SUPPLEMENTARY MATERIAL

Novel closed-loop process for simultaneous recovery of valuable metals and iron from mixed type of spent lithium-ion batteries

Xiangping Chen^{a*}, Jiazhu Li^a, Duozhi Kang^a, Tao Zhou^b and Hongrui Ma^a

^a School of Environmental Science and Engineering, Shaanxi University of Science & Technology, Xi'an 710021, P.R. China;

^b College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China.

Corresponding author: chenxiangping101@163.com (*X. Chen)

Pretreatment process

Spent LIBs with different sizes and models were collected from a local battery recycling center (Xi'an, China). In order to a completely metal recovery process, it is necessary to have a pretreatment process for these batteries before metal recycling process. The detailed pretreatment steps include: (1) Discharged completely (to prevent self-ignition and short circuiting). The used batteries was immersed in an electrolyte solution (10 % NaCl, w/v) for 24 hours, washed with deionized water and dried at 90 °Cfor 12 hours. (2) Then, these batteries manually disassemble, manually dismantled to separate the cathode and anode parts. (3) In addition, the cathode material coated on Al-foil was uncurled and cut to small parts, which immersed in NMP (N-methyl-2-pyrrolidone) at 90 °Cfor 2 hours to separate all the oxide deposit with Al-foil. (4) Finally, the active substance is filtered, dried and ground into fine particles. During the whole pretreatment process, it is required to wear gas masks, protective glasses and gloves. The detailed pretreatment process is illustrated in Fig.S1.



Fig. S1 Manual dismantling steps of spent LIBs (A: The spent LIBs after discharged; B: Remove the plastic shell; C: Release electrolyte; D, E, F: Mechanical separation of cathode, anode and separator; G: Positive and negative current collector; H: The film between the positive and negative components; I: Al-foils; J: The waste cathode materials; K: Cu-foils)

Leaching experiments

The leaching experiments were carried out in a three-necked flask, to ensure a complete reaction stirring with a mechanical stirrer, and the temperature was controlled with a water bath. The effects of phosphoric acid concentration, reaction time, slurry density, reaction temperature and dosage of H_2O_2 on the leaching process were studied. The specific experimental steps are as follows: (1).During the experiment, a certain amount of cathode active material was weighed by an analytical balance pour into a three-necked flask; (2).Take a certain amount of phosphoric acid solution prepared in advance in the cylinder, and then add H_2O_2 , and then add them into the three-necked flask. (3).After leaching for a given time, a slurry can be obtained and it was then subjected for filtration using a circulating water vacuum suction pump (SHB-111B), and leaching solution and leaching residues can be obtained after filtration. (4). 1 mL of the leaching solution was pipetted and diluted 100 times in a volumetric flask, and then filtered with a 0.45 µm disposable water filter, the filtered liquid was stored in a 10 mL centrifuge tube. (5).Finally, contents of metal ions of leaching solutions in above centrifuge tube were analyzed by ICP-AES to determine the leaching efficiency. All leaching experiments were conducted

in three parallel groups, and the average results will be used as the final leaching results. In this paper,

the specific operation equipment of the leaching experiment is as follows:



Fig. S2 The equipment of the leaching experiment.

Detailed redox reactions and corresponding redox potentials

Electrode reaction equation	Potential (E/V)
$Co^{3+}+e = Co^{2+}$	1.830
$Mn^{3+}+e = Mn^{2+}$	1.542
$MnO_4^{-}+8H^{+}+5e = Mn^{2+}+4H_2O$	1.507
$Fe^{3+}+e = Fe^{2+}$	0.771

Table S1 Standard electrode potential of metal at 25°C under acidic conditions.

Information of characterization devices

Table S2 The main detecting instruments and measure methods in this work.

Instrument	Model	Main remark
ICP-OES	Them, U.S.	Resolution ratio: <0.004nm; RSD: 0.2%;
		Limit of detection: ppb-ppm.
SEM	FEI Q45 ESEM	HV: 25.00 kV; spot: 4.5; HFW: 149.
EDS	EDAX Octane Prime.U.S.	KV: 20; Live Time(s):30;
		Resolution: (eV):125.2.
XRD	D8 Advance, Bruker company, Germany	Cu Ka radiation
		(λ=1.5418 A, 40 kV, 150 mA)
XPS	AXIS SUPRA, U.K.	Acceleration voltage: 500V~5kV, ion
		source Ar

Results of leaching experiments/ leaching kinetics

Condition	Laval	Mixed cathode material				
Condition	Level	Со	Li	Mn	Ni	Fe
	1.0	22.96	100.00	5.46	52.71	1.16
Constant's st	1.5	81.62	99.90	63.36	88.30	1.70
	2.0	88.40	100.00	85.05	90.10	2.96
(MOI/L)	2.5	87.44	98.16	86.97	85.17	3.21
	3.0	88.65	96.52	85.01	85.55	4.35
	0	4.85	29.03	7.69	8.90	1.41
Daduatant dagaga	1	27.64	45.90	30.14	37.05	3.09
Keductant dosage	2	47.98	78.71	39.48	66.85	3.25
(VOI. %0)	4	84.10	98.13	87.15	92.92	3.51
	6	85.79	99.84	88.61	93.28	3.29
	10	18.99	35.95	23.33	18.85	2.75
Pulp desity	20	82.98	90.71	75.48	86.85	3.05
(mL/g)	30	85.51	94.03	77.24	89.00	4.21
	40	85.67	94.30	78.74	90.26	4.03
	50	85.50	97.80	80.40	90.98	5.15
	10	31.79	65.84	56.80	31.05	1.44
	20	52.67	91.94	63.04	51.34	3.59
Time(min)	40	76.60	100.00	69.50	79.15	3.87
	60	89.06	100.00	90.22	95.23	3.21
	80	90.12	100.00	93.12	95.34	3.78
	30	51.98	89.58	61.71	69.98	1.41
Tomporatura	40	77.06	99.87	70.22	79.00	3.09
1 emperature	50	88.84	100.00	80.06	87.46	3.25
(°G)	60	90.47	100.00	88.37	94.08	3.51
	70	91.33	100.00	89.98	95.08	3.29
Optimal condition		96.30	100.00	98.80	95.50	2.70

 Table S3 Leaching results for Co, Li, Mn, Ni and Fe from mixed-cathode materials.

Tomporatura (90)	Time(min)	Leaching rate(%)			
Temperature("C)		Со	Li	Mn	Ni
	20	6.13	20.16	5.99	37.85
	30	9.48	32.11	9.23	39.84
30	40	14.74	48.49	12.66	46.03
	50	19.50	58.65	18.03	50.54
	60	23.62	64.57	22.99	54.94
	20	8.19	24.03	7.97	42.72
	30	15.68	46.70	15.14	45.64
40	40	24.73	61.27	24.28	55.30
	50	29.84	69.74	31.21	59.79
	60	36.51	75.91	35.91	64.39
	20	11.94	33.52	11.68	44.90
	30	24.22	51.69	20.96	50.35
50	40	33.00	64.96	32.23	60.00
	50	39.96	72.75	37.93	67.76
	60	45.82	77.28	44.20	72.47
	20	17.22	49.19	16.77	47.53
	30	29.19	56.94	29.43	51.06
60	40	39.90	68.58	40.05	62.50
	50	47.55	74.89	46.27	69.15
	60	55.47	78.73	53.10	74.60
	20	22.67	56.16	26.11	48.85
	30	35.72	63.21	36.52	54.77
70	40	45.10	72.32	44.76	67.74
	50	54.02	77.98	50.18	75.67
	60	59.09	81.55	54.77	78.99

Table S4 Kinetics leaching results for valuable metals (conditions: 2.0 MH₃PO₄, 20 mL/g, 4%H₂O₂).

Thermodynamic equilibrium calculation

To investigate the formation mechanism of $FePO_4$ after leaching in the phosphoric acidic medium, it is necessary to conduct a detailed thermodynamic equilibrium calculation in Fe-P-H₂O system. And the ϕ -pH formulas should be established in advance before the establishment of ϕ -pH diagram. Possible reactions in the Fe-P-H₂O system can be divided into the following three types:

(a). Redox reaction with electron transfer:

$$\Phi_{298.15K} = \frac{\Delta G_{298.15K}}{zF} \frac{0.0591}{z} \frac{a_C^c a_D^d}{a_A^a a_B^b}$$
(1)

(b). Hydrolysis neutralization reaction:

The relationship between pH and its ion activity can be obtained by the equilibrium constant of K.

$$\Delta G_{298.15K} = -2.303RT \lg K \tag{2}$$

(3). Redox and hydrolysis neutralization:

$$\Phi_{298.15K} = \frac{\Delta G_{298.15K}}{zF} \frac{0.0591}{z} \frac{a_C^c a_D^d}{a_A^a a_B^b z} \frac{h}{z \times 0.0591} h dt$$
(3)

Based on the above three kinds of reactions, possible reactions and the corresponding reaction formula and ϕ -pH formula can be obtained as the following table.

Table 55 φ -ph formulas of equilibrium feaction in Fe-P-H ₂ O system at 298.15	Table	e S5 φ-pH	formulas of	equilibrium	reaction in	n Fe-P-H ₂ O	system at 298.15 H	ζ.
--	-------	-----------	-------------	-------------	-------------	-------------------------	--------------------	----

No.	Reaction formula	φ-pH formula
1	$Fe^{3+}+e \rightarrow Fe^{2+}$	$\phi = 0.7690 - 0.05911gc(Fe^{2+}) + 0.05911gc(Fe^{3+})$
2	$Fe^{3+}H_3PO_4+2H_2O \rightarrow FePO_4 \cdot 2H_2O+3H^+$	pH=-1.0830-1/3lgc(Fe ³⁺)-1/3lgc(H ₃ PO ₄)
3	$FePO_4 \cdot 2H_2O + 3H^+ + e \rightarrow Fe^{2+} + H_3PO_4 + 2H_2O$	φ=0.5769-0.05911gc(Fe ²⁺)-0.17738pH
4	$Fe(OH)_4$ -+3H+ \rightarrow Fe(OH) ₃ +H ₂ O	pH=13.3165+lgc(Fe(OH) ₄ -)
5	$Fe(OH)_4$ -+3H++e \rightarrow Fe(OH)_3+2H_2O	φ=1.2634-0.1183pH+0.0591lgc(Fe(OH) ₄ -)
6	$Fe(OH)_3+H^++e \rightarrow Fe(OH)_2+H_2O$	φ=0.47611-0.0591pH
7	$H_2PO_4^-+H^+\rightarrow H_3PO_4$	pH=2.1459+lgc(H ₂ PO ₄ -)
8	$0.5O_2+2H^++2e \rightarrow H_2O$	φ=1.229-0.0591рН
9	$2H^++2e \rightarrow H_2$	φ=-0.0591pH
10	$3FePO_4 \cdot 2H_2O + 2H_2O + 2H^+ + 3e \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O +$	φ=0.3331143-0.03944pH-0.01972lgc(H ₂ PO ₄ ·)
	$H_2PO_4^-$	
11	$3FePO_4.2H_2O+2H_2O+H^++3e \rightarrow$	φ=0.19123585-0.01972pH-0.01972lgc(HPO ₄ ²⁻)
	$Fe_3(PO_4)_2 \cdot 8H_2O + HPO_4^{2-}$	
12	$Fe_{3}(PO_{4})_{2} \cdot 8H_{2}O \rightarrow 3Fe(OH)_{3} + 2H_{2}PO_{4} + 4H^{+} + 2H_{2}O$	pH=9.1371435+0.5lgc(HPO ₄ ²⁻)
13	$3Fe(OH)_3+2H_2PO_4-7H^++3e \rightarrow Fe_3(PO_4)_2\cdot 8H_2O+H_2O$	$\phi = 1.19681 - 0.13804 \text{pH} - 0.03944 \text{lgc}(\text{HPO}_4^{2-})$
14	$3Fe^{2+}+2H_2PO_4^{-}+8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O+4 H^+$	pH=2.4166+0.75lgc(Fe ²⁺)-0.5lgc(HPO ₄ ²⁻)
15	$3Fe_3(PO_4)_2 \cdot 2H_2O + 2H_2O + 3e \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O + PO_4^{3-}$	$\varphi = -0.0478746 - lgc(PO_4^{3-})$

Circulating leaching results



Fig. S3 Circulatory leaching with regenerated phosphoric acid on leaching rates of Co, Li, Mn and Ni.

Detailed economic analysis

Approximate 1.0 kg spent LIBs was taken as sample, economic assessment in laboratory-scale for spent LIBs recycling was performed based on proposed process. Input costs of energy consumption and chemical reagents are presented in Table S6-S7. Following calculations are based on exchange rate between RMB and US dollar of 1\$ = 6.8 RMB.

Fig.S4 (left) shows discharging and dismantling of spent LIBs. Here 250 g Na₂SO₄ were used to discharge 1.0 kg of spent LIBs. The cost of Na₂SO₄ is 0.88\$, based on current price of \$3.53/kg Na₂SO₄ provided by the Sino pharm Chemical Reagent Co., Ltd. (http://www.reagent.com.cn/?parentId=). Then, discharged batteries needed to be dried in a drying oven for 2 hours, the power of the drying oven is 1.6 kW. The electricity price in Beijing, China is $0.07/kW \cdot h$. Therefore, electricity cost for 1.0 kg spent LIBs is 2 h×1.6 kW× $0.07/kW \cdot h = 0.224$. Next, due to the manual dismantling process needed to be carried out in fume hood, the cost of energy consumption is 2 h×1.2 kW× $0.07/kW \cdot h = 0.168$. After pretreatment, 0.158 kg metallic shells, 0.232 kg graphite, 0.05 kg aluminum foil and 0.068 kg copper foil can be obtained, which can yield 0.16, 0.28, 0.11 and 0.53, respectively.

Fig.S4 (middle) shows that cathode materials need to be leaching by H_3PO_4 and H_2O_2 . Under the optimal extraction conditions, H_3PO_4 is required for 1.143 L, costing 1.143 L×5.71 \$/L=\$6.53, requiring $H_2O_21.55$ L, costing1.55 L×2.17 \$/L = \$3.38. The process consumes 7.297 L of water, and

the water price in Beijing, China is0.91 \$/t, which costs \$0.0067. The experiment needs to be heated in a water bath for 1 h, the water bath power is 27 KW, and the energy cost is 1 h×32 kW× \$0.07/kW· h=\$2.24. The total cost of filtration and evaporation is 0.483+0.692=1.175. Adjusting the proportion of metal in the leachate, adding 5.2 g of CoSO₄·H₂O and 197.13 g of NiSO₄·6H₂O, which would cost \$0.66. In the leachate, 0.402 kg H₂C₂O₄ was slowly added with a peristaltic pump, which cost 0.402 kg×0.56\$/kg=0.224\$, and the energy consumption was \$2.24. The obtained precipitate was ground and calcined, and the energy consumption was \$2.94, and finally 0.333 kg of Li (Ni_{1/3}Co_{1/3}Mn_{1/3})₂was obtained. Based on market prices, it can benefit from \$46.5.On the other hand, after leaching, 0.097 kg of FePO₄ can be obtained and added 0.025 kg of Li₂CO₃ in it. After calcination and grinding, 0.102 kg of LiFePO₄ would be obtained, and the benefit is \$1.33. Among them, the price of Li₂CO₃ is 118 \$/kg, which requires 0.025kg×118 \$/kg= \$2.95 and consumes energy of \$2.94.

Fig. S4 (right) shows the assessment of waste management. During the whole recycling process, a small amount of exhaust gases were produced during stripping, it does not produce wastewater. Therefore, active carbon was used for treatment and purification of exhaust gases. Simulating a waste disposal facility under laboratory conditions, 10 g of active carbon was needed for waste management. Thus, the cost of active carbon is \$0.085, according to the market price of active carbon (\$8.5/kg) provided by Sino pharm Chemical Reagent Co., Ltd. (http://www.reagent.com.cn/?parentId=). What is more economical is that active carbon can be used many times after restored meanwhile Na₂SO₄ and H₃PO₄ solution can be used repeatedly to discharge spent lithium-ion batteries. Finally, solid wastes, like organic separators and plastic frames can be disposed by incineration, according to incineration treatment standard of industrial solid wastes (\$0.54/kg), the input cost of 160 g of solid wastes was \$0.086. In the same way, the calories generated by incineration can also be used in other fields.

Therefore, the ultimate total profit for the whole recovery process was \$26.79 for recycling 1 kg of spent batteries. Some detailed calculation for energy consumption, chemicals consumption, waste minimization and corresponding profits can be found in Table S6 and Table S7.

Substance	Price (\$/kg)	Weight (kg)	Economic benefit (\$)
Spent LIBs	1	1	-1
Na_2SO_4	3.53	0.25	-0.88
H_3PO_4	5.71(\$/L)	1.143(L)	-6.53
35 wt.% H ₂ O ₂	2.17 (\$/L)	1.55 (L)	-3.38
Na ₂ CO ₃	4.12	0.172	-0.71
CoSO ₄ ·H ₂ O	119.1	0.005	-0.62
NiSO ₄ ·6H ₂ O	0.21	0.198	-0.041
$H_2C_2O_4$	0.56	0.402	-0.224
Li ₂ CO ₃	118	0.025	-2.95
Active carbon	8.5	0.01	-0.085
Industrial water	0.91(\$/t)	40 L	-0.036
Metallic shells	1.01	0.158	0.16
C powder	1.21	0.232	0.28
Cu foil	7.79	0.068	0.53
Al foil	2.2	0.05	0.11
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})_2$	139.6	0.333	46.5
LiFePO ₄	13.09	0.102	1.33
Total	-	-	32.454

 Table S7. The energy consumption to recycle material

Unit operation	Energy cost (kW)	Economic benefit (\$)
Drying	1.6	-0.224
Ventilating	1.2	-0.168
Leaching	32	-2.24
Filtering	12.5	-0.483
Evaporation	13.7	-0.692
Magnetic stirring	32	-2.24
Muffle furnace	84	-5.88
Total	177	-11.927



Fig. S4 Detailed economic analysis for current recycling process.

Comparison of different recycling processes

Type of spent LIBs	Method/ Leaching reagent		Condition	Product / Recycling rate	Ref.
LiFePO ₄	Direct regeneration		650 °Cfor 1 h under an Ar/H ₂ flow	LiFePO ₄	1
_		Solid phase sintering method	heat-treatment with doping of new LiFePO ₄ at the ratio of 3:7 at 700 °Cfor 8 h under N ₂ flow.	LiFePO ₄	2
	Oxalic a	icid	Milling time- 2 h, ball-to-powder mass ratio of 20:1, 30 min.	98.0 % Li and 94.0 % FeC ₂ O ₄ ·2H ₂ O	3
	H_2SO_4 (2)	5 M)	L/S ratio- 10 mL/g, 60 °C, 4 h; NH ₃ ·H ₂ O and Na ₂ CO ₃ .	FePO ₄ ·2H ₂ O and Li ₂ CO ₃	4
	CH ₃ COOH	(0.8 M)	S/L ratio- 120 g/L, 50 °C, 30 min.	95.05 % Li	5
Mixed cathode materials	Sulfuric a	acid (1 M)	95 °C,20 g/L, 40 min	96 % Li, 91% Co, 96 % Ni, 88% Mn.	6
	Lactic Acid (1	.5 M)	70 °C,20 g/L, 20 min	98% Li, 98% Ni, 99% Co, 98%Mn	7
	L-Tartaric a	acid (2.0 M)	70 °C, 17 g/L, 30 min	99% Li, 98% Co, 99% Mn, 99% Ni	8
This study	Phosphoric	acid (2.0 M)	60 °C,20 mL/g, 60 min	96.3% Co, 100% Li, 98.8% Mn, 99.5% Ni and 97.3 % FePO ₄	

Table S8 A brief comparison of different leaching systems.

References

- 1. J. Chen, Q. Li, J. Song, D. Song, L. Zhang and X. Shi, *Green Chemistry*, 2016, **18**, 2500-2506.
- 2. X. Song, T. Hu, C. Liang, H. L. Long, L. Zhou, W. Song, L. You, Z. S. Wu and J. W. Liu, *Rsc Advances*, 2017, **7**, 4783-4790.
- 3. E. Fan, L. Li, X. Zhang, Y. Bian, Q. Xue, J. Wu, F. Wu and R. Chen, ACS Sustainable Chemistry & Engineering, 2018, 6, 11029-11035.
- R. Zheng, L. Zhao, W. Wang, Y. Liu, Q. Ma, D. Mu, R. Li and C. Dai, *RSC Advances*, 2016, 6, 43613-43625.
- 5. Y. Yang, X. Meng, H. Cao, X. Lin, C. Liu, Y. Sun, Y. Zhang and Z. Sun, *Green Chemistry*, 2018, **20**, 3121-3133.

- 6. G. Granata, E. Moscardini, F. Pagnanelli, F. Trabucco and L. Toro, *Journal of Power Sources*, 2012, **206**, 393-401.
- 7. L. Li, E. Fan, Y. Guan, X. Zhang, Q. Xue, L. Wei, F. Wu and R. Chen, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 5224-5233.
- 8. L. P. He, S. Y. Sun, Y. Y. Mu, X. F. Song and J. G. Yu, Acs Sustainable Chemistry & Engineering, 2017, 5, 714-721.