



# Economical recycling process for spent lithium-ion batteries and macro- and micro-scale mechanistic study

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## HIGHLIGHTS

- An economical recycling process for spent lithium-ion batteries is proposed.
- The leaching mechanism is investigated at macro- and micro-scales.
- Environmental and economic analysis of the leaching process is investigated.

## ARTICLE INFO

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Recycle  
 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$   
 Leaching mechanism  
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## ABSTRACT

An economical effective method is developed for recycling spent  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathodes, where more than 98% Li, Co, Ni and Mn can be leached out with different organic acids, and resynthesized to  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . The leaching mechanism is investigated at macro- and micro-scales. The particles undergo a loosening-breaking-shrinking change for two acids, while the FTIR and UV-vis spectra indicate different coordination reactions. The performance of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  resynthesized from the leachate of the acetic acid leaching (NCM-Ac) and maleic acid leaching (NCM-Ma) are compared. The first discharge capacity of NCM-Ma and NCM-Ac at 0.2C are 151.6 and 115.0  $\text{mA h g}^{-1}$ , respectively. The much better performance of NCM-Ma than NCM-Ac results from the different coordination of the two acids in the sol-gel process, where the maleic acid can esterify to establish a stable network to chelate metal ions, while the weak chelation of acetic acid leads to the formation of impurities. The economics analysis including the cost of leaching acid and energy consumption shows that the price of organic acids and reducing agents, short leaching time, low temperature and high-valued products are the effective way to increase recycling and environmental benefits, which shows advantages in terms of resources cost and added value.

## 1. Introduction

High energy density, high voltage, long life span, and low self-discharge have been representative codes for lithium-ion batteries (LIBs) [1,2]. Satisfying human desire for sustainable development and safe energy [3,4], this eco-friendly technique has promoted the prosperity of electronics and electric vehicles (EV). According to the research of OFweek web, in 2015, the production of LIBs over the world has reached 100.75 GWh, of which power batteries accounted for 28.26% [5]. However, widespread use causes a sharp increase of spent LIBs [6]. The impacts on the environment and public health at the end of life stage, i.e., after certain cycles [7], cannot be ignored.

The development of cathode materials for LIBs can be divided into three stages. The first generation, based on  $\text{LiCoO}_2$ , appeared in the

early 1990s, and the next generation, based on  $\text{LiMn}_2\text{O}_4$  and  $\text{LiFePO}_4$ , was commercialized early in 21st century. In response to the high cost of Co and demand of high energy density, Ni-rich based cathodes,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) and  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  (NCM) appeared and is accounting for an increasingly large part of the market [8]. Meanwhile, the value of cathode materials accounts for ~40% of a whole LIB. As a result, it's necessary to pay more attention to the recycling of them.

Researchers have proposed a series of physical and chemical processes for recovering the valuable metals in LIB cathode materials. As shown in Fig. S1, a physical process is often used in the pretreatment stage, e.g., including mechanical separation [9–11], thermal treatment [2,12–14], mechanochemical process [15,16], and dissolution [17,18]. Chemical processes includes leaching, bioleaching [19,20], flotation

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[21,22], solvent extraction [23–25], chemical precipitation [11,26,27] and electrochemical process [28–30]. The leaching process can be divided into inorganic acid leaching such as HCl [31,32], H<sub>2</sub>SO<sub>4</sub> [33], and HNO<sub>3</sub> [34], and organic acid leaching such as citric acid [35–37], D,L-malic acid [8], ascorbic acid [38], succinic acid [39], oxalic acid [6], trichloroacetic acid [40], and iminodiacetic acid [41]. The acid leaching process is a highly effective process to recover the precious metals from the solid materials, and the choice of leaching agents is a key problem, as its not only related to the cost and efficiency, but also influences the following treatments. After chemical treatment, new cathode materials [8,42,43], metal oxide [44] and metal organic frameworks [45] could be synthesized to obtain the maximum values.

In the current studies of chemical recycling processes, researchers have focused more on the efficiency, while ignored the cost and the effects of leaching process on the follow-up treatments. For the industrial applications, low cost, high efficiency and high product value should be balanced for consideration. In this work, we designed an effective and economical recycling process based on leaching and re-synthesis process. Organic acids with different chelation abilities (acetic acid with weak chelation and maleic acid with strong chelation) were chosen as leaching agents to study the leaching performance. The leaching mechanism from the macro to micro scales were investigated by means of kinetics study and spectral analysis. After leaching, the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was resynthesized from the two respective leachate using a sol-gel method. The electrochemical performances of the resynthesized cathode materials were tested and compared. The cost of the leaching process in our study and of previous reported methods were compared.

## 2. Experimental

### 2.1. Leaching of cathode materials

As shown in Fig. 1, the spent LIBs were firstly discharged for safety reasons. After dismantling, the Al foil was dissolved in an alkaline solution. The residue was milled after dried and calcined at 700 °C for 5 h. The obtained materials were leached with acetic acid and maleic acid in a three-necked bottle with a stirrer and a Graham condenser. In this process, 1 g materials were dissolved in 50 mL acid solution.

Experiments were designed to determine the optimal conditions (Table 1). The effects of temperature (30–90 °C), H<sub>2</sub>O<sub>2</sub> volume (0–4 mL), acid concentration (0.5–4 M acetic acid; 0.5–2 M maleic acid), leaching time (30–120 min for acetic acid leaching; 30–75 min for maleic acid) and adding time of H<sub>2</sub>O<sub>2</sub> for acetic acid leaching (5–45 min).

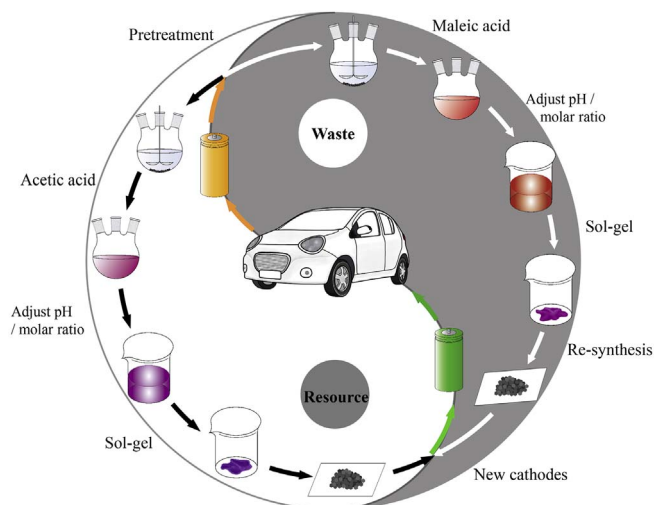


Fig. 1. The concept of the proposed recycling process.

Table 1

Operation conditions of orthogonal experiments for acid leaching process.

Level	Temperature	Maleic acid			Acetic acid		
		Time	Acid	H <sub>2</sub> O <sub>2</sub>	Time	Acid	H <sub>2</sub> O <sub>2</sub>
1	30 °C	30 min	0.5 M	0 mL	30 min	1 M	0.5 mL
2	50 °C	45 min	1.0 M	1 mL	60 min	2 M	1.0 mL
3	70 °C	60 min	1.5 M	2 mL	90 min	3 M	1.5 mL
4	90 °C	75 min	2.0 M	3 mL	120 min	4 M	2.0 mL

### 2.2. Study of kinetics and reaction mechanism of leaching process

The concentration of Li<sup>+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Mn<sup>2+</sup> were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 8300, Perkin Elmer, USA) after leaching for 1, 3, 5, 10, 20, 30, 40, 50, and 60 min at 70 °C, respectively. The reaction residue was examined by scanning electron microscopy (SEM; S-4800, Hitachi, Japan). Fourier Transform Infrared (FTIR) spectra and UV-vis spectra of the leachate after 1, 3, 5, and 60 min were recorded by Nicolet 6700 and UV-2550, respectively.

### 2.3. Re-synthesized of NCM

To maximize the value of the final product, NCM was resynthesized using a simple sol-gel method. Acetic acid and maleic acid acted as chelating agents. The Li<sup>+</sup>: Ni<sup>2+</sup>: Co<sup>2+</sup>: Mn<sup>2+</sup> molar ratios in the leachate under optimal conditions were adjusted to 3.05:1:1:1 by adding CH<sub>3</sub>COOLi, (CH<sub>3</sub>COO)<sub>2</sub>Ni, (CH<sub>3</sub>COO)<sub>2</sub>Co, and (CH<sub>3</sub>COO)<sub>2</sub>Mn. The pH was adjusted to 7, and the leachate was stirred at 80 °C to obtain a gel. A two-stage thermal treatment was then performed. The gel was calcined at 450 °C for 4 h and 900 °C for 12 h in a muffle furnace.

### 2.4. Material characterization and electrochemical performance test of NCM

The NCM synthesized from the leachate of acetic acid leaching (NCM-Ac) and maleic acid leaching (NCM-Mc) were characterized by scanning electron microscopy (SEM; S-4800, Hitachi, Japan) and X-ray diffractometry (XRD; Rigaku, Japan).

The electrochemical performance was tested in CR2025 coin cells. The cathode consists of 80 wt% resynthesized NCM, 10 wt% acetylene black and 10 wt% PVDF. The electrolyte is 1 M LiPF<sub>6</sub> in EC and DMC (1:1 v/v), and the anode is metallic lithium. The discharge capacity and cycle performance were tested by a Land battery test system (Land CT2001A, Wuhan, China) in the potential range of 2.8–4.3 V from 0.2C to 5C.

## 3. Results and discussion

### 3.1. Acid leaching

The data in Table S1(a and b) show that in the leaching process with acetic acid, H<sub>2</sub>O<sub>2</sub> volume has the greatest effect on leaching of the four ions, followed by temperature and acid concentration. The effect of leaching time is not significant. For maleic acid leaching process in Table S2(a and b), temperature influences most, then the H<sub>2</sub>O<sub>2</sub> volume, acid concentration and leaching time.

**Effect of H<sub>2</sub>O<sub>2</sub> volume.** Fig. 2(a) and (b) show the effects of H<sub>2</sub>O<sub>2</sub> volume on the leaching efficiency. For maleic acid leaching, the leaching efficiencies of the four ions increase with increasing of H<sub>2</sub>O<sub>2</sub> volume. However, above 2 mL the change is small and the efficiency is high enough. In terms of the economics, 2 mL of H<sub>2</sub>O<sub>2</sub> is the best choice. By comparison, the leaching efficiencies with acetic acid increase obviously from 0 to 3 mL H<sub>2</sub>O<sub>2</sub>, therefore 3 mL of H<sub>2</sub>O<sub>2</sub> is chosen. In addition, the positive effect of H<sub>2</sub>O<sub>2</sub> is clearly significant, especially in

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