

Lithium Carbonate Recovery from Cathode Scrap of Spent Lithium-ion Battery – a Closed-loop Process

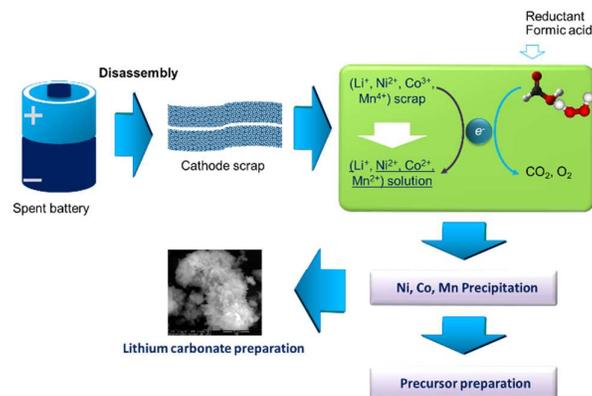
Wenfang Gao, Xihua Zhang, Xiaohong Zheng, Xiao Lin, Hongbin Cao, Yi Zhang, and Zhi H.I. Sun

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35

36 **1. Introduction**

37 The demand of lithium-ion batteries (LIBs) is directly driven by their extensive applications on
 38 electrical and electronic products including laptops, mobile phones, electric bikes and vehicles (EVs) ¹.
 39 In 2014, the production of LIBs had reached 5.287 billion units only in China². It has subsequently
 40 resulted in a large amount of spent LIBs and production scrap required to be treated. On one hand, this
 41 type of waste is considered to be hazardous due to the high content of heavy metals ³ and
 42 fluoride-bearing electrolyte. On the other hand, significant amount of valuable metals ⁴ including Li,
 43 Ni, Co, Al, Cu, are ready to be recycled from such waste which has therefore attracted worldwide
 44 attentions to develop various technologies, aiming to either minimize the management risks or
 45 maximize the recovery rate of the valuable metals.

46 Typical recycling technologies can be classified into three categories: pyrometallurgy,
 47 hydrometallurgy and biometallurgy. Prior to metal recovery, spent battery is usually pre-treated via
 48 disassembling and/or mechanical shredding. Among different fractions of the spent LIBs after
 49 pretreatment, cobalt-based cathode scrap together with its production scrap is considered to be the
 50 most valuable fraction to be recycled because of the content of cathode materials and high purity
 51 aluminum foil ⁵. In the pyrometallurgical processes, for instance in Umicore ⁶, the spent batteries are
 52 smelted with flux to form a metal phase containing most of the Co, Ni and partial Fe to be refined and
 53 a slag phase containing Li and small amount of other metals to be further recovered. However, the
 54 recovery rate of Co is relatively low due to its complicated recycling route and the difficulty in
 55 selective recovery of Li⁷⁻¹¹. At the same time, its high capital cost, potential hazardous gas emission,
 56 relatively high energy consumption and rather complex extraction procedures limit the flexibility of
 57 this technology. The extraction of metals, especially minor elements (metals), is significantly
 58 constrained by their partitioning behaviour between metal phase and molten slag. Hydrometallurgy
 59 with leaching and extraction as the main steps similar to treatment of other types of waste ¹²⁻¹⁴ is
 60 therefore attracted more attention than pyrometallurgy recently ¹⁵, in which the inorganic acids (e.g.,
 61 H₂SO₄ ¹⁶⁻²¹, HCl ²²⁻²⁴ and HNO₃) and organic acids (e.g., citric acid ²⁵⁻²⁸, DL-malic acid ²⁹, ascorbic
 62 acid ²⁷, oxalic acid ^{30,31}, succinic acid ³² and trichloroacetic acid ³³) were used as leachants. During the
 63 leaching process, reductants such as H₂O₂ ^{19,21,22,32-35}, NaHSO₃ ¹⁶ and glucose ^{17,18,25} are usually added

64 to the solution to increase the recovery rate of different metals. Inorganic acids are readily leaching
65 almost all metals from the cathode scrap with low leaching selectivity (selectively leaching the
66 targeted metals), and the metal recovery depends largely on the subsequent solvent extraction steps ³⁶.
67 Different from inorganic acids, organic acids can be employed as leachant, reductant, precipitant or
68 chelating agent during cathode scrap processing. Zeng et al. ³⁰, Sun and Qiu ³¹ used oxalic acid as both
69 leachant and precipitant to recover cobalt and lithium from LiCoO₂. Yao et al. ²⁸ introduced citric acid
70 as both leaching and chelating agents to treat the cathode material which was already separated from
71 Al foil using N-methyl pyrrolidone (NMP) dissolution at 80 °C. Since NMP can only dissolve polar
72 organic binders (e.g., polyvinylidene fluoride, PVDF), rather than the highly non-polar binders such as
73 polytetrafluoroethylene (PTFE) ³⁷, thermal treatment at 600 °C is required in order to reach effective
74 separation of the aluminum foil and cathode material ²⁸. However, the resulted NMP contained
75 solution is rather difficult to be recirculated which finally has to be disposed as organic liquid waste.
76 In addition, in the aforementioned hydrometallurgical processes, it mostly requires to manually
77 disassemble the battery and then either peel the cathode materials off the aluminum foil or dissolve
78 and burn the binders to obtain cathode powder for further recycling ^{19, 21-23, 32-34}. Research on cathode
79 scrap after effective mechanical processing (e.g., shredding and separation) or such scrap from LIBs
80 production in a practical approach with minimized environmental impact is limited. Two aspects,
81 leaching selectivity and closed-materials-loop, are therefore critical to be considered in order to
82 develop an effective near-to-industry process for spent LIBs recycling.

83 In previous work ³⁷, we have tried to close the materials loop for recycling and resynthesizing
84 LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ from the LIBs cathode scrap, in which trifluoroacetic acid (TFA) was employed to
85 dissolve the organic binder PTFE and then separate the cathode material from Al foil. However, it is
86 found that considerable amount of aluminum could be co-leached during the separation of cathode
87 material from the Al foil. The aluminum needs to be removed before further recycling of Ni, Co, Mn
88 and Li from the leachate. Furthermore, TFA is relatively expensive which might bring economic
89 uncertainties to the further scaling-up of this process if the purification and re-circulation of TFA
90 cannot be achieved. With this research, we demonstrate a process for cathode scrap recycling by
91 designing the materials flow in order to improve the materials efficiency of the recycling process,
92 minimize aluminum loss and environmental impact, with fully recycling of the cathode scrap. Formic
93 acid which can be both functioned as reductant and leachant is introduced. The following aspects are
94 focused in this research: 1) identifying the behavior of formic acid as partially a reductant; 2) the
95 effects of different factors on cathode scrap leaching and aluminum loss by considering the kinetics
96 behavior; 3) characterization of the recycled products including Li₂CO₃ that its purity reaching the
97 requirements for LIB production has not yet been reported to our best knowledge. However, the
98 preparation of cathode materials as well as the electrochemical performance is not included in this
99 research.

100

101 2. Experimental

102 2.1 Materials and reagents

103 Supplied by a local lithium-ion battery recycling company (Brunp Recycling Co. Ltd.), the active
104 material of the disassembled polytetrafluoroethylene (PTFE)-based cathode scrap is
105 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Figure S1, S2)^{33,37}. All chemicals (HCOOH-based, H_2O_2 , NaOH, Na_2CO_3) were
106 of analytical grade and all solutions were prepared with ultrapure water (Millipore Milli-Q).

107 2.2 Characterization of experimental materials

108 The cathode scrap was cut into pieces with the size of approximately 10 mm×10 mm. After drying at
109 60 °C for 24 h, the cathode scrap pieces were dissolved in the aqua regia solution ($\text{HNO}_3\text{:HCl}=1\text{:}3$, v/v)
110 to determine the contents of metals by inductive coupled plasma-optical emission spectrometry
111 (ICP-OES). The metal contents were found to be 18.32% nickel, 18.65% cobalt, 17.57% manganese,
112 6.15% lithium and 7.86% aluminum, respectively.

113 2.3 Selective leaching of cathode scrap

114 The leaching experiments were performed in a 1000 mL three-necked round bottom flask installed
115 with a reflux condenser to avoid the loss of formic acid. A heating bath with a magnetic stirrer was
116 used to ensure optimized kinetics condition and temperature control. During the experiments, a certain
117 amount of cathode scrap was added into a 250 mL mixed solution including formic acid-based leaching
118 solution and H_2O_2 . After reacting for a preset period, the mixture (leachate and reaction residue) was
119 filtered immediately. During the leaching experiments, the effects of a range of factors including the
120 temperature, acid concentration, liquid-to-solid ratio and reductant amount were considered.

121 2.4 Lithium carbonate precipitation and Ni, Co, Mn precipitation

122 The leachate and residue were treated separately following the procedures as below-mentioned.
123 Lithium carbonate was prepared after the remaining Ni, Co and Mn were precipitated out from the
124 leachate following traditional procedures for Ni-Co-Mn hydroxide precursor preparation²¹. The
125 leachate and sodium hydroxide solution (5 M) were simultaneously pumped into the reactor with the
126 speed of 2 mL/min under the protection of nitrogen at 65 °C with stirring speed of 1300 rpm.
127 Afterwards, the pH value of the mixture was first adjusted to 6.45 in order to precipitate Al^{3+} by
128 adding NaOH and NH_4OH solution into the reactor, and then the pH was further adjusted and
129 maintained at 11 for 24 h after vacuum filtration. After centrifuging, the mixture of Ni, Co, Mn
130 hydroxide precipitate (precipitate II) was obtained, after which it was thoroughly washed with ultrapure
131 water and dried in a vacuum oven at 80 °C for 10 h. The raffinate was adjusted to neutral with formic
132 acid and saturated Na_2CO_3 of stoichiometric amount was subsequently added into the raffinate at
133 20~60 °C with a speed of 1~5 mL/min. The precipitated Li_2CO_3 was washed with boiling ultrapure

134 water and dried in a vacuum oven for 12 h.
 135 The leaching residue that contains Al foil, precipitates during leaching and leaching residue of very
 136 small amount (mainly undissolved organic binder and conductive reagent) was sieved using a sieving
 137 mesh of 0.5 mm pore size. Al foil was subsequently collected for metal recycling. The separated
 138 precipitate and Ni, Co, Mn hydroxide precipitation (precipitate I) were collected for Ni-Co-Mn
 139 precursor preparation²¹.

140 2.5 Characterisation

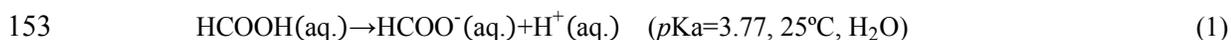
141 The concentrations of all metals in solutions were measured by inductively coupled plasma optical
 142 emission spectrometer (ICP-OES, iCAP 6300, Radial, Thermo Scientific). The morphology was
 143 observed by a mineral liberation analyzer (MLA 250, FEI) which contains an energy dispersive
 144 spectrometer (EDS, EDAX GenesisSiLi) and a scanning electron micrometer (SEM, Quanta 250). The
 145 crystal structures of solid materials were characterised by an X-ray diffractometer (X'pert PRO,
 146 PANalytical) with Cu K α radiation.

147 3. Results and discussion

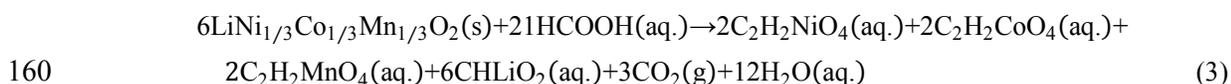
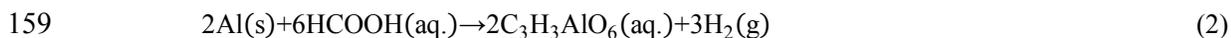
148 As the simplest carboxylic acid with an aldehyde, the formic acid can be used as leachate and
 149 reductant to 1) separate the cathode materials from aluminum foil of the cathode scrap and 2)
 150 selectively recover lithium from the cathode scrap.

151 3.1 Selective leaching of cathode scrap

152 The acid ionization equation of formic acid is described by

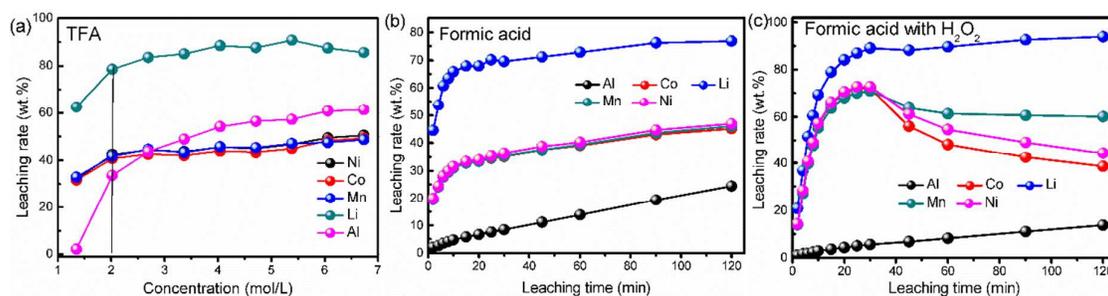


154 Other than a weak acid, formic acid is also reductive to metal ions with high oxidative potentials
 155 because of its aldehyde. Different from other acids, the formic acid can selectively leach lithium with a
 156 lower leaching rate of the aluminum to obtain high purity aluminum foil, while most of the nickel,
 157 cobalt, manganese can be precipitated out as hydroxides. The chemical reactions during the leaching
 158 process can be described as



161 To illustrate the selectivity of formic acid to aluminum leaching, two exploratory experiments were
 162 carried out under following conditions: using formic acid concentration of 2 mol/L, reaction
 163 temperature of 70 °C, solid to liquid ratio (S/L) of 50 g/L and reaction time of 120 min, while the 2
 164 vol.% of 30 wt.% H₂O₂ was only added to one of the experiments. In comparison with TFA leaching
 165 process (Figure 1(a)) which had a longer time of 240 min and the stronger acidity (pK_a=0.23, 25 °C,

166 H_2O)³³, the leaching rate of Ni, Co and Mn was nearly 45% at 120 min by formic acid process (Figure
 167 1(b)) while TFA consumed 240 min to reach the same rate, proving that the reduction ability of formic
 168 acid can enhance the leaching effects of the metals of spent cathode materials. In order to improve the
 169 leaching rate of cathode scrap (Co^{3+} and Mn^{4+} need to be converted to Co^{2+} and Mn^{2+} respectively³⁸),
 170 additional reductant (H_2O_2) can be introduced³⁹. The leaching rates of Ni, Co, Mn and Li increase
 171 within 20 min as the Figure 1(c) shows, while the rates except that of Li decrease after 30 min because
 172 of the formation of hydroxide precipitations. During leaching, it was noticed that the solubility of
 173 $\text{Co}(\text{COOH})_2$, $\text{Ni}(\text{COOH})_2$ and $\text{Mn}(\text{COOH})_2$ are relatively small comparing with LiCOOH , although
 174 comprehensive solubility data could not be found in literature. At the end of leaching, amorphous
 175 precipitate of Co/Ni/Mn together with small amount of organic binder and Al foil were obtained with
 176 minimized Co/Ni/Mn in the solution which enable effective recovery of lithium in the next stage.
 177 Further investigation on the solubility behavior of formic salts will be given in our future research.



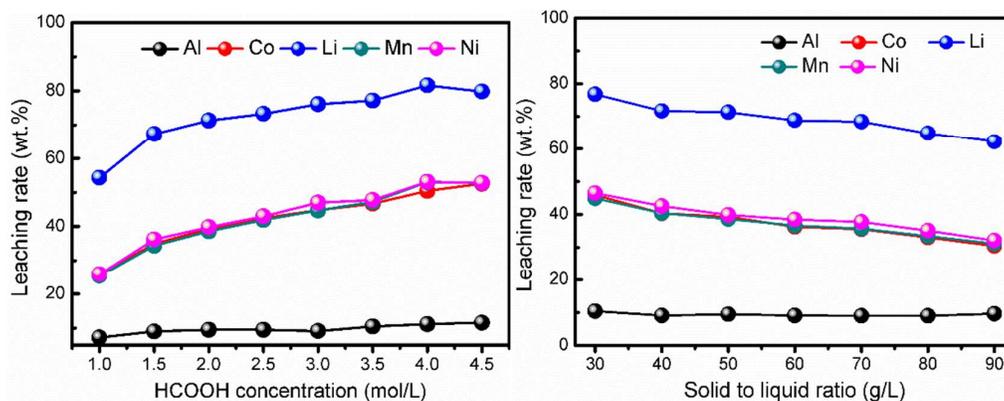
178

179 **Figure 1** The leaching rate of metals using different acids: (a) TFA³³, (b) formic acid, (c) formic acid
 180 with H_2O_2

181 In order to find the optimized leaching conditions, the effects of formic acid concentration, solid-liquid
 182 ratio (S/L) and reaction temperature were evaluated before addition other reductants, in the first stage
 183 of experiments.

184 3.1.1 Effect of formic acid concentration and solid to liquid ratio (S/L)

185 To study the effect of formic acid concentration on the leaching of cathode scrap, experiments were
 186 carried out to optimize the conditions for the extraction of nickel, cobalt, manganese, lithium and
 187 aluminum under the condition as follows: the ratio of the cathode scrap to acid solution (S/L) of 50
 188 g/L, formic acid concentration ranging from 1.0 mol/L to 4.5 mol/L, acid solution volume of 250 mL,
 189 leaching temperature of 60 °C and reacting time of 120 min. The leaching rate of each element under
 190 the different formic concentrations is presented in Figure 2(a).



191

192 **Figure 2** The leaching rate of each metal under varying formic concentration (a) and solid to liquid
 193 ratio (S/L) (b).

194 When increasing the formic acid concentration from 1.0 mol/L to 4.5 mol/L, clear increase of the
 195 leaching rates for Ni, Co, Mn and Li can be observed while the leaching rate of Al is always below

196 10%. According to the changing of leaching rate against the acid concentration, i.e. $\frac{dy_M}{dC_A}$, the

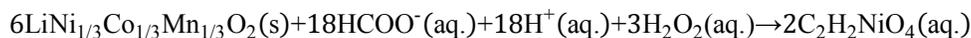
197 concentration of formic acid has insignificant effect on the leaching of Al comparing with other
 198 elements from the cathode scrap. This indicates that aluminum is relatively stable in this solution of
 199 weak acid and enables formic acid leaching to separate the Al foil from the cathode materials. For the
 200 sake of optimized leaching conditions, 2 mol/L for the formic acid concentration was chosen in the
 201 following experiments.

202 To investigate the effect of S/L, the leaching experiments were performed under the following
 203 conditions: S/L ratio of 30 to 90 g/L, acid concentration of 2 mol/L of 250 mL formic acid solution and
 204 60 °C for 120 min. As given in Figure 2(b), with the increasing of the S/L from 30 g/L to 90 g/L, the
 205 leaching rates of Ni, Co, Mn, Li all decrease slightly with a fixed reaction time which indicates the
 206 reaction requires sufficient formic acid to ensure the reaction speed⁴⁰. The phenomenon of
 207 insignificant effect on the leaching rate of Al with different S/L indicates that the reaction between
 208 formic acid and Al is trivial. However, a large amount of S/L is usually required to facilitate proper
 209 operational efficiency in practical applications and therefore the S/L was chosen to be 50 g/L in
 210 accordance to Figure 2(b).

211 3.1.2 Effect of reductant amount

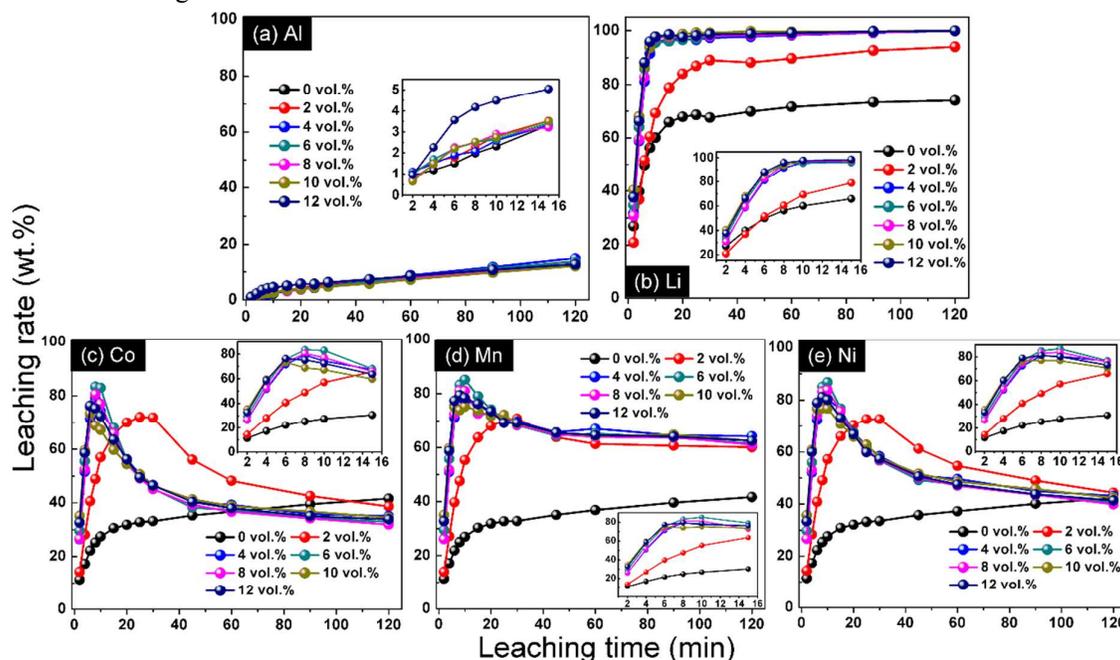
212 In literature, the reducing reagents for spent lithium ion battery leaching can be sodium thiosulfate
 213 ($\text{Na}_2\text{S}_2\text{O}_3$)³³, sodium bisulfite (NaHSO_3)^{16,17} and hydrogen peroxide (H_2O_2)^{19,21,22,32-34}. According to
 214 our preliminary experiments, hydrogen peroxide was the selected as the reductant in order not to
 215 introduce impure ions.

216 With the addition of 30 wt.% hydrogen peroxide, the leaching reaction of cathode scrap with formic
 217 acid is shown below in addition to equation (3).



218 $+2\text{C}_2\text{H}_2\text{CoO}_4(\text{aq.})+2\text{C}_2\text{H}_2\text{MnO}_4(\text{aq.})+6\text{CHLiO}_2(\text{aq.})+3\text{O}_2(\text{g})+12\text{H}_2\text{O}(\text{aq.})$ (4)

219 Under the conditions of 2 mol/L formic acid S/L of 50 g/L, temperature of 60 °C and the addition of
 220 H_2O_2 was from 2 vol.% to 12 vol.%, the leaching rates of different elements from the cathode scrap
 221 are shown in Figure 3.



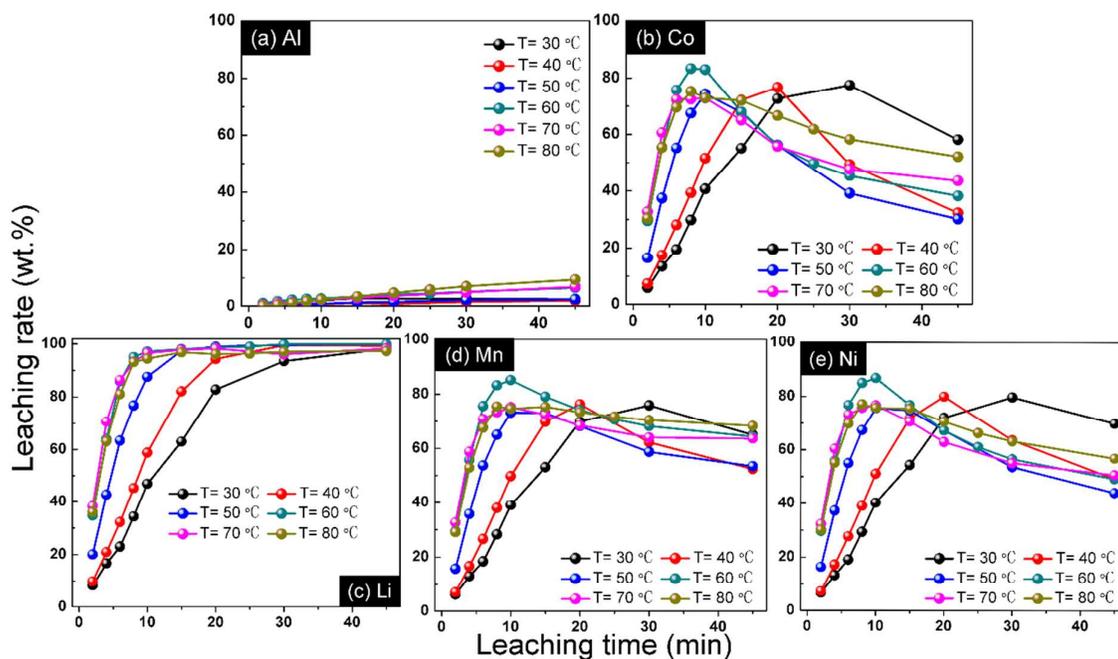
222
 223 **Figure 3** Leaching rate of (a) Al, (b) Li, (c) Co, (d) Mn and (e) Ni from the cathode scrap under
 224 different hydrogen peroxide concentration and time

225 The leaching rate of Al was not affected obviously by the concentration of H_2O_2 (Figure 3(a)), while
 226 the leaching rate of Li increased significantly and arrived almost 100% within 10min (Figure 3(b)).
 227 Different from all of other acid leaching processes, the leaching rate of Ni, Co and Mn under any
 228 hydrogen peroxide concentration increased rapidly within 10 min, and then decreased steadily before
 229 reaching certain levels. While hydrogen peroxide as a reductant helps to dissolve manganese and
 230 cobalt in crystal of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the dissolution of lithium and nickel are at the same time
 231 promoted²⁹. The best condition of H_2O_2 (concentration of 30 wt.%) was chosen to be 6 vol.%.
 232 Comparing the recovered Al foil with formic acid leaching with and without hydrogen peroxide is
 233 given in Figure S3, indicating clean Al foil can be obtained by adding H_2O_2 .

234 3.1.3 Effect of reaction temperature

235 The effect of reaction temperature on leaching efficiencies of metals was investigated under the
 236 following experimental condition: 2 mol/L formic acid, 6 vol. % of 30 wt. % H_2O_2 , S/L ratio of 50 g/L
 237 and the temperature ranging from 30 °C to 90 °C. As shown in Figure 4, the leaching rate of Al is not
 238 effectively affected by temperature and there is only slightly increment of the leaching at 90 °C. With
 239 the increase of temperature from 30 °C to 60 °C, the slope of leaching curves for all the metals are
 240 noticed to be increased suggesting the fact that the leaching process is an endothermic reaction

241 process²⁹. The leaching behavior of Ni, Co and Mn was found to be very different from that of Li and
 242 Al, where peak extraction rate in the leach solution can be noticed at the early stage of the leaching.
 243 Afterward, the leaching rates of Ni, Co and Mn decrease significantly especially at high temperatures
 244 (60 °C to 80 °C), which can be attributed to the decomposition of hydrogen peroxide when the reaction
 245 temperature is higher than 60 °C⁴¹ (Figure 4). It can also be noticed that the leaching rate is not
 246 significantly improved after 60 °C by further increasing the leaching temperature (detailed leaching
 247 rate against time at the early stage can be found in Table S1).



248 **Figure 4** Leaching rate of (a) Al, (b) Co, (c) Li, (d) Mn and (e) Ni from the cathode scrap under
 249 different reaction temperature and time
 250

251 3.2 Apparent mechanisms of metal recovery

252 To identify the apparent leaching mechanisms of the cathode scrap using formic acid, kinetics analysis
 253 was carried out in accordance to the leaching behavior of different metals. During the decomposition
 254 of the cathode materials in formic acid solution, the binder (PTFE) and the acetylene black conductive
 255 agent remain to form a gray residue layer with loose and porous structure after the leaching reaction is
 256 completed. As shown in Figure S4, the dissolution of a particle of the cathode material includes the
 257 following steps: (1) mass transfer of reactive ions through liquid film, (2) diffusion from residue-film
 258 interface to the reaction interface through the residue layer, (3) chemical reaction at the
 259 residue-particle interface, (4) products diffuse through the residue layer, (5) products transfer through
 260 the liquid film to the bulk solution.

261 Leaching of metal values from the cathode scrap is a solid-liquid-gas heterogeneous process, and it is
 262 a combination of mass transfer, diffusion, and chemical reaction following⁴², so the leaching rate can
 263 be assumed to be controlled by liquid boundary layer mass transfer (Eq.5), surface chemical reaction
 264 (Eq.6) or residue layer diffusion (Eq.7)

$$265 \quad X = k_1 \cdot t \quad (5)$$

$$266 \quad 1 - (1 - X)^{\frac{1}{3}} = k_2 \cdot t \quad (6)$$

$$267 \quad 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) = k_3 \cdot t \quad (7)$$

268 where, k_1 , k_2 and k_3 are the slopes of the fitted lines, t is the reaction time (min).

269 As shown in Figure S5, the equation (6) (surface chemical reaction control) exhibits the best fitting
270 relevance among the three rate controlling assumptions (the fitting data of equation (5) and (7) are
271 given in Figure S6 and S7, Table S2 and S3, respectively).

272 Figure S8 as well as Table 1 gives the fitting lines by assuming chemical reaction control leaching. It
273 can be found that two distinctive stages exist for the leaching rate against temperature in the range of
274 30 °C to 80 °C. From 60 to 80 °C, the values for k_2 (indicating the reaction rate constant) are nearly
275 identical proving that the temperature has insignificant effect on the leaching process when the
276 temperature is high enough. In the range of 30–60 °C, the data can be described by the empirical
277 Arrhenius law as

$$278 \quad k = A e^{\frac{-E_a}{RT}} \quad (8)$$

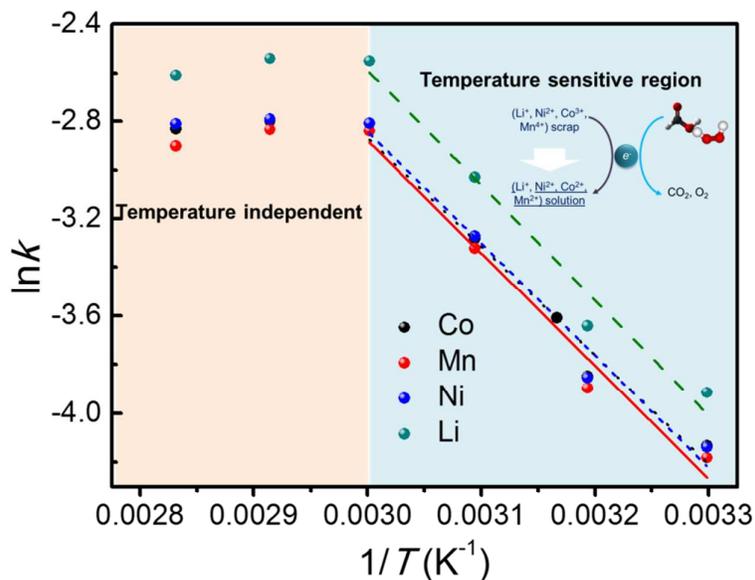
279 where R is the universal gas constant, A is the pre-exponential factor, E_a is the apparent activation
280 energy and $T(K)$ is the absolute temperature. The equation can be further converted into

$$281 \quad \ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

282 By plotting $\ln k$ vs. $1/T$ in Figure 5, the apparent activation energy with H_2O_2 for Co, Mn, Ni and Li can
283 be obtained as 37.17 kJ/mol, 39.38 kJ/mol, 38.47 kJ/mol and 38.29 kJ/mol, respectively (Table S4).
284 Similarly, the apparent activation energy without H_2O_2 addition for Co, Mn, Ni and Li (based on the
285 data of Figure S9) was 41.52 kJ/mol, 41.64 kJ/mol, 41.16 kJ/mol and 43.61 kJ/mol, respectively (as
286 shown in the Figure S10 and S11, Table S5 and S6).

287 **Table 1** Kinetic parameters during the leaching process with H_2O_2 calculated using the surface
288 chemical control model

T(K)	Co		Li		Mn		Ni	
	k(min ⁻¹)	R ²						
303.15	0.01607	0.98776	0.01995	0.98296	0.01529	0.98876	0.01595	0.98788
313.15	0.02136	0.98592	0.02621	0.98059	0.02033	0.98623	0.02118	0.98534
323.15	0.03751	0.99746	0.04831	0.9964	0.03611	0.99787	0.03795	0.99802
333.15	0.05850	0.99684	0.07810	0.99774	0.05845	0.99684	0.06033	0.99758
343.15	0.06085	0.99476	0.08129	0.9989	0.0588	0.99504	0.06143	0.99633
353.15	0.05603	0.99845	0.07078	0.99994	0.05333	0.99908	0.05615	0.99886



289

290 **Figure 5** Arrhenius plots for leaching of Co, Mn, Ni and Li from the cathode scrap under the surface
 291 chemical control model with the addition of H₂O₂

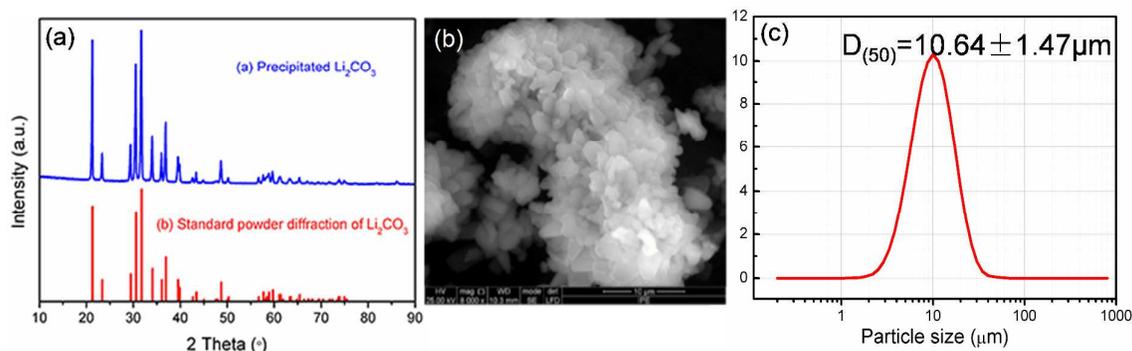
292 3.3 Recover of lithium carbonate

293 After formic acid leaching, the Al foil in the residue can be easily separated by sieving (Figure S3).
 294 The mass fraction of each element in the Al foil can be analyzed by ICP-OES and given in Table S7
 295 where the mass fraction of Al is found to be 99.98%.

296 The leach solution is processed according to aforementioned procedures to precipitate out the
 297 remaining Ni, Co and Mn. Subsequently, lithium carbonate can be obtained by adding excessive
 298 (110%) saturated Na₂CO₃ to obtain lithium carbonate which is slightly soluble in water and the
 299 solubility decreases with the increasing of temperature⁴³.

300

301 The XRD pattern of the obtained lithium carbonate is shown in Figure 6(a) and it agrees well with the
 302 standard pattern peaks.



303

304 **Figure 6** XRD patterns of the precipitated Li₂CO₃ and standard powder diffraction peaks of Li₂CO₃ (a),

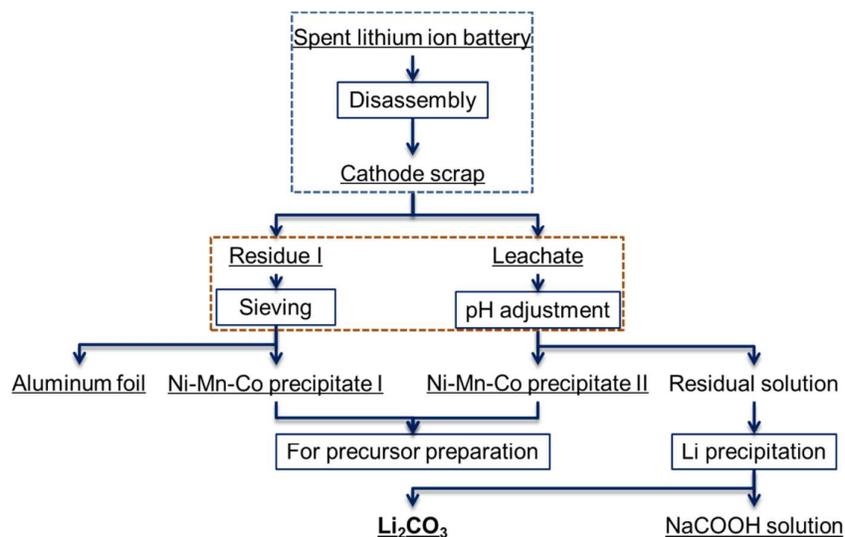
305 SEM images of the precipitated Li_2CO_3 (b), particle size distribution (c)
 306 To accurately calculate the purity of lithium carbonate, the precipitated Li_2CO_3 was further dissolved
 307 by aqua regia and its mass fraction of metals was measured by ICP-OES (Table S8). From Table S8,
 308 the mass fraction of lithium is accounted for 99.90 wt.%.
 309 The SEM images of the precipitated Li_2CO_3 are illustrated in Figure 6(b) and it can be noticed that the
 310 precipitated Li_2CO_3 was presented as massive agglomerates of numerous primary sheets. The particle
 311 size distribution (Figure 6(c)) is found to be $10.64 \pm 1.47 \mu\text{m}$.
 312 The mass fraction of Na^+ among the metallic ions in the solution after precipitation is found to be
 313 98.20%, where the anion through all the leaching process is mainly HCOO^- . The solution can be
 314 further processed to prepare NaCOOH or directly used for leather processing after pH adjustment⁴⁴
 315 and the Ni-Co-Mn precipitates are ready for precursor preparation of cathode materials (detailed
 316 investigation is out of the scope of current research).

317 3.4 Development of a new lithium-ion battery production process

318 Based on previous theoretical and experimental results, a new lithium-ion battery production process
 319 under the leaching of formic acid was schematically plotted in Figure 7.
 320 The global recovery rates of all the metals are all over 90% and the main products are shown in Table
 321 2. The Ni, Co and Mn of the cathode scrap were mainly recovered as hydroxide precipitates
 322 (Ni-Co-Mn precipitates I and II) with minor loss in the residue solution (Table S9). In the process to
 323 separate Ni-Co-Mn precipitate I and Al foil, it was found that about 0.005 wt.% Ni-Co-Mn was lost as
 324 the impurity of Al foil (Table S7). So the global recovery rates of the Ni, Co and Mn in this process
 325 were 99.96%. The product form of Al in the whole recovery process is in its foil form with only 4.54
 326 wt.% dissolved in the leaching process. The XRD result of the Ni, Co, Mn hydroxide precipitate is
 327 shown in Figure S12 and no $\text{Al}(\text{OH})_3$ phase is identified in the precipitate. Furthermore, it was found
 328 helpful for increasing the rate performance and cycle stability of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with an improved
 329 lamellar structure even small amount of Al remaining in the precipitates which may be later in the
 330 cathode materials¹⁸. The loss of Li happened in the leaching process (0.07%, Table S9), the Ni-Co-Mn
 331 precipitation process (0.60%, Table S9) and the Li_2CO_3 precipitation process (around 1.11% remains
 332 in the residual solution). Therefore the global recovery rates of the Al and Li in this process were
 333 95.46% and 98.22%, respectively. Based on the results, the process exhibits no secondary waste
 334 emission and reaches closed-loop by using formic acid as the leaching reagent.

335 **Table 2** The global recovery rates of different metals from the cathode scrap in this research

Element	Al	Li	Ni	Co	Mn
Recovery rate (wt.%)	95.46	98.22	99.964	99.964	99.947
Product form	Al foil	Li_2CO_3	Precursor		
Major loss	$\text{Al}(\text{OH})_3$	NaCOOH solution	Al foil		



336

337

Figure 7 Simplified flow-sheet of recovery process based on formic acid

338 Associated content

339 Supporting Information

340 Details about the leaching and kinetics analyses are given. The Supporting Information is available
 341 free of charge on the ACS Publications website at DOI:

342

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