgy works to crush and dissolve spent batteries, and then uses suitable chemical reagents to selectively separate the metal elements in the leaching solution, yielding high-grade cobalt metal or lithium carbonate. Hydrometallurgy is more suitable for recycling spent LIBs with single chemical composition, and its equipment investment cost is low, suitable for the recycling of small- and medium-scale spent LIBs. Therefore, this method is widely used at present.

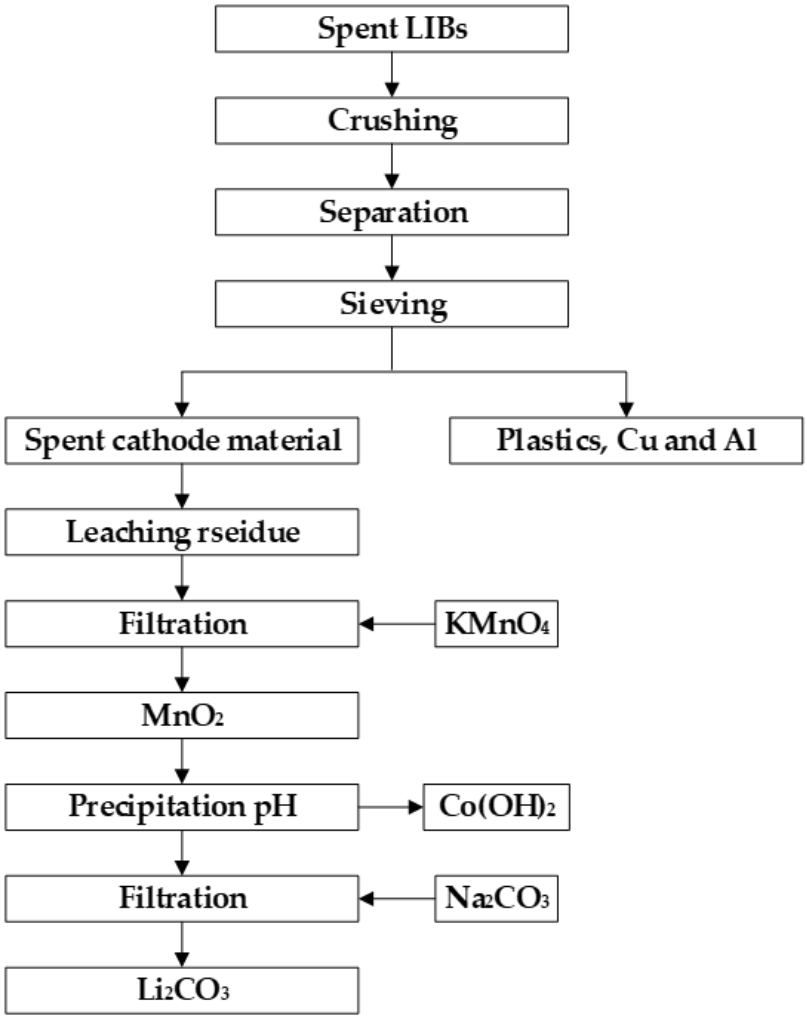

Figure 1. Flow chart of the hydrometallurgical process for recovering battery cathode material.

The valuable metals, mainly lithium, cobalt, and manganese, are extracted from the spent LIB cathode material by the acid leaching process, as concluded in **Table 1**.

Once the valuable metal has been leached, the metal can be recovered through a series of processes including precipitation and solvent extraction. After the leaching process, the recovered material can be reformulated to regenerate the lithium cathode material.

Table 1. Several major acid leach recovery processes.

Leaching Treatment		**Auxiliary Means**	**Leach Temp**	**Leach Efficiency (%)**			**Reference**
Inorganic Leaching Agent	Reducing Agent			Li	Co	Mn	
4 mol/L HCl			80 °C	99	99		[1]
4 mol/L HCl			80 °C	99	99	99	[2]
2 mol/L H_2SO_4				76	76		[3]

2 mol/L H_2SO_4	H_2O_2		80 °C	99	99		[3]
2 mol/L H_2SO_4	H_2O_2				99.9		[4]
4 mol/L H_2SO_4	H_2O_2		70 °C	99	99	100	[5]
2 mol/L H_2SO_4	H_2O_2	ultrasound	30 °C	98.6	94.6		[6]
1 mol/L HNO_3			75 °C	75	40		[7]
1 mol/L HNO_3			75 °C	75	40		[8]
1 mol/L HNO_3	H_2O_2		75 °C	95	95		[9]
1.5mol/L H_3PO_4	$C_6H_{12}O_6$		80 °C	98	100		[10]
1.5mol/L malic acid	grape seed		80 °C	99	92		[11]
10 mol/L HCOOH	H_2O_2		80 °C	99.5			[12]
0.5mol/L ascorbic acid		microwave	125 °C	100	100	100	[13]
57.8%(v/v) lemon juice	H_2O_2	ultrasound	40 °C	100	96	96	[14]
citric acid		microwave				94	[15]
$H_2C_2O_4$-H_3PO_4				100	98.2	100	[16]
H_2SO_4-$FePO_4{\cdot}2H_2O$			80 °C	96	96	96	[17]
0.5 mol/L HCl-0.5mol/L ascorbic acid			90 °C	97.72	97.25		[18]
0.5 mol/LCH_3COOH-0.2mol/L ascorbic acid	bagasse pith	ultrasound	50 °C	98	98	98	[19]

2. Acid Leaching

Most of the active cathode materials in LIBs can be dissolved in acid. Thus, the pretreated electrode material can be leached with an acid solution to achieve separation of the active material from the collector fluid, and then combined with the principle of a neutralization reaction to precipitate and purify the target metal, thereby achieving recovery of high-purity components. Acid solutions utilized by the acid leaching method are conventional inorganic acids, including hydrochloric acid, sulfuric acid, and nitric acid.

The leaching of spent LIBs using inorganic strong acids generates large amounts of spent liquids, as well as some harmful gases such as chlorine gas (Cl_2) and sulfur trioxide (SO_3), which can pollute the environment. These spent liquids are difficult in terms of being treated harmlessly. Researchers have tried to treat spent LIBs using organic acids, such as malic acid, citric acid, oxalic acid, malic acid, and ascorbic acid.

The selective recovery of the metal from the leachate is carried out in multiple steps. First, the Mn in the leachate reacts selectively with the $KMnO_4$ reagent and nears comple-tion, and the Mn is recovered as MnO_2 and manganese hydroxide. Second, nickel in the leachate is selectively extracted by dimethylglyoxime near completion. Third, the pH is adjusted by using a sodium hydroxide solution to selectively precipitate cobalt hydroxide. The addition of a saturated Na_2CO_3 solution precipitated Li_2CO_3. The purity of lithium, manganese, cobalt, and nickel is 96.97 wt%, 98.23 wt%, 96.94 wt%, and 97.43 wt%, respec-tively.

Almost all leaching processes require large amounts of acid and the reducer/oxidizer to achieve the desired leaching results, with acid concentrations ranging from 1.0 M to 3.0 M and high consumption of the reducer/oxidizer (e.g., 2–6 vol% hydrogen peroxide). Furthermore, large amounts of acid or the reductant/oxidizer are practically ineffective for accurate recovery of the target metal, and any unreacted acid or reductant/oxidizer ends up in the effluent and causes secondary contamination. It can be observed that different additives are used to reduce or oxidize the corresponding spent cathode materials (e.g., reductants for LCO and oxidizers for LFP), resulting in a single batch of different types of cathode materials that cannot be recovered synergistically. Therefore, the balance between simplifying the recycling process and saving chemical/energy consumption should be fully considered in order to pursue the efficient and green recycling of different metals from spent LIBs. Unlike conventional leaching processes that require reducing or oxidizing agents, the different redox properties of LCO and LFP are fully utilized to avoid the use of additional reducing or oxidizing agents. Moreover, due to the intrinsic motivation of the redox reactions of LCO and LFP and the transformation of transition metals, especially Fe, the amount of acid is presumed to be significantly reduced. The dissolved metals in the leachate can then be recovered efficiently and selectively as different products depending on the differences in solubility.

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