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## Process for recycling mixed-cathode materials from spent lithium-ion batteries and kinetics of leaching

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### ABSTRACT

A “grave-to-cradle” process for the recycling of spent mixed-cathode materials (LiCoO<sub>2</sub>, LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, and LiMn<sub>2</sub>O<sub>4</sub>) has been proposed. The process comprises an acid leaching followed by the resynthesis of a cathode material from the resulting leachate. Spent cathode materials were leached in citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Optimal leaching conditions were obtained at a leaching temperature of 90 °C, a H<sub>2</sub>O<sub>2</sub> concentration of 1.5 vol%, a leaching time of 60 min, a pulp density of 20 g L<sup>-1</sup>, and a citric acid concentration of 0.5 M. The leaching efficiencies of Li, Co, Ni, and Mn exceeded 95%. The leachate was used to resynthesize new LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> material by using a sol-gel method. A comparison of the electrochemical properties of the resynthesized material (NCM-spent) with that synthesized directly from original chemicals (NCM-syn) indicated that the initial discharge capacity of NCM-spent at 0.2 C was 152.8 mA h g<sup>-1</sup>, which was higher than the 149.8 mA h g<sup>-1</sup> of NCM-syn. After 160 cycles, the discharge capacities of the NCM-spent and NCM-syn were 140.7 mA h g<sup>-1</sup> and 121.2 mA h g<sup>-1</sup>, respectively. After discharge at 1 C for 300 cycles, the NCM-spent material remained a higher capacity of 113.2 mA h g<sup>-1</sup> than the NCM-syn (78.4 mA h g<sup>-1</sup>). The better performance of the NCM-spent resulted from trace Al doping. A new formulation based on the shrinking-core model was proposed to explain the kinetics of the leaching process. The activation energies of the Li, Co, Ni, and Mn leaching were calculated to be 66.86, 86.57, 49.46, and 45.23 kJ mol<sup>-1</sup>, respectively, which indicates that the leaching was a chemical reaction-controlled process.

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### 1. Introduction

Since commercialized in 1991, lithium ion batteries (LIBs) have become increasingly attractive as power sources for portable electronic devices and electric vehicles, as they provide advantages of a high voltage, a high specific capacity and a long lifespan (Chen et al., 2015a; Goncalves et al., 2015; Sun and Qiu, 2012). The increased usage of LIBs makes their recycling an urgent requirement. It is predicted that by 2020, 13 828 tonnes of LIBs will need to be recycled in the European Union alone (Träger et al., 2015). The most commonly used cathode materials are based on LiCoO<sub>2</sub> (LCO), LiMn<sub>2</sub>O<sub>4</sub> (LMO), LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM), and LiFePO<sub>4</sub> (LFP). The value of 1 tonne of waste LIBs is \$7708, and the cathode materials comprise \$6101 of the total, as shown in Fig. 1 (Gratz

et al., 2014). The inappropriate management of spent LIBs poses a threat to biological health and to the environment, and wastes resources (Zhang et al., 2014).

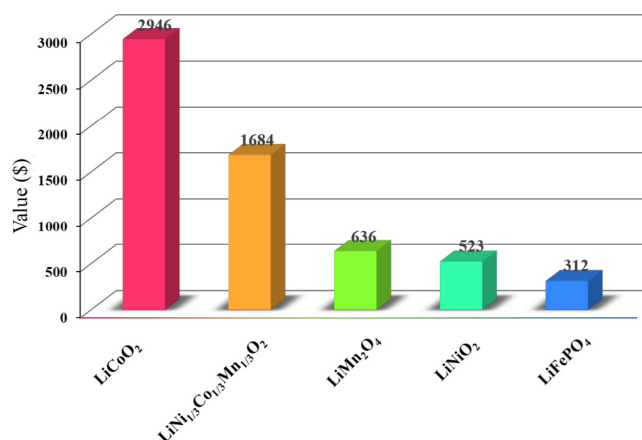
As an important recycling method, hydrometallurgical processes provide a high metal-recovery efficiency with a high purity and less energy consumption compared with pyrometallurgical processes (Zhang et al., 2013). Hydrometallurgical processes usually include pretreatment, leaching, and post-treatment steps (He et al., 2017b).

Pretreatment involves mechanical, dissolution and thermal treatments. Mechanical treatment aims to separate steel shells, cathodes, anodes, and separators (Guo et al., 2016; Meshram et al., 2015). Dissolution by alkaline solution or N-methyl pyrrolidone (NMP) is used to separate active materials from aluminum or copper foils (Meshram et al., 2016b; Nayaka et al., 2016a). Thermal treatment can burn off impurities such as acetylene black, electrolyte, and binder residues (Li et al., 2010a).

For the leaching process, researchers have proposed acid leaching (organic or inorganic acids) and bioleaching methods. Inorganic

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**Fig. 1.** Intrinsic value of cathode materials in 1 tonne of lithium ion batteries. (Georgi-Maschler et al., 2012; Gratz et al., 2014).

acid leaching often results in secondary pollution with toxic gas, so increased attention has been given to environmental-friendly organic acid leaching, as shown in Table 1. Citric acid, tartaric acid, ascorbic acid, oxalic acid, lactic acid, and succinic acid have been used to recycle LiCoO<sub>2</sub> or LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub>. Leaching efficiencies of as high as 98–100% can be achieved. Bioleaching is in its early development, and is a green method to extract metals by using microorganisms. Its low cost and minimal industrial requirements make it a promising method for future use (Zhang et al., 2013).

After the leaching process, chemical precipitation, solvent extraction, electrochemical process, and the resynthesis of new materials are applied to obtain the final products (Chen et al., 2015a; Fan et al., 2016; Lupi et al., 2005; Wang et al., 2016). The first three methods can separate the metals and produce raw materials, such as Li<sub>2</sub>CO<sub>3</sub>. The resynthesis of new cathodes or metal-organic frameworks can yield higher values (Perez et al., 2016).

Most studies to date have focused on the recycle of single spent-cathode materials, which is unsuitable for practical application. Currently, LCO comprises 37.2% of cathodes in the LIB market, followed by NCM (29%), LMO (21.4%), and LFP (5.2%) (Zou et al., 2013). An investigation of recycling processes for mixed materials is therefore practical and critical.

In this work, we investigated a simple and green closed-loop process to recycle spent mixed-cathode materials (LCO, LMO, NCM) from “cradle to grave” which has potential value for practical

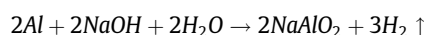
application. After pretreatment, citric acid was used as the leaching medium and H<sub>2</sub>O<sub>2</sub> was used as the reductant to transform powdered spent cathode into an aqueous solution that contains Li<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, and Mn<sup>2+</sup>. NCM was resynthesized directly from the leachate by a simple sol-gel process which exhibited good performance. A new equation for the kinetics of the leaching process was proposed and the investigation of the leaching mechanism provided new insight into the recycling of spent LIBs.

## 2. Experimental

### 2.1. Experimental process

#### 2.1.1. Pretreatment of spent lithium ion batteries

The spent LIBs were 18650 and pouch-type cells. The pretreatment process is shown in Fig. 2. After being discharged in saturated Na<sub>2</sub>SO<sub>4</sub> solution, the spent LIBs were dismantled manually in a fume hood to remove plastic and steel casings. The active cathode materials were separated from the Al foil after immersion in 2 M alkaline NaOH solution for 2 h. The Al foil was dissolved in NaOH according to the following reaction:



After filtration, the residue was dried at 80 °C in a vacuum drying oven for 24 h, and calcined at 700 °C for 5 h in a muffle furnace to burn off the acetylene black, binder, and other organic impurities. Because leaching is an interfacial reaction between the solid and the liquid, the boundary area of the two phases can affect the reaction rate significantly. Therefore, the materials were milled to a fine particle size to increase the contact surface area and to accelerate the reaction rate. The pretreatment process was conducted under sealed conditions to prevent electrolyte decomposition and alkaline gases from leaking into the environment. The mass ratio of spent LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was set to 1:1:1 in this study.

#### 2.1.2. Acid leaching of cathode materials

As shown in Fig. 2, acid-leaching experiments were carried out in a 150-mL three-necked round-bottomed flask equipped with a reflux condenser to avoid loss of water by evaporation. A water bath was used to control the reaction temperature. The solution was agitated by an electrical stirrer. Mixed-cathode material (1 g) was used each time. An orthogonal experiment (Table A.1) was designed to study the influence of five factors on the leaching.

**Table 1**  
Summary of conditions and leaching efficiencies of some organic acids used for the leaching of spent Li-ion batteries.

Ref.	Sample	Leaching agent	Leaching efficiency
Li et al. (2010b)	LiCoO <sub>2</sub>	1.25 M Citric acid 1.0 vol% H <sub>2</sub> O <sub>2</sub>	100% Li, 90% Co
Li et al. (2010a)	LiCoO <sub>2</sub>	1.5 M d,l-malic acid 2.0 vol% H <sub>2</sub> O <sub>2</sub>	100% Li, 90% Co
Li et al. (2012)	LiCoO <sub>2</sub>	1.25 M Ascorbic acid	98.5% Li, 94.8% Co
Sun and Qiu (2012)	LiCoO <sub>2</sub>	1.0 M Oxalic acid	98% Li, 98% Co
Nayaka et al. (2015)	LiCoO <sub>2</sub>	1.0 M Citric acid 0.2 M Ascorbic acid	100% Li, 80% Co
Li et al. (2015)	LiCoO <sub>2</sub>	1.5 M Succinic acid 4.0 vol% H <sub>2</sub> O <sub>2</sub>	96% Li, 100% Co
Zhang et al. (2015)	LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	3.0 M Trichloroacetic acid 4.0 vol% H <sub>2</sub> O <sub>2</sub>	93% Ni, 91.8% Co, 91.8% Mn, 89.8% Li
Yao et al. (2016)	LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	1.0 M D,L-malic acid 3 ml H <sub>2</sub> O <sub>2</sub>	Resynthesized LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>
Nayaka et al. (2016b)	LiCoO <sub>2</sub>	1 M maleic acid 0.02 M Ascorbic acid; 1 M Iminodiacetic acid 0.02 M Ascorbic acid	99% Li, 91% Co; 100% Li, 97% Co
He et al. (2017a)	LiNi <sub>x</sub> Co <sub>y</sub> Mn <sub>z</sub> O <sub>2</sub>	2 M L-tartaric acid 4 vol% H <sub>2</sub> O <sub>2</sub>	99.07% Li, 98.64% Co, 99.31% Mn, 99.31% Ni
Gao et al. (2017)	LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	2 M Fomic acid 2 vol% H <sub>2</sub> O <sub>2</sub>	95.46% Al, 98.22% Li, 99.96% Ni, 99.96% Co, 99.95% Mn
Li et al. (2017)	LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	1.5 M Lactic acid 0.5 vol% H <sub>2</sub> O <sub>2</sub>	98.2% Ni, 98.9% Co, 98.4% Mn, 97.7% Li

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