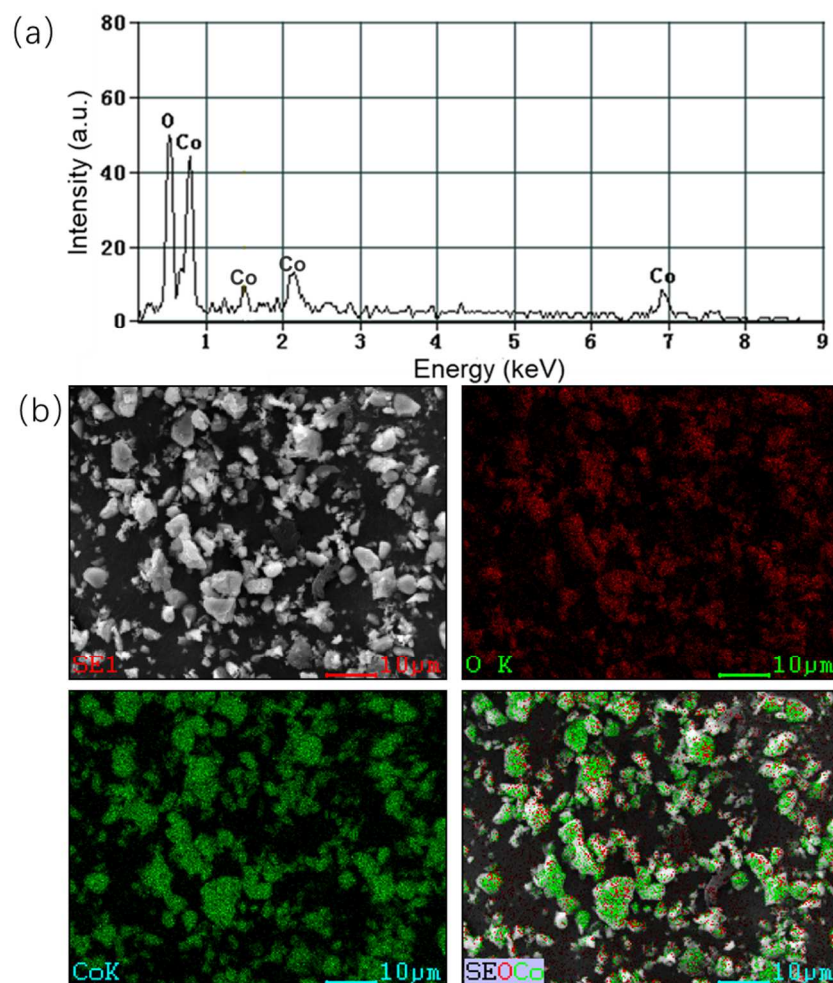1   **Environmentally benign process on selective recovery of**

2   **valuable metals from spent lithium-ion batteries by using**

3   **conventional sulfation roasting**

4   Jiao Lin, Chunwei Liu, Hongbin Cao, Renjie Chen, Yongxia Yang, Li Li, Zhi Sun

5

6   **Results**

7

8

9   **Figure S1. (a) EDS spectrum of the recycled Co_3O_4 sample, (b)mapping of various elements**

10   **of obtained on the recycled Co_3O_4 sample**

11

12   **Discussion**

13   Through the calculation of the lithium content of the $LiCoO_2$ scrap and the amount of H_2SO_4

14   required, and the amount of H_2SO_4 required for the conversion of lithium to lithium sulfate, the

15 problem of sulfur in the sulfuric acid of the process route developed in this paper is determined.

16 Specifically, 5 g of $LiCoO_2$ cathode scrap was taken, mixed with 1.370ml of H_2SO_4 (98%,

17 25.21mmol) in a ratio of 2:1, and then dried at 393 K for 720 minutes. After drying, the slurry was

18 refined to obtain 7.0046 g of a mixed homogeneous powder. The material was placed in a tube

19 furnace and roasted under a set procedure, and roasted to obtain 6.6835 g of calcined clinker. After

20 leaching for 180 minutes at a solid-liquid ratio of 400 g/L at room temperature, the concentration of

21 Li^+ in the leachate was analyzed by ICP-6300. The results showed that the concentration of Li^+ in

22 the total volume of 16.71 ml of the leachate was 19.96 g/L.

23 $$m_{Li} = \rho_{Li} v_{Li} \qquad\qquad (S1)$$

24 where m_{Li}, ρ_{Li} and V_{Li} are the mass of the element "i" in the leachate, the concentration of Li^+ in the

25 leachate and the volume of the leachate, respectively.

26

27 According to the formula of S1, the total mass of Li in the leachate is 0.3335 g, and the molar mass

28 thereof is 48.05 mmol, and the SO_4^{2+} ion theoretically bound to Li^+ is at least 24.02 mmol. The

29 actual amount of H_2SO_4 added in the 5g scrap powder is 25.21mmol. Ignoring the loss error and

30 test error in the experiment, it can be considered that the sulfur in the added H_2SO_4 is completely

31 combined with Li^+, and there is no loss or escape of sulfur.

32
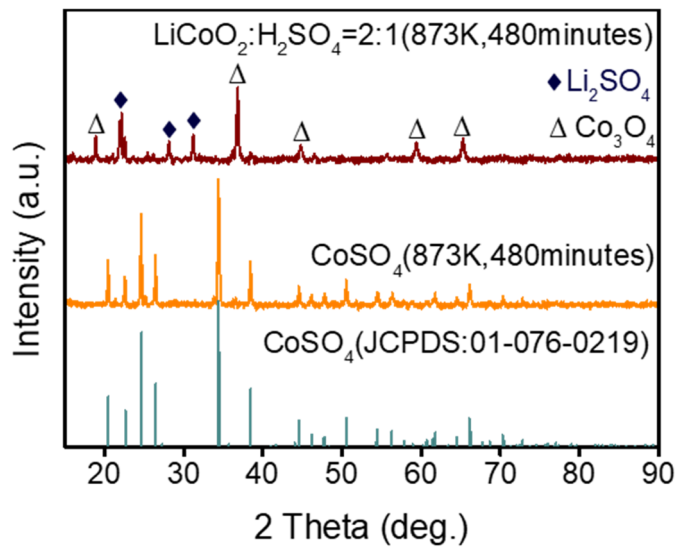
33

34 **Figure S2.** XRD pattern of the roasted materials ($LiCoO_2$:H_2SO_4=2:1, roasting temperature=873 K, roasting

35 time=480minutes) and the roasted $CoSO_4$ material (roasting temperature=873 K, roasting time=480 minutes)

36

Table S1. Leaching rate of metal elements in different lithium ion batteries

Element	Li	Co%	Ni	Mn
L(%)	99.22	0.02	0.08	0.05

[a] the roasted powders were leached by water with S:L of 400 g/L just the once.

41

Economic feasibility. The recycling process in this study can be divided into four parts: Drying; High temperature roasting; Leaching and filtering; Precipitation and purification. Assume that 1 ton of spent $LiCoO_2$ scrap were treated by the proposed green recycling process in China. The working day is 300 days per year (average 25 days per month) while the work time is about 8 hours every day. And the average wage of per labor is 74318 CNY per year ($39 per day, 1$=6.367 CNY) in china. And the industrial electricity charge is $0.20 /kWh (maximum), the industrial water charge is $0.40/t (maximum), the industrial H_2SO_4 cost is $70/t.[1]

Considering the residuals rate and interest rate, depreciation cost of equipment is calculated as Eq. (S2) while the cost of equipment maintenance cost is calculated as Eq. (S3):

$$C_D = C_o \cdot (1 - r) \cdot \frac{i}{1 - (1 + i)^{-n}} \qquad (S2)$$

C_D ——— Depreciation cost of equipment

C_O ——— Acquisition cost of equipment

r ——— Residuals rate of equipment, 4%

i ——— Interest rate, 10%

n ——— Service life, year

$$M_c = 0.05 \cdot C_o \qquad (S3)$$

M_C ——— Maintenance cost of equipment

C_O ——— Acquisition cost of equipment

And the energy consumption, the cost of energy, water and labor are calculated as Eq. (S4), (S5), (S6) and (S7):

$$E_P = P \cdot t \cdot n \qquad (S4)$$

E_p ——— Energy consumption of the process

65   P —— — Equipment power, Kw

66   t —— — Working time of equipment

67   n —— — number of equipments

68

69      $C_P = E_P \cdot p_e$ (S5)

70   C_p —— — Cost of energy

71   E_p —— — Energy consumption of the process

72   p_e —— — Electricity price for industrial uses,\$0.20/kWh

73

74      $C_W = m \cdot p_w$ (S6)

75   C_w —— — Cost of water

76   m —— — Water consumption, ton

77   p_w —— — Water price for industrial uses, \$0.91/t

78

79      $C_l = n \cdot p_l$ (S7)

80   C_l —— — Cost of labor

81   n —— — number of workers

82   p_l —— — Wage of per labor, \$39/day

83   Finally, the energy consumption and the cost of every process and revenue of products in this study

84   were calculated in detailed and then a profit was obtained by recycling 1 ton spent $LiCoO_2$ batteries

85   with the current process as follows in China.

86   **Process I: Drying**

87   **Drying requirement:** Four conveyor drier (P=20Kw, per price=\$15180, maximum capacity =
88   300kg/per, service life = 5 years) is needed to work for 12h.

89      $C_D = C_o \cdot (1-r) \cdot \dfrac{i}{1-(1+i)^{-n}} = (\$15180 \times \dfrac{1}{300}) \times (1-4\%) \times \dfrac{10\%}{1-(1+10\%)^{-5}} = \$12.81$

90      $M_c = 0.05 \cdot C_o = 0.05 \times (\$15180 \times \dfrac{1}{300}) = \$2.53$

91      $E_P = P \cdot t \cdot n = 20kW \times 12h \times 4 = 960kW \cdot h$

         $C_P = E_P \cdot p_e = 960kW \cdot h \times \$0.2/kWh = \$192$

93   $C_l = n \cdot p_l = 1 \times \$39 = \$39$

94   The H_2SO_4 solution and water were used in this process, and 500 kg of H_2SO_4 and 400 kg of water

95   are required for per ton of $LiCoO_2$ scrap recovered.

96   $C_h = m \cdot p_h = 0.5 \times 70 = \$35$

97   $C_W = m \cdot p_w = 0.4 \times 0.91 = \$0.36$

98   Total costs: $281.7

99   After this process, the dried powders are about 1.4ton.

100   **Process II: High temperature roasting**

101   **High temperature roasting requirement:** Three heating equipment (Pw = 55 kW, per price =

102   $216000, maximum capacity = 300 kg/per, service life = 5 years) are needed to respectively work

103   for 4h every day. In this process, the obtained mixed electrode materials were roasted, which means

104   every device needs to work 2 times every day.

105   Electric power charge: the working time including temperature rise and hold is 3 hour and the

106   cooling time is 1 hour.

107   $C_D = C_o \cdot (1-r) \cdot \dfrac{i}{1-(1+i)^{-n}} = (\$216000 \times 3 \times \dfrac{1}{300}) \times (1-4\%) \times \dfrac{10\%}{1-(1+10\%)^{-5}} = \$546$

108   $M_c = 0.05 \cdot C_o = 0.05 \times (\$216000 \times 3 \times \dfrac{1}{300}) = \$108$

109   $E_P = P \cdot t \cdot n = 55kW \times 4h \times 6 = 1320kW \cdot h$

    $C_P = E_P \cdot p_e = 1320kW \cdot h \times \$0.2 / kWh = \$264$
110

111   $C_l = 1 \cdot p_l = 1 \times \$39 = \$39$

112   Total costs: $957

113   After this process, the calcined powders are about 1.27 ton

114   **Process III: Leaching and filtering**

115   **Leaching and filtering requirements**: the calcined powders are leached by water once with S: L

116   of 400 g/L for 180 min. A set of frame filter (Pw =10 Kw, per price=$8350, maximum capacity =

117   30 m²/per, service life = 5 years) is needed to work for 1 h. About 3.65 ton of water is consumed.

118   $C_D = C_o \cdot (1-r) \cdot \dfrac{i}{1-(1+i)^{-n}} = (\$8530 \times \dfrac{1}{300}) \times (1-4\%) \times \dfrac{10\%}{1-(1+10\%)^{-5}} = \$7.05$

119   $M_c = 0.05 \cdot C_o = 0.05 \times (\$8530 \times \dfrac{1}{300}) = \$1.42$

120   $E_P = P \cdot t \cdot n = 10kW \times 1h \times 1 = 10kW \cdot h$

121      $C_P = E_P \cdot p_e = 10kW \cdot h \times \$0.2 / kWh = \$2$

122      $C_W = m \cdot p_w = 3.65t \times \$0.91 / t = \$3.32$

123      $C_I = n \cdot p_I = 1 \times \$39 = \$39$

124   Total costs: $52.79

125

126   **Process VI: Precipitation and purification**

127   Precipitation requirement: two set of glass lining reactors (Internal Electric Heater) (P=25 Kw, per

128   price=$1955, maximum capacity =500 L/per, service life = 5 years) are needed to respectively work

129   for 4 h including temperature rise and hold. About 5 ton water was consumed.

130      $C_D = C_o \cdot (1-r) \cdot \dfrac{i}{1-(1+i)^{-n}} = (\$1955 \times \dfrac{1}{300}) \times (1-4\%) \times \dfrac{10\%}{1-(1+10\%)^{-5}} = \$1.65$

131      $M_c = 0.05 \cdot C_o = 0.05 \times (\$1955 \times \dfrac{1}{300}) = \$0.33$

132      $E_P = P \cdot t \cdot n = 25kW \times 4h \times 2 = 200kW \cdot h$

133      $C_P = E_P \cdot p_e = 100kW \cdot h \times \$0.2 / kWh = \$20$

134      $C_W = m \cdot p_w = 5t \times \$0.91 / t = \$4.55$

135      $C_I = n \cdot p_I = 0.5 \times \$39 = \$39$

136   After this process,456 kg of Li_2CO_3 can be recycled.

137   Purification requirement: Purification of Co_3O_4(II, III) in leaching slag by wet magnetic flotation

138   technology. Purification equipment (P = 40 kW, per price = $36000, maximum capacity = 1ton/hour,

139   service life = 5 years)

140      $C_D = C_o \cdot (1-r) \cdot \dfrac{i}{1-(1+i)^{-n}} = (\$36000 \times \dfrac{1}{300}) \times (1-4\%) \times \dfrac{10\%}{1-(1+10\%)^{-5}} = \$30.38$

141      $M_c = 0.05 \cdot C_o = 0.05 \times (\$36000 \times \dfrac{1}{300}) = \$6$

142      $E_P = P \cdot t \cdot n = 40kW \times 3h \times 1 = 120kW \cdot h$

143      $C_P = E_P \cdot p_e = 120kW \cdot h \times \$0.2 / kWh = \$24$

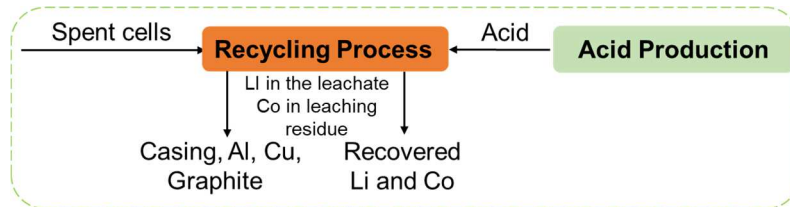144 $C_I = n \cdot p_I = 0.5 \times \$39 = \$39$

145   Total costs: $115.53

146   After this process,741 kg of Co_3O_4(II, III) can be recycled.

147   In summary, when dealing with 1ton spent $LiCoO_2$ scrap, the total cost in this study is \$1407.
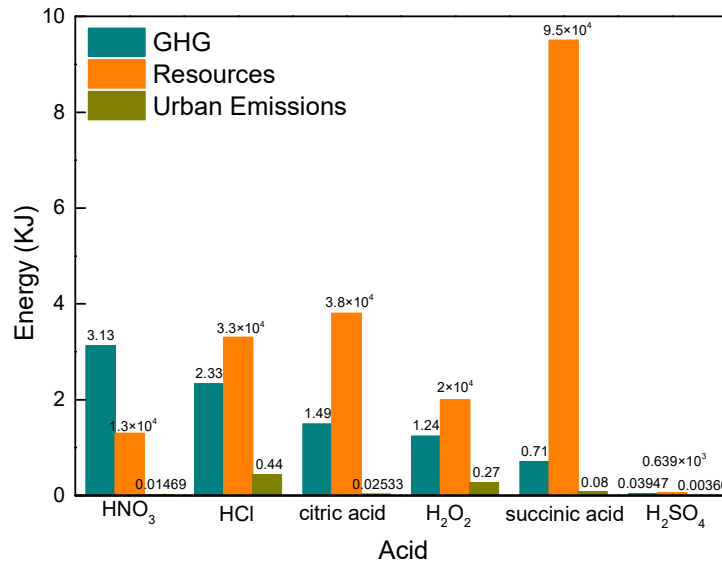
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149   **Environmental Assessment**

150

151
152   **Figure S3. Recycling processes environmental analysis boundary**

153

154
155   **Figure S4. Environmental impact of different acid production processes**

156   [a] The environmental impact is modeled using Argonne National Laboratory's Greenhouse Gases,

157   Regulated Emissions, and Energy use in Transportation (GREET) model

158

159   In this document, we provide details of parameter development for the environmental analysis of

160   the sulfation roasting recycling process.

161

162   <u>Discharging</u>

163   In the first step of this recycling process, spent LIBs are deconstructed into cells. The cells are discharged,

164   then physically separated into constituents of cathode, anode, and casing. To estimate the energy intensity

165   of the discharging step, we calculate the energy intensity of the discharge step from Equation S8:

166 $$EI_{Co,R} = \frac{a_{cathode} EI_{discharge}}{f_{cell} f_{AM} f_{AM,Co} f_R}$$ (S8)

167 where $EI_{Co,R}$ is the energy intensity of the discharge step in units of mmBtu/ton recovered Co;

168 $a_{cathode}$ is the allocation factor for Co (0.50);

169 $EI_{discharge}$ is the energy intensity of the cycling step in battery manufacturing (0.034 mmBtu/ton battery);

170 f_{cell} is the fraction of the battery mass made up of cells (0.67);

171 f_{AM} is the fraction of active material per mass of battery (38%);

172 $f_{AM,Co}$ is the fraction of cobalt in the active material (56.96%); and

173 f_R is the fraction of cobalt that is recovered (98%).

174

175 The battery cells being discharged comprise the casing, the cathode (active materials and aluminum foil),

176 copper, and graphite. Although these cells were taken from laptop batteries, we assume that their makeup

177 is similar to vehicle cells and we use parameters in a model developed by Nelson et al. to determine the

178 ratio of the mass of cathode to the mass of the entire cell, which is $a_{cathode}$ in Equation S8. The mass of

179 active material in the spent lithium-ion batteries was 380 g.[2]

180

181 <u>NMP Bath</u>

182 After discharging, the copper sheet and graphite of the anode are manually (at the laboratory scale)

183 separated from the cathode and the casing. The cathode is soaked in warm N-methylpyrrolidone (NMP)

184 at 100°C to separate it from the aluminum foil. To determine the energy intensity for this step, we use

185 Equation S9:

186 $$EI_{Soak} = \frac{a_{AM} \Delta T}{m_{AM} f_{AM,Co} \eta} \sum C_{p,i} m_i$$ (S9)

187 where EI_{Soak} is the energy intensity of the NMP soaking stage;

188 a_{AM} is the allocation ratio for the active material (0.87);

189 ΔT is the change in temperature (75 °C);

190 η is the efficiency of the natural gas boiler that is providing steam to heat the vessel (80%);

191 m_{AM} is the mass of active material;

192 $C_{p,i}$ is the heat capacity of either NMP (2.1 J/g °C), the active material (1.0 J/g °C), or aluminum (0.90

193   J/g °C); and

194   m_i is the mass of NMP, the active material, or aluminum.

195

196   We assumed a mass ratio of NMP to active material of 1:1 and used the mass ratio of aluminum foil to

197   active material in Table S2 to calculate m_i values. The heat capacity of the active material is based upon

198   solid-compound heat capacity data. Further, we assume NMP losses are negligible because residual NMP

199   filtered from the active material can be reused.

200

201   **Table S2.   Mass ratios of cell components to active material**

Component	Mass ratio of component to active material
Casing	0.12
Copper	0.34
Graphite (anode)	0.37
Aluminum foil (cathode)	0.16

202

203

204   <u>Crushing</u>

205   Next, the active material undergoes crushing in a planetary ball mill. To estimate the energy intensity of

206   this step that precedes roasting, we calculated the energy intensity per ton of recovered cobalt by dividing

207   the energy intensity per ton of total material by the fraction of cobalt in the active material (56.96%) and

208   again by the recovery efficiency (95%).

209     $$EI_{crush,Co} = \frac{Q_{crush}}{\eta} \times m_{Co} \qquad \text{(S10)}$$

210   where $EI_{crush,\,Co}$ is the energy intensity of the crushing step (mmBtu/ton cobalt);

211   Q_{crush} is the energy input per mass of battery (0.65mmBtu/ton cobalt);

212   η is the grinding efficiency of the ball mill (95%); and

213   m_{Co} is the mass fraction of cobalt in the alloy (0.57).

214

215   <u>Roasting</u>

216   To determine the energy intensity of the roasting step allocated to cobalt, we used Equation S11.

217 $$EI_{roast,Co} = \frac{Q_{roast}}{f_{Co,batt}} \times m_{Co} \qquad \text{(S11)}$$

218 where $EI_{smelt, Co}$ is the energy intensity of the roasting step (mmBtu/ton cobalt);

219 Q_{roast} is the energy input per mass of battery (5.45mmBtu/ton cobalt);

220 $f_{Co,batt}$ is the mass fraction of cobalt in the fed batteries (0.57); and

221 m_{Co} is the mass fraction of cobalt in the alloy (0.43).

222

223 To select an energy intensity for the calcining step, we chose a best value to use in the analysis of the

224 recycling process of 2.3 MJ/kg. Calcining processes also consume electricity. We adopted the average

225 electricity consumption of the processes 0.09 MJ electricity/kg. We used the stoichiometric ratio of Co

226 in $LiCoO_2$ (0.57 kg Co/kg $LiCoO_2$) and the recovery efficiency to calculate an energy intensity for this

227 step per mass of recovered cobalt.

228

229 <u>Leaching</u>

230 We calculated the energy intensity of the leaching steps with Equation S12.

231 $$EI_{leaching,Co} = \frac{EI_{leaching}}{m_{Co}} \times a_l \qquad \text{(S12)}$$

232 where $EI_{leaching, Co}$ is the energy intensity of the leaching steps allocated to cobalt (mmBtu/ton cobalt);

233 EI_{leach} is the energy intensity of the leaching step (0.12mmBtu/ton alloy);

234 a_l is the mass allocation ratio for cobalt for the leaching step (0.9)

235 We used the stoichiometric ratio of Co in $LiCoO_2$ (0.57 kg Co/kg LiCoO2) and the recovery efficiency

236 to calculate an energy intensity for this step per mass of recovered cobalt.

237

238

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240

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243

244

Table S3. The purchased energy intensity of different recycling process

Hydrometallurgical Process			Pyrometallurgical Process			Sulfation Roasting Recycling Process		
Step	Purchased Energy Intensity (mmBtu/ton recovered product)		Step	Purchased Energy Intensity (mmBtu/ton recovered product)		Step	Purchased Energy Intensity(mmBtu/ton recovered product)	
	Lithium	Aluminum		Lithium	Cobalt		Cobalt	Aluminum
Discharging	1.02	0.46	Smelting	0.41	1.45	Discharging	0.12	0.12
NMP soak	2.91	0.63	Leaching	0.15	0.52	NMP soak	0.7	0.63
Crushing	1.74	0	Solvent Extraction	0	0	Crushing	0.39	0
Calcination	3.25	0	Oxidation	0	0	Roasting	4.11	0
Grinding	0.2	0	Firing	2.4	8.0	Leaching	0.19	0
Leaching	0.2	0						
Total	9.32	1.09	Total	3.0	9.9	Total	5.51	0.75

[a] British thermal units (Btu, 1 quadrillion Btu = 293 TW h)[3]

1. Yang Y, Meng X, Cao H, Lin X, Liu C, Sun Y, *et al.* Selective recovery of lithium from spent lithium iron phosphate batteries: a sustainable process. *Green Chemistry* 2018, **20**(13)**:** 3121-3133.

2. Li L, Dunn JB, Zhang XX, Gaines L, Chen RJ, Wu F, *et al.* Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. *Journal of Power Sources* 2013, **233:** 180-189.

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