Supporting Information

Novel Approach for *In-situ* Recovery of Lithium Carbonate from Spent Lithium Ion Batteries Using Vacuum Metallurgy

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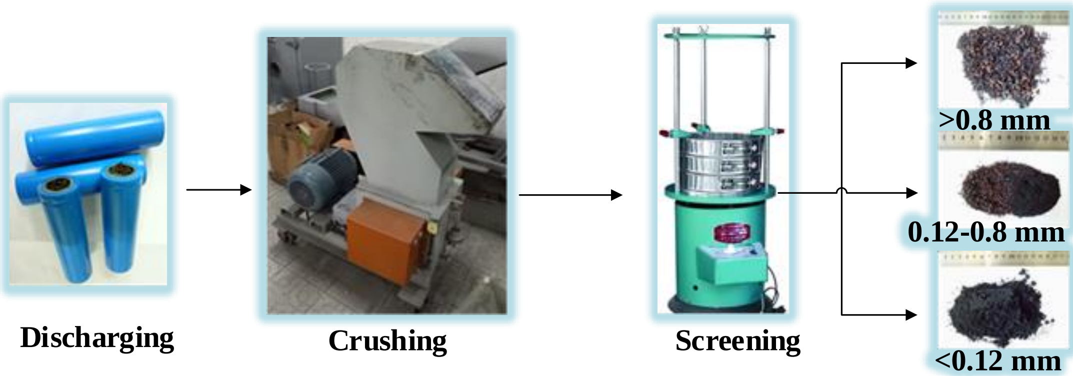

Figure S1 The pre-treatment processes to obtain mixed electrode materials from spent batteries

After discharging, the batteries are fully crushed and screened to obtain mixed electrode materials whose ingredients are anode powders "graphite" and cathode powders "$LiMn_2O_4$" (powders size<0.12 mm) as shown in Figure S1.

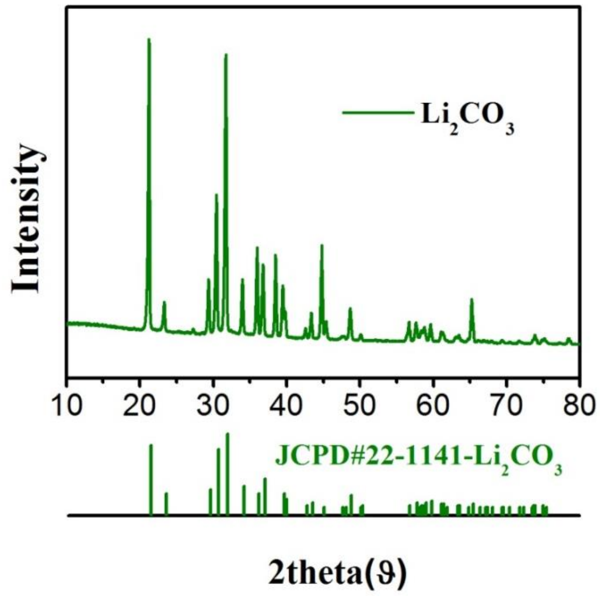

Figure S2 XRD pattern of white crystals

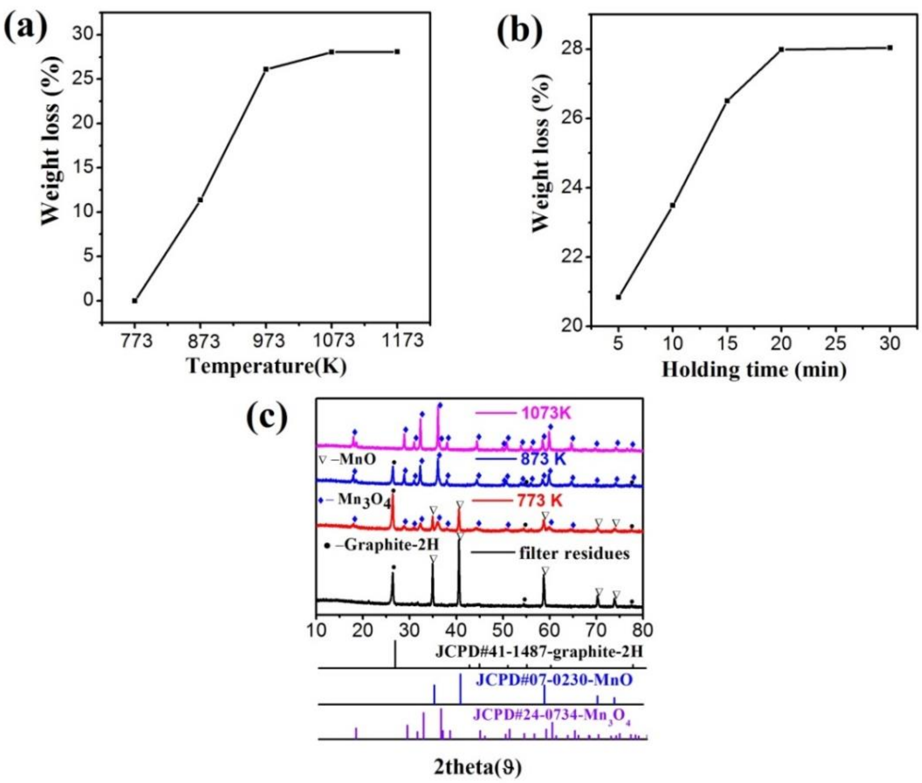

Figure S3 (a), (b) effect of temperature and holding time on graphite removal, and (c) XRD patterns of burned powders at different condition.

After Li recovery by water leaching process, effects of temperature and holding time on the purity of Mn resource in the filter residues were investigated. In the process, the purity ratio of Mn resource depended on the removal ratio of graphite, so the weight loss rate was used to replace the purity rate. As shown in Figure 3(a), a series of experiments were conducted at different temperatures and the results showed that graphite can be completely removed at 1073 K for 30 min. Besides, Figure 3(c) showed that MnO was oxidized into Mn_3O_4 as the final product during the graphite removal. Furthermore, effect of holding time was studied as Figure 3(b). With the rise of holding time, the weight loss gradually increased and then reached a plateau. When holding time was 20 min, the weight loss rate of residues reached the maximum and the purity rate of Mn_3O_4 was 96.51%. In a word, the graphite in filter residues was totally burned away at 1073 K for 20 min and the final product as Mn_3O_4 was obtained as precursor of cathode materials.

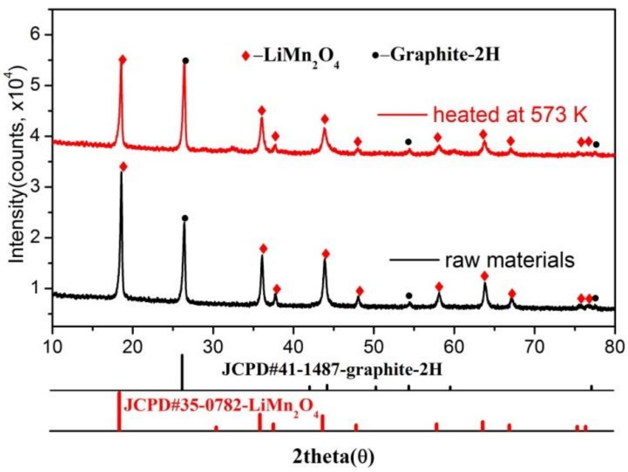

Figure S4. XRD patterns of mixed electrode materials and calcined mixed electrode materials

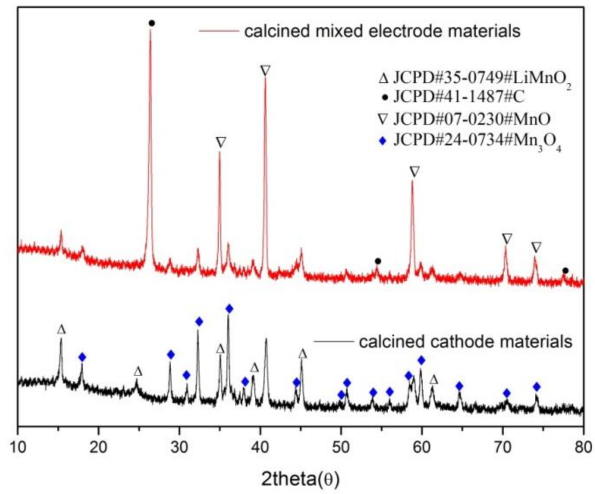

Figure S5. XRD patterns of cathode material and mixed materials calcined at 873 K for 45 min

Table S1. Main Composition of Mixed Electrode Powders Gained by Mechanical Separation

Elements	Li	Mn	Cu	Al	Fe	Co	Ni	C
Content (wt. %)	2.371	37.22	0.2307	0.2276	0.0627	0.0095	0.0062	30.83

Table S2. Li-element Recovery Rate [a] from Different Spent LIBs

	$LiMn_2O_4$	$LiCoO_2$	$LiCo_xMn_yNi_zO_2$
R (%)	81.90	82.70	66.25

[a] the pyrolysis powders were leached by water with S:L of 25 g/L just the once.

Economic Assessments

Assume that the treatment capacity is 10 ton (18650) spent $LiMn_2O_4$ per day in China. And the cost of collection and transportation of every battery is $0.15. And the total amount of batteries was about 27400. So the collection and transportation costs were calculated as the following:

$$C_{C\&T} = \$0.15 \times 27400 = \$4110$$

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 industrial electricity charge is $0.20 /kWh (maximum), the industrial water charge is $0.40/t (maximum), the industrial NaCl cost is $58/t. The average wage of per labor is $900 every month ($36 per day, 25 day per month).

Considering the residuals rate and interest rate[1], depreciation cost of equipment is calculated as Eq. (1) while the cost of equipment maintenance cost is calculated as Eq. (2):

$$C_D = C_o \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} \quad (1)$$

C_D ——— depreciation cost of equipment

C_o ——— acquisition cost of equipment

r ——— Residuals rate of equipment, 4%

i ——— interest rate, 10%

n ——— sevice life, year

$$M_c = C_o \times 0.05 \quad (2)$$

M_c ——— maintenace cost of equipment

C_o ——— acquisition cost of equipment

And the cost of electric power, water and labor are calculated as Eq. (3), (4) and (5):

$$C_P = P \times t \times p_e \quad (3)$$

C_P ——— cost of electric power

p_e ——— electricity price for industrial uses, $0.20/kWh

t — — — working time of equipment

P — — — Equipment power, Kw

$$C_w = V \times p_w \qquad (4)$$

C_w — — — cost of water

p_w — — — water price for industrial uses, \$0.4/t

V — — — water consumption, ton/day

$$C_L = m \times p_s \qquad (5)$$

C_L — — — cost of labor

p_s — — — wage of per labr, \$30/day

m — — — number of workers

Finally, the cost of every process and revenue of products in this study were calculated in detailed and then a day's profit was obtained as follows.

Process I: NaCl-discharging:

Requirement: discharging in 5 w.t. % NaCl solution for 12 h, batteries/solution = 1:10 w/w (assume that the discharging is done at the night before); about 5 ton of NaCl and 30 ton of water were needed in the discharging process; two sets of automatic conveyor belts (P_w=7.5kW, per price= \$2000, 2.0 m/s, maximum capacity= 1000 m^3/h, service life=5 years) work for 1 hour every day.

$$C_D = C_o \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}}$$
$$= (\$2000 \times 2 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$3.38$$

$$M_c = C_o \times 0.05$$
$$= \left(\$2000 \times 2 \times \frac{1}{300}\right) \times 0.05 = \$0.67$$

$$C_P = P \times t \times p_e$$

$$= 7.5 \text{ kW} \times 1\text{h} \times \$0.20/\text{kWh} \times 2 = \$3.0$$

$$C_{NaCl} + C_w = 5 \text{ t} \times \$58/\text{t} + 100 \text{ t} \times \$0.4/\text{t} = \$330$$

$$C_L = 2\text{per} \times \$36/\text{per} = \$72$$

Total costs: $409.05

Besides, the NaCl solution can be used repeatedly to reduce the consumption.

Process II: Crushing and Screening

Requirements: One crusher (P_w=11 kW, price= $14400, maximum capacity = 8 ton/hour, service life = 5 years) works for 2 h every day.

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

$$= (\$14400 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$12.16$$

$$M_c = C_o \times 0.05$$

$$= \left(\$14400 \times \frac{1}{300}\right) \times 0.05 = \$2.4$$

$$C_P = P \times t \times p_e$$

$$= 11 \text{ kW} \times 2\text{h} \times \$0.20/\text{kWh} = \$4.4$$

$$C_L = m \times p_s$$

$$= 2 \text{ per} \times \$36/\text{per} = \$72$$

Total costs: $90.96

After this process, 3.223 ton mixed electrode materials can be obtained by mechanical separation in this study.

Process III: Vacuum pyrolysis

Requirements: four heating equipment (P_w = 55 kW, per price = $216000, maximum capacity = 250 kg/per, service life = 5 years) are needed to respectively work for 4 h every day. In this process, the obtained mixed electrode materials were heated in batches of 16 by four devices, which means every device needs to work 4 times every day. About 200 kg was heated in every device every time.

Electric power charge: the working time including temperature rise and hold is 1 hour every time and the cooling time is 0.5-1 hour.

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

$$= (\$216000 \times 4 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$730$$

$$M_c = C_o \times 0.05$$

$$= (\$216000 \times 4 \times \frac{1}{300}) \times 0.05 = \$144$$

$$C_P = P \times t \times p_e$$

$$= 55 \text{ kW} \times 1\text{h} \times \$0.20/\text{kWh} \times 16 = \$176$$

$$C_L = m \times p_s$$

$$= 2 \text{ per} \times \$36/\text{per} = \$72$$

Total costs: $1122

After this process, the calcined powders are about 2.836 ton.

Process IV: leaching and evaporation

Requirements: the calcined powders are leached by water twice with S: L of 25 g/L for 20-30 min. The supernatant liquor was filtered by 4 self-discharging filtering machines (P_w = 20 kW, per price = $5800, maximum capacity = 4 ton/hour, service year = 3 years) while the slurry was bag-type filtered; about 123.6 ton of water is consumed

At the first leaching, 73.22% of Li_2CO_3 was soluble in water and about 300 kg Li_2CO_3 crystals can be obtained by evaporation. Then, the filter residues are washed again and total 85 % Li_2CO_3 was leached by water. The water consumptions are both 56.8 ton. Every filtering machine needed to work about 4 hours every day.

Specially, the first leaching liquid is mechanically evaporated, which is achieved by two multiple-stage evaporators (P_w = 48 kW, per price = $72000, maximum capacity = 7ton/hour, service life = 5 years), while the second one is naturally evaporated.

Filtering:

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

$$= (\$5800 \times 4 \times \frac{1}{300}) \times (1-4\%) \times \frac{10\%}{1-(1+10\%)^{-3}} = \$30$$

$$M_c = C_o \times 0.05$$

$$= (\$5800 \times 4 \times \frac{1}{300}) \times 0.05 = \$3.87$$

$$C_P = P \times t \times p_e$$

$$= 20\ \text{kW} \times 4\text{h} \times \$0.20/\text{kWh} \times 4 = \$64$$

Evaporating:

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

$$= (\$72000 \times 2 \times \frac{1}{300}) \times (1-4\%) \times \frac{10\%}{1-(1+10\%)^{-5}}$$

$$= \$122$$

$$M_c = C_o \times 0.05$$

$$= (\$72000 \times 2 \times \frac{1}{300}) \times 0.05 = \$24$$

$$C_P = P \times t \times p_e$$

$$= 48\ \text{kW} \times 5\text{h} \times \$0.20/\text{kWh} \times 2 \ \ = \$96$$

$$C_L = m \times p_s$$

$$= 4\ \text{per} \times \frac{\$36}{\text{per}} \ = \$144$$

$$C_w = V \times p_w$$

$$= 56.8\ \text{t} \times 2 \times \$0.4/\text{t} = \$45.44$$

Total costs: $529.31

After this process, about 297.83 kg of Li_2CO_3 (s) can be obtained by mechanical evaporation and about 47.93 kg of Li_2CO_3 (s) can be obtained by natural evaporation. Finally, the filter residues are about 2.490 ton.

Process V: purifying

Requirements: the filter residues are heated by 4 furnaces (P_w= 20 kW, per price=$20000, maximum capacity=200 kg/per, service life=5 years). In this process, the filter residues are heated in batches of 16 by four devices. About 170 kg was heated in every device every time. Electric power charge: the working time including temperature rise and hold is 1 hour every time and the cooling time is 0.5-1 hour.

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

$$= (\$20000 \times 4 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$68$$

$$M_c = C_o \times 0.05$$

$$= (\$20000 \times 4 \times \tfrac{1}{300}) \times 0.05 = \ \$13.33$$

$$C_P = P \times t \times p_e$$

$$= 20\ \text{kW} \times 1\text{h} \times \$0.20/\text{kWh} \times 16 = \$64$$

$$C_L = m \times p_s$$

$$= 2 \text{ per} \times \$36/\text{per} = \$72$$

Total costs: $217.33.

After this process, about 1.76 ton Mn_3O_4 powders can be obtained and the purity rate of Mn_3O_4 is 93 %.

Therefore, the total costs of whole processes (C_T) in this study can be calculated:

$$C_{T=}\$409.05 + \&90.96 + \$1122 + \$529.31 + \$217.33 = \$2368.65.$$

Further, revenues of products including Li_2CO_3 and Mn_3O_4 are calculated as shown in Table SI.

Table S3. Revenues of Products by This Recycling Process

Product	Daily production (kg)	Purity rate (%)	Prices(/t)	Revenue
Li_2CO_3 [a]	297.83 47.93	99.7	$17554	$5228.11 $841.36
Mn_3O_4	1.76	93	$1430	$2517
Total revenues				$8587

[a] Li_2CO_3(s) was obtained by two ways: mechanical evaporation and natural evaporation.

Thus, the day's profit (P) can be obtained:

$$P = R - C_{C\&T} - C_T = \$8587 - \$4110 - \$2368.65 = \$2108.35$$

In summary, the day's profit of this recycling process in this study is $2108.35.

Reference

1. Turton R., Bailie R. C., B. W. W., A. S. J. Analysis, synthesis and design of chemical processes [M]. PTR Upper Saddle River, New Jersey, USA: Prentice Hall, ***1998***.