A sustainable delamination method to completely separate the spent cathode foil via biomass-derived γ-valerolactone

Zheng Fang, Qiangling Duan*, Qingkui Peng, Zesen Wei, Lihua Jiang, Jinhua Sun, Qingsong Wang

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, 230026, China

* Corresponding authors: Qiangling Duan

E-mail addresses: duanql@ustc.edu.cn (Q. Duan).

Table S1

The prices of various solvents mentioned in the text. (Source: http://english.macklin.cn/)

Solvent	Prices (USD/ kg)
NMP (98%, pack size:2.5 kg)	23.73
DMF (99%, pack size:2.5 L)	21.33
DMAC (99%, pack size:2.5 L)	11.87
Cyrene^{TM} (98.5%, pack size:2.5 L)	202.35
DMI (98.5%, pack size:2.5 L)	178.53
GVL (98%, pack size:2.5 kg)	76.27

Table S2

Hansen solubility parameters (HSPs) and Hildebrand solubility parameters (δ) of PVDF and various solvents are shown in **Fig. 1(a)** of the manuscript. R_a represents the distance of the respective compound to PVDF in Hansen space.

Compound	δ_d	δ_p	δ_h	δ	R_a
PVDF	17.2	12.5	9.2	23.17	\
NMP	18	12.3	7.2	22.96	2.16
DMF	17.4	13.7	11.3	24.86	2.43
DMAC	16.8	11.5	10.2	22.77	1.47
Cyrene	18.5	11.6	6.6	22.81	3.04
GVL	16.7	14	8	23.21	1.98

Table S3

Ecotoxicity comparison between GVL solvent and other conventional dipolar aprotic solvents (NMP, DMF, DMAC).

Test system	EC50 (2.5% CI-97.5% CI)				
	GVL[a]		NMP	DMF	DMAC
	mg L^{-1}	mmol L^{-1}	mmol L^{-1}		
IPC-81	≈1000 (n.a.)	100 (n.a.)	n.a.	n.a.	n.a.
Aliivibrio fischeri	257 (251-269)	25.7 (25.1-26.9)	n.a.	257[c]	27.6[c]
Lemna minor	>1135	>114	n.a.	n.a.	n.a.
Daphnia magna	>680	>68	0.012[b]	169 (130-208)[d]	n.a.

[a] According to Kerkel et al.[1] [b] According to Lan et al.[2] [c] According to Jennings et al.[3]

[d] According to LeBlanc and Surperenant.[4] The half-minimal inhibitory concentration (EC50) is given, whenever the effects allowing for its determination were observed. Additionally, 2.5% and 97.5% confidence intervals are specified in the brackets, whenever such could be calculated.

Table S4

Comparison of different solvents for cathode foil delamination.

Methodology	Solvents	Operating conditions	Delamination efficiency	References
Ultrasound-assisted	NMP	70 °C, 90 min, 240W	~99%	(He et al., 2015)[5]
Organic solvent	Cyrene	100 °C, 1 hour	-	(Bai et al., 2020)[6]
Organic solvent	triethyl phosphate	150 °C, stirring and sonication for 30 min	-	(Bai et al., 2021)[7]
Ultrasound-assisted	0.05 M citric acid	high-intensity ultrasonication (>1000 W)	-	(Lei et al., 2021)[8]
Eutectic salts	LiOAc:$LiNO_3$ (3:2)	300 °C, 30 min	98.5%	(Ji et al., 2022)[9]
Organic solvent	glycerol	200 °C, 350 rpm, 15 min	95.0%	(Gu et al., 2022)[10]
This study	γ-valerolactone	80 °C, 90 W, 8 min	99.2%	

Table S5

Element composition of the spent cathode foil, Al foil, and delaminated CAMs. (wt%).

	Li	Ni	Co	Mn	Al
Cathode foil	5.44	25.91	10.65	13.70	6.10
Al foil	0.89	0.27	0.08	0.12	96.22
Delaminated CAMs	3.73	37.13	14.97	20.28	0.19

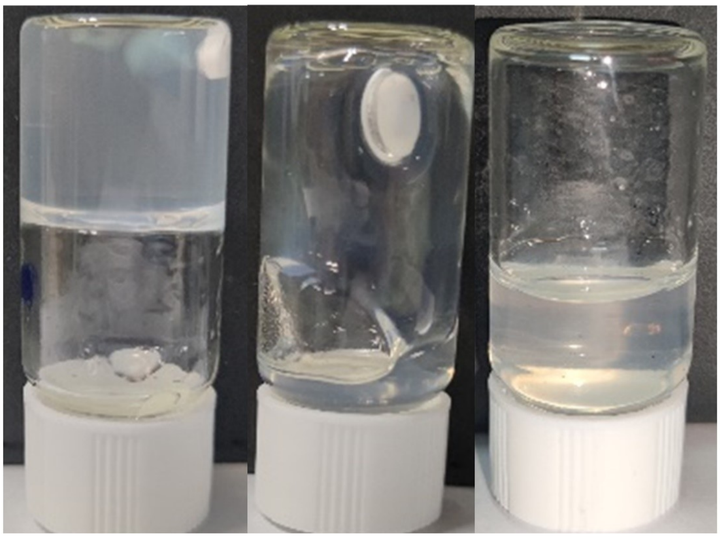

Fig. S1. Photos showing samples #1, #2, #3 (10 wt%, 5 wt%, 2 wt%) after the apparent solubility test (at room temperature).

(a) **(b)**

Fig. S2. Photos showing the spent cathode foil before and after the delamination process in GVL (80 °C, 600 rpm).

(a) **(b)**

Fig. S3. Ultrasound-assisted delamination of the spent cathode foils in (a) deionised water and (b) GVL (P_{ul} = 150 W, T_{op} = 80 °C, t_{op} = 5 min).

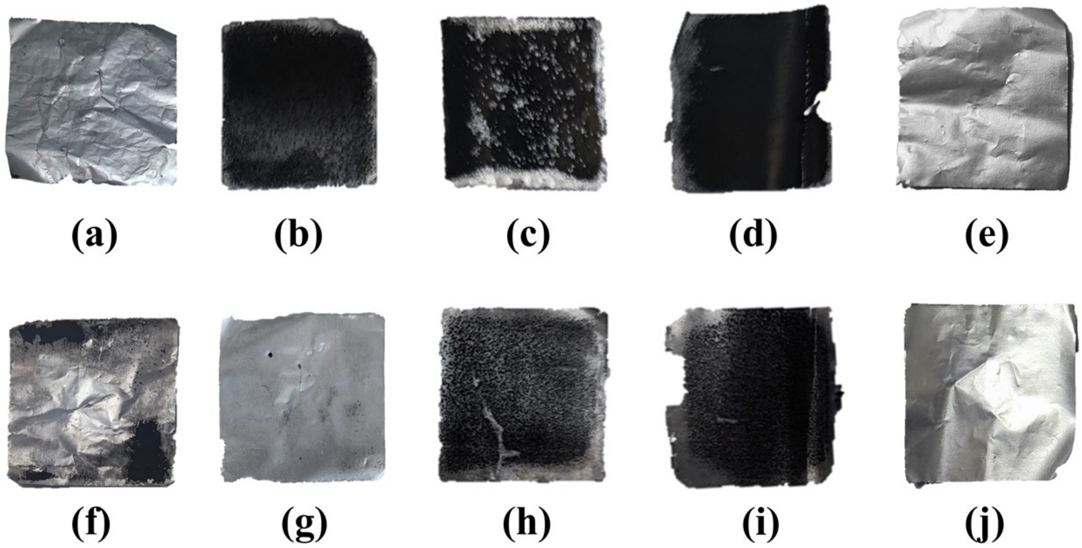

Fig. S4. (a)-(i) Orthogonal experimental designs of ultrasound-assisted GVL delamination (Exp. number 1-9), and (j) the validation experiment of theoretical optimal condition (P_{ul} = 90 W, T_{op} = 80 °C, t_{op} = 8 min).

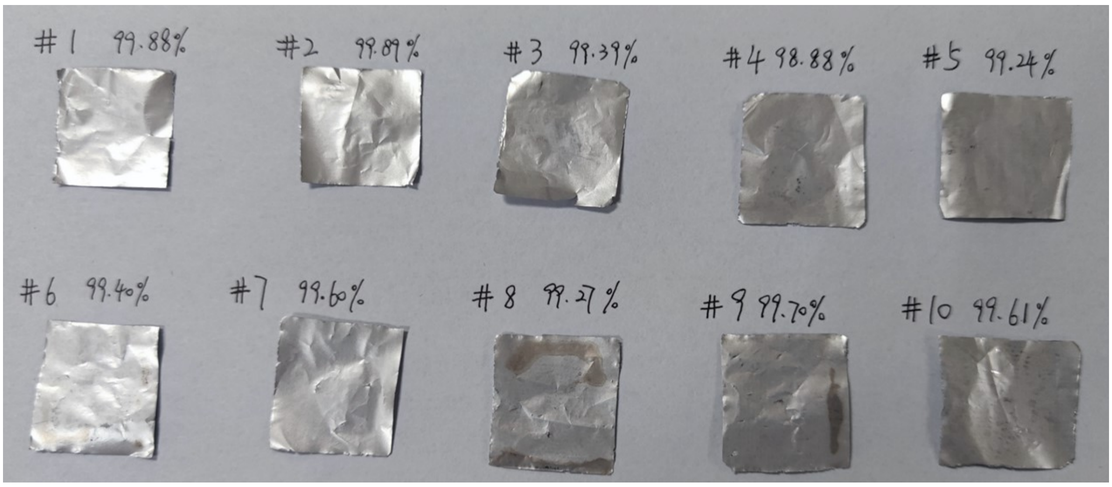

Fig. S5. Cyclic experiments and corresponding delamination efficiency (E_d) after multiple cycles (optimal condition: P_{ul} = 90 W, T_{op} = 80 °C, t_{op} = 8 min).

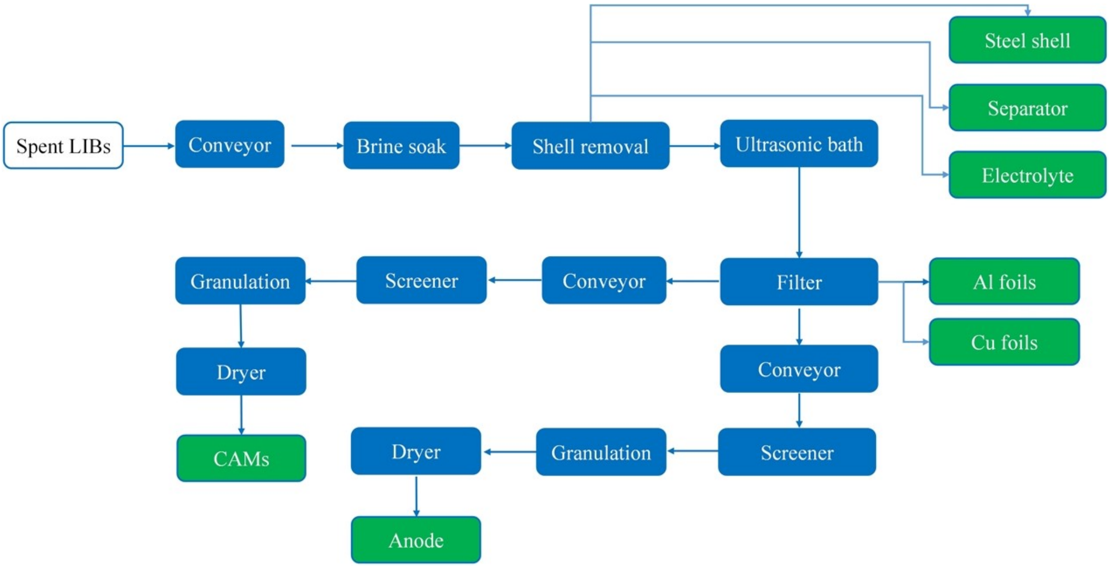

Fig. S6. Process diagram of GVL-based direct recycling method of spent LIBs.*

* Lithiated graphite (LiC_x) in the anode will react exothermically with H_2O to produce hydrogen and LiOH, and the graphite will be rapidly stripped from the surface of the copper foil without other treatments.[11]

Table S6

Revenue comparison between GVL-based direct recycling and pyrometallurgical recycling methods

Method \ Recycled material	Steel shell 0.28 $/kg	Separator 0.1$/kg	Cu foil 5.43 $/kg	Al foil 1.45 $/kg	Graphite 0.2 $/kg	CAMs 20 $/kg	Total
GVL-based direct recycling	164.10 g 0.046 $	17.36 g 0.002 $	69.57 g 0.377 $	26.15 g 0.038 $	241.30 g 0.048 $	347.47 g 6.949 $	7.46 $
Pyro recycling			0.85 $			Ni, Co, Mn products 3.91 $	4.76 $

Table S7

Energy consumption, water consumption, and gas emissions of GVL-based direct recycling and pyrometallurgical recycling methods

Method \ Recycled material	Energy Consumption (MJ/kg)	CO_2 (g)	NO_x (g)	SO_x (g)	Water Consumption (L)
GVL-based direct recycling	11.98	987	0.71	2.17	11.73
Pyro recycling	18.23	2399	1.22	2.25	6.06

References

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