A closed-loop zero-liquid-discharge process for the precipitative separation of all valuable metals from waste lithium-ion batteries of mixed chemistries at room-temperature[†]

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Materials and Methods

A variety of used mobile batteries were gathered from a local recycling centre in Bhavnagar, Gujarat, India. These batteries were discharged and disassembled manually to separate cathode, anode, metal casings, and plastic separators. The whole cathode, which is aluminium foil with cathode active material, was heated in air at 450 °C for 5h to remove the binder. For leaching experiments, either the whole cathode (aluminium foil with active cathode material) or cathode powder was utilized separately. Acetic acid, hydrogen peroxide (35 % v/v), dimethylglyoxime, sodium sulfide, sodium hydroxide, and sodium carbonate, all chemicals of the analytical grade, were purchased from TCI Chemicals Pvt. Ltd.

Analytical methods

In this study, the concentration of metal ions in the leached liquor was analyzed using an ICP-MS Thermofisher icap Qnova series instrument. The morphologies of the recovered metal salts were characterized through scanning electron microscopy (SEM-Leo series 1420 VP). The FT-IR spectra of the samples with KBr pellets were measured using a Perkin-Elmer GX spectrophotometer, which was manufactured in the USA. Additionally, powder X-ray diffraction profiles were recorded at 20 angles ranging from 10° to 80° using a MiniFlex-II (FD 41521) powder diffractometer from Rigaku, Japan. To ensure accuracy and minimize errors (within \pm 5 %), all leaching experiments and subsequent downstream processing to recover metal ions through precipitation were repeated three times, and the average results were considered as the final results.

Experimental procedure:

Battery discharging & dismantling

The collected lithium-ion batteries (from mobile phones) were immersed in the NaCl solution (1 M) for 48 hrs to discharge the batteries. Then these batteries were washed with tap water, followed by deionized water, and dried in a vacuum oven at 70 °C for 12h. Batteries were dismantled manually to obtain cathode (aluminum foil with metal oxides, 34.28 %), anode (copper foil with graphite, 18.98 %), and separator (5.14 %), aside from the steel casing and other parts (42 %) (Fig. S1†).

Selective precipitative separation of metals from leached liquor of cathode material

Separation of Nickel:

After leaching, the metal-enriched liquor is used as the feed source for separation of the metal ions sequentially (Ni, Co, Al, Mn, Li) by selective chemical precipitation method. Initially, the filtered leached liquor having a pH of ~3.5 was used for the recovery of nickel as Ni(DMG)₂. In a typical precipitation method, DMG (dimethyl glyoxime) (2.24 g, 19.29 mmol) was dissolved in 100 mL water containing sodium hydroxide (0.77 g). This solution was added slowly with constant stirring into the above liquor (1 L) under warm conditions for 1h and the red precipitate was filtered, washed, and dried to obtain the Ni(DMG)₂ complex (2.64 g, yield = 99.32 %). Recovered Ni(DMG)₂ was characterized by elemental analysis; 32.9 % C (33), 4.80 % H (4.84), and 20.00 % N (19.38) found (calculated) are matched with the Ni(DMG)₂ complex with the formula C₈H₁₄N₄NiO₄. Powder XRD also confirms the pure form of Ni(DMG)₂ complex. ICP-MS analysis of the acid-digested solution indicates a purity of ~ 99 ± 0.26 %.

Separation of Cobalt:

The obtained filtrate after the recovery of nickel having a pH ~ 3.7 was used for the precipitation of cobalt as cobalt sulfide. In a typical precipitation method, sodium sulfide (6.65 g) was added under warm conditions, to obtain black precipitates of cobalt sulfide. The black precipitate thus obtained was centrifuged and finally collected by vacuum filtration followed by washing with hot water and drying in a vacuum oven at 70 °C to get Co_xS_y (7.43 g, yield = 99.77 %). The cobalt sulfide retrieved was determined to possess an amorphous structure initially. It was then subjected to calcination to enhance its crystallinity, resulting in the identification of Co_9S_8 species through powder XRD analysis. Additionally, it is characterized by EDX elemental mapping and ICP-MS results indicated the absence of other metallic impurities, demonstrating a purity of ~98 ± 0.56 %.

Recovery of excess lixiviant acetic acid:

The filtrate obtained from the above step after the recovery of cobalt was distilled under a vacuum at 120 °C to recover the unreacted acetic acid. Recovered acetic acid was titrated against 1N NaOH volumetrically and molarity was found to be \sim 1.72 M (800 Ml). The remaining residue was used further for the recovery of manganese and lithium.

Recovery of Manganese:

The residual part obtained from the above step was dissolved in 200 mL of water to get a clear solution. A saturated solution of sodium hydroxide was added to the above solution to raise the pH of the solution initially to ≥ 6 which gives small amount of Al(OH)₃, which was filtered and discarded. Then additional amount of NaOH was added to raise the pH of the solution ≥ 12 to precipitate out Mn(OH)₂ (1.70g). Al and Mn are not valuable products and can be separated together as a mixture (total: 2.97 g) by directly raising the pH of the solution ≥ 12 to reduce the number of steps. Mn(OH)₂ was characterized by PXRD, EDX, and ICP-MS analysis.

Recovery of Lithium:

The filtrate obtained from the above step after removal of manganese was used for the recovery of lithium as lithium carbonate or lithium phosphate from boiling solution. A little excess stoichiometric amount of a saturated solution of sodium carbonate was added to obtain white precipitates of Li_2CO_3 (3.91 g, yield = 85.40%). In separate experiments, the treatment with trisodium phosphate gives Li_3PO_4 (4.25 g, yield = 88.87%). The above salts were characterized by PXRD, EDX, and ICP-MS analysis. The ICP-MS results of Li_2CO_3 revealed the absence of other metallic impurities, signifying a purity of 99 ± 0.24%.

Recovery of the by-product Sodium acetate:

The filtrate obtained after lithium recovery was neutralized (pH \sim 7) with acetic acid. The neutralized filtrate was treated with activated charcoal powder (0.5 % w/v) and stirred vigorously for 30 minutes on a magnetic stirrer followed by filtration. The volume of the filtrate was reduced under a hot plate to obtain a saturated solution, which resulted in white crystalline sodium acetate (332.8 g) upon cooling. The obtained sodium acetate was analyzed by PXRD, EDX and ICP-MS analysis. The ICP-MS results revealed a purity of ~97±0.86 %. As the quantity of sodium acetate is in large excess compared to other salts, the remaining lithium and other unrecovered salts do not affect its purity drastically. Based on weight loss on drying indicates a mixture of sodium acetate trihydrate (65%) and sodium acetate (35%).

Metal leaching from spent anode material:

In this study, the spent anode material was initially calcined in a muffle furnace in an air atmosphere at 500 °C for 1 hour to volatilize the electrolyte and the binder (PAA), which decomposes when the temperature reaches approximately 400 °C. The recovered acetic acid

(1.7 M CH₃COOH) from cathode leached liquor was employed as a leachate to recycle lithium, graphite, and copper foil from the calcined anode materials. The calcined spent anode material was then treated with recovered acetic acid in a beaker. The reaction mixture was stirred with a mechanical stirrer at 500 rpm and a temperature of 75 °C for 100 minutes. Finally, the mother liquor was separated by vacuum filtration after completing the reaction. The graphite and copper foil solid residue was washed with plenty of distilled water. The blue colour of the filtrate showed that the copper acetate leached into the solution.



Fig. S1 The discharging and dismantling of mixed type mobile batteries.



Fig. S2 Plot of leaching efficiency (%) versus time (h) at different temperatures under optimized conditions for Li (A), Mn (B), Ni (C) and Co (D).



Fig. S3 Plot between 1- $(1-X)^{1/3}$ versus time (h) for Li, Mn, Ni and Co under optimized conditions (S/L ratio: 20 g/L; H₂O₂ conc: 5 %; Acetic acid conc: 4 M; time: 5 h) varying temperature.



Fig. S4 Plot between $\ln k (h^{-1})$ versus $1/T (K^{-1})$.



Fig. S5 The FT-IR (A) & EDX (B) characterization plots for recovered Ni(DMG)₂ complex.



Fig. S6 The characterization plots for recovered for Co₉S₈ salt.



Fig. S7 The characterization plots for recovered Mn(OH)₂.



Fig. S8 The characterization plots for recovered Li₂CO₃.



Fig. S9 The PXRD & EDX spectrum of recovered sodium acetate.



Fig. S10 (A) PXRD pattern of recovered graphite and (B) Li₂CO₃ from anode.

Table. S1 The leaching of metal ions from cath	hode material using various lixiviants.
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<i>S</i> .	Type of	Acid/DES as	Reducing	Reaction condition	Leaching	Metals	Ref.
No.	Battery	leachant	agent		efficiency	Recovered	
1	LCO/	ChCl:EG	-	100 mg NMC, 5 g	Li 89.8	Co only	6
	NCM			ChCl:EG, 180 °C, 24	%, Co		
				h /	50.3 % /		
				10 mg NMC, 5 g	Li 53.6		
				ChCl:EG, 180 °C, 24	%, Co		
				h	23.4 %,		

					Ni 18.8,		
					Mn 40.9		
					%		
2	NCM	Phosphoric	H ₂ O ₂	3 M H ₃ PO ₄ , 6 %	Li 100 %,	-	14
	/LPF	acid		H ₂ O ₂ , 50 g/L S/L, 80	Co 96.3		
				min, 70 °C	%, Ni		
					95.5, Mn		
					98.8 %,		
					Fe 2.70		
3	LFP	Acetic acid	H ₂ O ₂	0.8 M AcOH, 6 %	Li 94.08	Li only	20
				H ₂ O ₂ , 120 g/L S/L,	%, Fe 5.5		
				30 min, 50 °C	%,		
4	LCO	Sulfuric acid	H ₂ O ₂	2 M H ₂ SO ₄ , 0.5 %	Li 99.1	-	21
				H ₂ O ₂ , 20 g/L S/L, 20	%, Co 70		
				min, 70 °C	%		
5	NCM	Mixed system	-	0.4 mol/L (HTTA),	Li 2.8 %,	-	22
				0.4 mol/L (TOPO)	Co 99.5		
				and IL, $O/A = 1/1, 20$	%, Ni		
				min, 25 °C	99.6, Mn		
					99.8 %		
6	NCM	Lactic acid	H ₂ O ₂	1.5 M C ₃ H ₆ O ₃ , 6 %	Li 97.7	-	23
				H ₂ O ₂ , 50 g/L S/L, 80	%, Co		
				min, 70 °C	98.9 %,		
					Ni 98.2,		
					Mn 98.4		
1					%		
7	NCM	Formic acid	H ₂ O ₂	2 M HCOOH, 2 %	Li 98.2	Li only	27
7	NCM	Formic acid	H ₂ O ₂	2 M HCOOH, 2 % H ₂ O ₂ , 50 g/L S/L,	Li 98.2 %, Co	Li only	27

					Ni 99.9,		
					Mn 99.9		
					%		
8	LCO	Sulfuric acid	H ₂ O ₂	3 M H ₂ SO ₄ , 1.6 mL/g	Co 85.5	Co only	30
				H ₂ O ₂ , 7 mL/g L/S,	%		
				2.5 h, 70 °C			
9	NCM	Sulfuric acid	H ₂ O ₂	3 M H ₂ SO ₄ , 3 %	Li 99 %,	Li, Co,	31
				H ₂ O ₂ , 7 20 g/L S/L,	Co 99 %,	Ni, Mn	
				60 min, 80 °C	Ni 99,		
					Mn 99 %		
10	LCO	ChCl:LA	-	1:3 ChCl:LA , 1:100	Li 97.1	Li and Co	36
				S/L, 24 h, 90 °C	%, Co		
					95.2 %		
11	LCO	PTSA-ChCl	-	PTSA·2H ₂ O·ChCl _{DES,}	Li 100 %,	Co only	37
				60 g/L S/L, 15 min,	Co 100 %		
				90 °C			
12	LCO	nitrilotriacetic	Ascorbic	0.1 M AA, 0.02 M	Li 92 %,	Co only	44
		acid/ Adipic	acid	ascorbic acid, 0.2 g	Co 85 %,		
		acid (AA)		LCO, 20 min, 80 °C			
13	LPF	Sulfuric acid	-	pH- 3.5, 10 g/mL S/L,	Li 99.3 %	Li only	45
				5 h, 25 °C, air flow			
				600 mL/min			
14	NCM	Sulfuric acid	H ₂ O ₂	1 M H ₂ SO ₄ , 0.62 wt	Li 99 %,	Li only	46
				% H ₂ O ₂ , 25 ml/g L/S,	Co 99 %,		
				60 min, 51 °C	Ni 99,		
					Mn 99 %		
15	LCO/LMO	Acetic acid	H ₂ O ₂	3 M C ₃ H ₆ O ₃ , 7.5 %	Li 99.9	Li, Co,	47
				H ₂ O ₂ , 20 g/L S/L, 40	%, Co	and Mn	
				min, 70 °C	98.7 %,		
					Mn 99.5		
					%		
16	LCO	Phosphoric	H ₂ O ₂	0.7 M H ₃ PO ₄ , 7 %	Li 98.7	Li	50

		acid		H_2O_2 , 30 mL/g L/S,	%, Co		
				40 min, 40 °C	0.69 %,		
17	LCO	EDTA	-	$0.8 \text{ M} \text{ C}_{10} \text{H}_{16} \text{N}_2 \text{O}_8,$	Li 97.1	Li, Co	56
				50 g/L S/L, 4 h, 90 °C	%, Co		
					93.5 %,		
18	NCM	Acetic acid	H ₂ O ₂	4 M AcOH, 5 %	Li 99.1	Li _, Co, Ni	This
				H ₂ O ₂ , 20 g/L S/L, 5	%, Co	, Mn	work
				h, 30 °C	98.1 %,		
					Ni 98.3,		
					Mn 99.5		
					%		

Table. S2 The leaching of metal ions from anode material using various lixiviants.

<i>S</i> .	Type of	Acid/ DES	Reducing	Reaction	Leaching	Elements	Ref
No.	material	Leachant	agent	conditions	efficiency	recovered	
	considered						
1	Both	Acetic acid	H ₂ O ₂	Pulp	99.9 % Li	Li,	47
	cathode and			density 20		graphite	
	anode			g/L, 3 M			
				AcOH, 70			
				°C, 40 min			
2	LIB (Only	HC1	H ₂ O ₂	S/L ratio	99.4 % Li	Li,	59
	anode)			1:50 g/mL,		graphite	
				90 min,			
				3M, 80 °C			
3	LIB (Only	aqueous		ultrasonic	>90.00%	Li,	S1

	cathode)	solutions		leaching	Li	graphite	
4		HCl,			96.6 %	Li, Cu	S2
		HNO ₃			Li, Cu		
					(97.6%)		
5	A mixture	0.8 M		70 °C	100 %	Li, Co	S3
	of cathode	acetic acid					
	and anode						
6	A mixture	2 M acetic	H ₂ O ₂	70 °C, S/L	98.56 %	Al, Co,	S4
	of cathode	acid		ratio of 20	Li	Mn, Ni,	
	and anode			g/L, 30 min		Li	

Supporting Information References

- S1 T. Ren, K. Lin, M. Zhao, B. Lai and J. Ruan, *ACS Sustain. Chem. Eng.*, 2024, **12**, 15240–15249.
- S2 S. Agarwal, S. Dhiman and H. Gupta, *Environ. Sci. Pollut. Res.*, 2024, **31**, 34249–34257.
- S3 S. Sahu and N. Devi, *RSC Adv.*, 2023, **13**, 7193–7205.
- S4 K. Wang, G. Zhang and M. Luo, *Separations*, 2022, 9, 259.

Mass balance & Economic viability calculations:

In our process, a 1 kg batch of whole cathode (including Al foil) is used for leaching, with a total of 50 L: 2.5 L of H_2O_2 and 47.5 L of 4M acetic acid. This leaching process allows for the concurrent leaching of metals while effectively separating the undissolved Al foil. The resulting leached liquor from the whole cathode is then processed in 1 L batches for the selective and sequential precipitation of metals. For every 1 kg of cathode, 3.6 kg of used LIBs, 1.15 kg of anode, 1.22 kg of external parts, and 0.2 kg of separator are processed.

In the material balance calculations, we assume that the input and output water are the same if collected, and thus H_2O_2 and water are not included in the calculations. It was observed that for an input of 17.382 kg, 17.52 kg of product was obtained. Economic evaluations were made based on the local market prices of some commodities and the price information from cited literature. Since no market price is available for Co_9S_8 , we used the price for cobaltous sulphide as a reference. For Ni(DMG)₂, this material is recycled to recover Ni(OH)₂ and DMG, but we have excluded it from the cost calculation. Similarly, Mn(OH)₂ and Al(OH)₃, due to their lower economic value and small quantities, were not included in the cost calculation. The solid separator and external parts were also excluded from the cost evaluation. Based on the input cost of 218.46 USD, the output revenue amounts to 460.15 USD, yielding a net profit of 241.69 USD.

Material balance for dismant	ing of 3.6 Kg ba	ttery to get 1 Kg cathode materia	ıl
INPUT MATERIALS	Weight	OUTPUT MATERIALS	Weight
	(Kg)		(Kg)
Battery	3.6 Kg	Cathode	1 Kg
		Anode	1.15 kg
		[0.544kg (Cu foil) +	
		0.520kg (C powder)]	
		Separator	0.21 kg
		External Parts	1.22 kg
Total	3.6 kg	Total	3.58 kg
Material balance for processing	ng of 1 Kg catho	de material for metal recovery	
INPUT MATERIALS	Weight	OUTPUT MATERIALS	Weight

Table S3. Mass balance for processing of 3.6 Kg of used LIBs in our study.

	(Kg)		(Kg)
Cathode	1 Kg	Al foil	0.107 kg
		Carbon residue	0.069 Kg
4 M Acetic acid (47.5 L)	11.41 kg	Recovered Acetic Acid (1.72 M, 40 L)	4.12 Kg
35 wt % H ₂ O ₂	2.5 L		
(Not considered for mass balance)			
DMG	0.11 Kg	Ni(DMG) ₂	0.13 Kg
Na ₂ S	0.332 Kg	Co ₉ S ₈	0.372 Kg
NaOH (for neutralization & precipitation of Mn &Al	4.2 Kg	$Mn(OH)_2 + Al(OH)_3$	0.148 Kg
Na ₂ CO ₃	0.330 Kg	Li ₂ CO ₃	0.195 Kg
	1	NaOAC.3H ₂ O (65%)/NaOAC (35%)	16.64 Kg
Total	17.382 Kg		21.819 Kg
Total	17.382 Kg	Subtracting water content in NaOAC.3H ₂ O (4.3 Kg)	21.819 – 4.3 = 17.52 Kg
	<u> </u>		<u> </u>

Notes:

H₂O₂ & Water is not considered for mass balance (The input water will same as output water if collected).

Table S4. Economic evaluation for processing of 3.6 Kg of used LIBs in our study.

Cost calcul	lation for I	nput Materials		
Input Material	Quantit y	Cost (USD/Kg)	Total Cost (USD)	Source of Values
Battery	3.6 Kg	4	14.4	(Local market, India)
4M Acetic	47.5 L = 11.41	0.81 USD/Kg	9.24	Local market price (www.indiamart.com)

acid	Kg			
35 %	2.5 L	0.14 USD/L	0.35	J. Hazard Mater , 2024, 474 , 134794,
H ₂ O ₂	-			······································
	0.11 V~	$2 \text{ USD}/W_{\alpha}$	0.22	Legal market migg (www.indiamont.com)
	0.11 Kg	3 USD/Kg	0.55	
Na2S	0.332	0.80 USD/Kg	0.26	Local market price (www.indiamart.com)
	Kg			
NaOH	4.2 Kg	0.42 USD/Kg	1.76	J. Hazard. Mater., 2024, 474, 134794.
Na2CO3	0.33 Kg	0.37 USD/Kg	0.12	I Hazard Mater 2024 474 134794
	0.0001128	0.07 0.027118	0.112	<i>b</i> . 11(20) (<i>b</i> . 11(10)), 202 (<i>b</i> . 17), 10 (<i>b</i> . 17) (<i>b</i> . 10)
T (1			26.46	
Total input	t material c	cost	26.46	
			USD	
Operation	cost for 3.H	Kg of spent LIBs	that tak	es 2 days for complete separation
Electricit	1170		112	
v (in	kwH		USD	
KWH)	I KWII			
Mannarra	2	10	60	
Manpowe	3			
r		USD/Person/Da	USD	
		У	20	
Capital			20	
cost/per			USD	
process				
Total Cost	(material +	- operation)	218.4	
		1 /	6	
			USD	
			0.50	
Cont onlog	- 4°	······································		
	ation for t	hitniit Materiais		
Cost calcul				
Output	Quantity	Cost	Total	Source of Values
Output Material	Quantity	Cost (USD/Kg)	Total Cost	Source of Values
Output Material	Quantity	Cost (USD/Kg)	Total Cost (USD	Source of Values
Output Material	Quantity	Cost (USD/Kg)	Total Cost (USD)	Source of Values
Output Material	Quantity	Cost (USD/Kg)	Total Cost (USD) 0.23	Source of Values
Output Material	Quantity 0.107	Cost (USD/Kg) 2.19 USD/Kg	Total Cost (USD) 0.23	Source of Values J. Hazard. Mater., 2024, 474, 134794.
Output Material	Quantity 0.107 Kg	Cost (USD/Kg) 2.19 USD/Kg	Total Cost (USD) 0.23	Source of Values J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil	Quantity 0.107 Kg 0.544	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg	Total Cost (USD) 0.23 4.43	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil	Quantity 0.107 Kg 0.544 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg	Total Cost (USD) 0.23 4.43	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil Carbon	Quantity 0.107 Kg 0.544 Kg 0.520	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg	Total Cost (USD) 0.23 4.43 0.11	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil Carbon powder	Quantity 0.107 Kg 0.544 Kg 0.520 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg	Total Cost (USD) 0.23 4.43 0.11	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil Carbon powder Recovere	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market
Output Material Al foil Cu foil Carbon powder Recovere d Acetic	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com))
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1 72	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M 401)	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L)	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba It-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 0.195	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 0.372 Kg 0.195 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba It-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm J. Hazard. Mater., 2024, 474, 134794.
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 0.195 Kg 16.64	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 17.5 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm J. Hazard. Mater., 2024, 474, 134794.Local market
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 0.195 Kg 16.64 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 17.5 USD/Kg 1 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba It-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm J. Hazard. Mater., 2024, 474, 134794. Local market (www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 16.64 Kg	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 17.5 USD/Kg 1 USD/Kg	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htmJ. Hazard. Mater., 2024, 474, 134794.Local market (www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc Total outpu	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 16.64 Kg ut material	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 17.5 USD/Kg 1 USD/Kg cost	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD 460.1	Source of Values J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. J. Hazard. Mater., 2024, 474, 134794. Local market ((www.indiamart.com) https://www.ibuychemikals.com/product/coba It-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htm J. Hazard. Mater., 2024, 474, 134794. Local market (www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc Total outpu	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 16.64 Kg ut material	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 17.5 USD/Kg 1 USD/Kg cost	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD 460.1 5	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htmJ. Hazard. Mater., 2024, 474, 134794.Local market (www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc Total outpu	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 16.64 Kg ut material	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 1 USD/Kg 1 USD/Kg cost	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD 460.1 5 USD	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htmJ. Hazard. Mater., 2024, 474, 134794.Local market (www.indiamart.com)
Output Material Al foil Cu foil Carbon powder Recovere d Acetic acid (1.72 M, 40L) Co ₉ S ₈ Li2CO3 NaOAc Total output	Quantity 0.107 Kg 0.544 Kg 0.520 Kg 4.12 Kg 0.372 Kg 16.64 Kg ut material	Cost (USD/Kg) 2.19 USD/Kg 8.15 USD/Kg 0.21 USD/Kg 0.81 USD/Kg 1163 USD/Kg 1 USD/Kg 1 USD/Kg cost	Total Cost (USD) 0.23 4.43 0.11 3.33 432 USD 3.41 USD 16.64 USD 460.1 5 USD	Source of ValuesJ. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.J. Hazard. Mater., 2024, 474, 134794.Local market ((www.indiamart.com)https://www.ibuychemikals.com/product/coba lt-(ii)-sulphide-cobaltous https://www.chemicalbook.com/Price/COBA LT-SULFIDE.htmJ. Hazard. Mater., 2024, 474, 134794.Local market (www.indiamart.com)

NET Profit = Total output cost - Total input cost = 460.15 - 218.46 = 241.69 USD

 Co_9S_8 : There is no market price available for Co_9S_8 . So, we have considered price for cobaltous sulphide.

Ni(DMG)₂: This material is recycled to recover Ni(OH)₂ & DMG. However, we have not considered in cost calculation.

Mn(OH)₂ & Al(OH)₃: Considering less economic values and small amount not considered in cost calculation.

Water: The quantity of input water will be same as output water if collected. So, we have not considered in cost calculation.

Separator: Not considered in cost calculation

External Parts: Not considered in cost calculation

 Table. S5 A comprehensive analysis of mass balance & economic evaluation

INPUT MATERIALS		Input	OUTPUT MATERIALS		Output Cost (USD)
		Cost (USD)			
Battery	3.6 Kg	14.4 USD	Cathode	1 Kg	Used for metal recovery
		(4 USD/Kg)	Anode	1.15 kg	[4.43 USD (Cu foil)+
		(As per local market pricing)	[0.544kg (Cu foil) +		0.11USD (C powder)]
			0.520kg (C powder)]		= 4.54 USD
					[8.15 USD/Kg (Cu foil), 0.21 USD/kg (C powder)] (Pricing: <i>J. Hazard.</i> <i>Mater.</i> , 2024, 474 , 134794.)
			Separator	0.21 kg	
			External Parts	1.22 kg	
Total	3.6 kg	14.4 USD	Total	3.58 kg	4.54 USD
Downstream processing	of obtained 1	1 kg cathode from 3	.6 kg of used LIBS (Total volume	50 L)	
Cathode	1 Kg		Al foil	0.107 kg	0.23 USD [2.19/Kg] (Pricing: J.
			Carbon residue	0.069 Kg	Hazard. Mater., 2024, 474 , 134794)
4 M Acetic acid (47.5 L)	11.41 kg	9.24 USD	Recovered Acetic Acid (1.72 M, 40 L)	4.12 Kg	3.33 USD
		(0.81 USD/Kg)			(0.81USD/Kg) (local market)

35 wt % H ₂ O ₂	2.5 L	0.35 USD			
(Not for mass balance)		(0.14 USD/L) (Pricing: J. <i>Hazard. Mater.</i> , 2024, 474 , 134794.)			
DMG	0.11 Kg	0.33 USD (3 USD/Kg) (local market)	Ni(DMG) ₂	0.13 Kg	Recycled
Na ₂ S	0.332 Kg	0.26 USD (0.80 USD/Kg) (local market)	Co ₉ S ₈	0.372 Kg	432 USD (1163 USD/Kg) (There is no market price available for Co ₉ S ₈ . So, we have considered price for cobaltous sulphide) https://www.ibuychemikals.com/product/cobalt-(ii)- sulphide-cobaltous https://www.chemicalbook.com/Price/COBALT- SULFIDE.htm
NaOH (for neutralization & precipitation of Mn &Al	4.2 Kg	1.76 USD (0.42 USD /Kg) (Pricing: J. <i>Hazard. Mater.</i> , 2024, 474 , 134794)	Mn(OH) ₂ + Al(OH) ₃	0.148 Kg	
Na ₂ CO ₃	0.330 Kg	0.12 USD (0.37 USD/Kg) (Pricing: J. Hazard. Mater.,	Li ₂ CO ₃	0.195 Kg	3.41 USD (17.5 USD/Kg) (Pricing: <i>J. Hazard. Mater.</i> , 2024, 474,

		2024, 474 , 134794)			134794)			
			NaOAC.3H ₂ O (65%)/NaOAC (35%)	16.64 Kg	16.64 USD (1 USD/Kg) (Pricing: local market)			
Total	17.382 Kg	26.46 USD		21.819 Kg	460.15 USD			
Total	17.382 Kg		Subtracting water content in NaOAC.3H ₂ O (4.3 Kg)	21.819 - 4.3 = 17.52 Kg				
Operation cost for handling 3.6 Kg of sent LIBs in 2 days up to the end (up to recovery of sodium acetate)								
Electricity (in KWH)	1170 kwH	112 USD						
Manpower	3	60 USD						
Capital cost/per process		20 USD						
Total		218.46 USD	NET Profit : 460.15 - 218.46 = 241.69 USD		460.15 USD			