



Succinic acid-based leaching system: A sustainable process for recovery of valuable metals from spent Li-ion batteries



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HIGHLIGHTS

- A new hydrometallurgical method is designed to recover spent Li-ion batteries.
- Succinic acid is employed as leaching agent and H₂O₂ as reductant.
- Nearly 100% of cobalt and more than 96% of lithium are leached.
- Results are given for fitting of experimental data to acid leaching kinetic models.

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ABSTRACT

A hydrometallurgical method involving natural organic acid leaching has been developed for recovery of lithium and cobalt from the cathode active materials in spent lithium-ion batteries. Succinic acid is employed as leaching agent and H₂O₂ as reductant. The cobalt and lithium contents from the succinic acid-based treatment of spent batteries are determined by inductively coupled plasma-optical emission spectroscopy to calculate the leaching efficiency. The spent LiCoO₂ samples after calcination and the residues after leaching are characterized by X-ray diffraction and scanning electron microscopy. The results show that nearly 100% of cobalt and more than 96% of lithium are leached under optimal conditions: succinic acid concentration of 1.5 mol L⁻¹, H₂O₂ content of 4 vol.%, solid-to-liquid ratio of 15 g L⁻¹, temperature of 70 °C, and reaction time of 40 min. Results are also given for fitting of the experimental data to acid leaching kinetic models.

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1. Introduction

In the 1990s Japan's SONY Corp. developed lithium-ion batteries (LIBs). Compared with nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH), lead-acid, or other secondary batteries, LIBs have found wide application as electrochemical power sources in mobile communications and portable electronic devices due to their high power and energy density, long storage life, low self-discharge rate, high cell voltage, and wide operating temperature range [1]. As a consequence, the world's production of LIBs reached 2.05 billion in 2005 and 4.6 billion in 2010 [2]. In 2012 the output of LIBs increased

to 5.86 billion. The production of LIBs in South Korea, Japan, and China accounted for more than 90% of global output. With the steady development of China's economy, large-scale battery manufacturers in the world have settled in China, which is gradually becoming one of the manufacturing centers of the world's batteries [3,4].

As an important cathode active material, layered LiCoO₂ is usually employed in commercial LIBs. As a result, the consumption of lithium and cobalt has increased dramatically in parallel with the growth in demand for electronic equipment [5–7]. Both lithium and cobalt are regarded as significant strategic metals that are expensive. Cobalt, in particular, is of relatively low abundance and costly. In addition, the tremendous expansion of the LIB market has resulted in a great deal of battery waste. In accordance

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with the classification method formulated by the National Environmental Protection Agency with regard to the solid waste in China, Ni–Cd, Ni–MH, and LIBs and their production waste belong to the category of hazardous waste [8]. What's more, spent LIBs are considered waste electrical and electronic equipment (WEEE), which is defined as hazardous waste by many countries [9]. The continued disposal of spent LIBs without recycling will bring about severe environmental issues on account of their hazardous components, such as metals and electrolyte. Given the need to debase the consumption cost of lithium and cobalt resources and reduce associated environmental problems, effective recycling and recovery processes for lithium and cobalt are required for spent LIBs [10]. A few years after the development of lithium-ion technologies, Contestabile et al. [11] published one of the early papers devoted to the description of a multi-step process for the treatment and recovery of spent lithium primary batteries [4]. Since then, many researchers have applied various methods to the development of recovery processes for spent LIBs batteries [12]. Iizuka et al. [10] separated lithium and cobalt from spent LIBs by bipolar membrane electro dialysis coupled with chelation. Li et al. [13] recycled lithium and cobalt from used LIBs with natural organic acids as leaching reagents. Zhu et al. [14] used sodium citrate and acetic acid to leach the paste components of spent LIBs. It is important to note that, because LiCoO₂ has become the leading and typical cathode active material of LIBs, most of the established recovery technologies have concentrated on the treatment of LiCoO₂.

From an environmental and health viewpoint, hydrometallurgical treatment is the favored technology for recycling of the metals from LIBs compared with pyrometallurgical and biometallurgical processes, because it offers such advantages as low energy consumption, no air emissions, complete recovery of valuable components with high purity, and the minimization of wastewater. [15] Of hydrometallurgical techniques for recovering metals, acid leaching is the most cost-effective, simple, and environmental friendly. Several studies have reported on the leaching of LiCoO₂ cathodic material from spent LIBs using inorganic acids, such as sulfuric (H₂SO₄) [16–19], nitric (HNO₃) [21,22], and hydrochloric (HCl) [20] acids, and natural organic acids, such as citric (C₆H₈O₇) [23], DL-malic (C₄H₅O₆) [15], L-aspartic [12], ascorbic [1], and oxalic acids [5], as shown in Table 1. Table 1 summarized the leaching systems ever applied to recovery of lithium and cobalt from spent LIBs. Different leaching systems possessed various reaction conditions with mostly higher lithium efficiency than cobalt.

Our research is focused on introducing a natural organic acid to develop a leaching system for the recovery of metals from spent LIBs. The advantages of this process are elimination of contamination and low damage to the experimental equipment, as well as easy bio-degradation. Succinic acid is a valuable four-carbon platform chemical and considered as one of the twelve building-block organic compounds with applications in many fields [24]. In this work, we established an acid leaching system using succinic acid and hydrogen peroxide with the purpose of finding optimum reaction conditions for recycling lithium and cobalt from LiCoO₂ cathode material. This recycling process can be advanced beyond the laboratory scale to achieve large-scale reclamation of LIB solid wastes.

2. Experimental

2.1. Experimental procedure

For safety considerations, before dismantling, the spent cells were discharged to avoid potential dangers of short-circuiting or

Table 1
Summary of leaching systems applied to metals recovery from spent LIBs.

Leaching reagents	Reaction conditions	Efficiency (%)	References
Sulfuric acid (H ₂ SO ₄)	2 M H ₂ SO ₄ , 5 vol.% H ₂ O ₂ , 60 min, S/L ratio of 100 g L ⁻¹ , and 75 °C	99.1% Li 70.0% Co	[16]
	6 vol.% H ₂ SO ₄ , 5 vol.% H ₂ O ₂ , 60 min, S/L ratio of 1/30 g mL ⁻¹ and 65 °C	95% Li 80% Co	[17]
Hydrochloric acid (HCl)	2 M H ₂ SO ₄ , 5 vol.% H ₂ O ₂ , 40 min, S/L ratio of 100 g L ⁻¹ , and 75 °C	94% Li 93% Co	[18]
	15 vol.% H ₂ O ₂ , 20 min, S/L ratio of 50 g L ⁻¹ and 75 °C	100% Li 95% Co more than 99%	[19]
Nitric acid (HNO ₃)	4 M HCl, 60 min, S/L ratio of 20 g L ⁻¹ , and 80 °C	Li and Co more than 95%	[20]
	1 M HNO ₃ , 1.7 vol.% H ₂ O ₂ , 30 min, S/L ratio of 20 g L ⁻¹ , and 75 °C	Li and Co	[21]
Citric acid (C ₆ H ₈ O ₇)	2 M HNO ₃ , 60 min, and 80 °C	100% Li 95% Mn	[22]
	1.25 M C ₆ H ₈ O ₇ , 1.0 vol.% H ₂ O ₂ , 30 min, S/L ratio of 20 g L ⁻¹ , and 90 °C	nearly 100% Li more than 90% Co	[23]
DL-malic acid (C ₄ H ₅ O ₆)	1.5 M C ₄ H ₅ O ₆ , 2.0 vol.% H ₂ O ₂ , 40 min, S/L ratio of 20 g L ⁻¹ , and 90 °C	nearly 100% Li more than 90% Co	[15]
Oxalic acid (H ₂ C ₂ O ₄)	1.5 M H ₂ C ₂ O ₄ , 120 min, S/L ratio of 50 g L ⁻¹ , and 80 °C	reaction efficiency more than 98%	[5]
Ascorbic acid (C ₆ H ₈ O ₆)	1.25 M C ₆ H ₈ O ₆ , 20 min, S/L ratio of 25 g L ⁻¹ , and 70 °C	98.5% Li 94.8% Co	[1]
L-aspartic acid (C ₄ H ₇ O ₄ N)	1.5 M C ₄ H ₇ O ₄ N, 4.0 vol.% H ₂ O ₂ , 120 min, S/L ratio of 10 g L ⁻¹ , and 90 °C	60% Li 60% Co	[12]

self-ignition. A flowsheet of the procedure designed for metal recovery is illustrated in Fig. 1.

Firstly, the spent LIBs were manually dismantled to remove the plastic and steel cases that cover the batteries. Secondly, once dismantled the anodes and cathodes were uncurled and separated, the cathode parts were immersed in NMP at 100 °C by ultrasonication for 1 h in order to separate the cathode materials from the aluminum foil effectively. After centrifugation, filtration of the solution and drying of the filtrate at 60 °C for 24 h, a thermal pretreatment was necessary to eliminate impurities, such as carbon and polyvinylidene fluoride (PVDF), in the cathodic active materials. Subsequently, the cathode materials were calcined at 700 °C for 5 h in a muffle furnace and cooled to room temperature. The powders of lithium cobalt oxide were then ground in a planetary ball mill for 2 h to obtain smaller and higher-surface-area particles, a step that was beneficial in increasing the dissolution rate and leaching efficiency. The metal leaching test was conducted subsequently. All leaching experiments were carried out in a 100 mL three-necked and round-bottomed thermostatic Pyrex reactor placed in a water bath with a temperature controller. The reactor was assembled with an impeller stirrer and a reflux condenser to reduce the loss of water via evaporation at a high temperature. Succinic acid in a known concentration and quantity was poured into the reactor. Then, a measured amount of spent LiCoO₂ powders and H₂O₂ solution were added to the reactor, which was followed by agitation by the stirrer. The leaching experiment was conducted under variations in the following conditions: succinic acid concentration (0.25–2.0 mol L⁻¹), amount of H₂O₂ (0–6 vol.%), solid/liquid ratio (5–30 g L⁻¹), reaction time (10–60 min), and temperature (50–90 °C). Finally, after leaching, the product solution and undissolved residue were separated by filtration and washed with distilled water, yielding a pink filtrate and a black residue for analysis.

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