A STUDY ON THE RECYCLING OF LITHIUM-ION BATTERIES FROM NEWLY GENERATED RECHARGEABLE SMALL ELECTRONIC DEVICES

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- **I** — Innovative to Future
- **G** — Globalization to Leader
- **A** — Alternation to Smartness
- **M** — Mobility to Convergence

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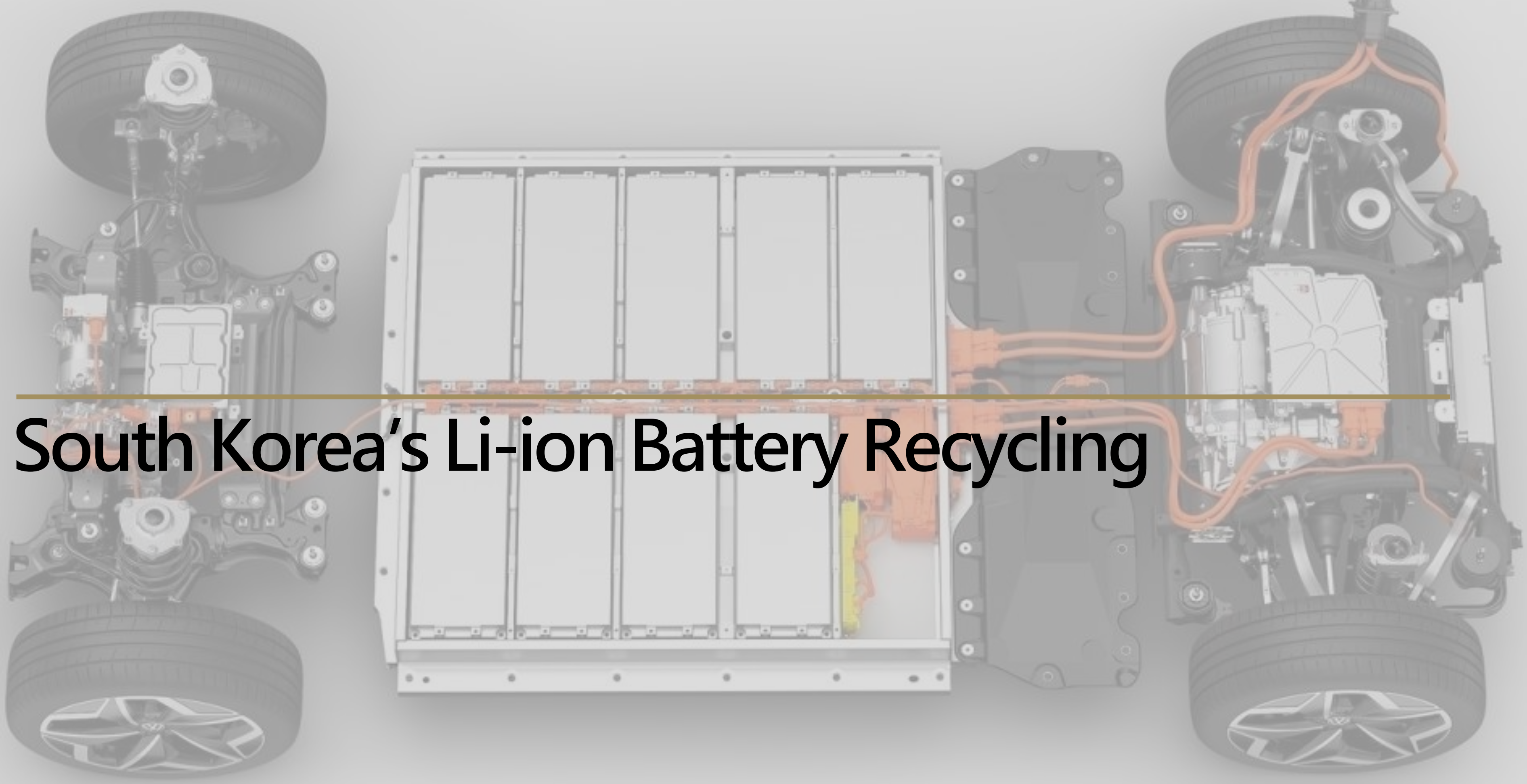
- Geology Division
- Climate Change Response Division
- Resources Utilization Division
- Marine Geology & Energy Division
- Mineral Resources Division
- Geologic Hazards Division

Contents



South Korea's Li-ion Battery Recycling

Battery Recycling

Recycle vs. Re-Use

Korean battery circular economy is classified into **recycling** (extracting and recycling rare metals by decomposing waste batteries into cells) and **reuse** (using waste batteries in their original form for other purposes), and there are differences in necessary facilities and requirements.

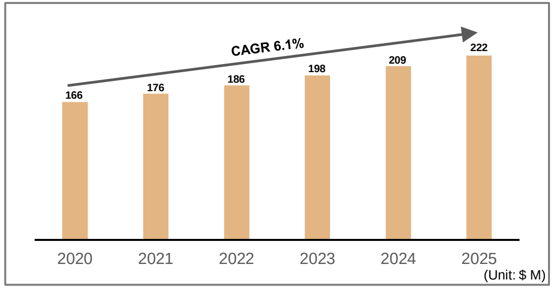
RECYCLING		RE-USE
• A method of extracting and recycling rare metals by decomposing waste batteries in cell units	Definition	• How to use waste battery modules and packs as ESS or UPS
• Small IT device battery	Target	• Medium and large batteries (electric vehicle batteries, etc.)
• Waste battery discharge system required • Required to secure recovery process technology	Requirements	• Waste battery diagnosis and analysis equipment • Advantageous for ESS production and operation know-how
• Reduction of raw material cost • Sales \$600-900/24kWh battery packs by extracting metals	Expected Effects	• No need to dismantle the module and cell • Stable dismantling process and low cost

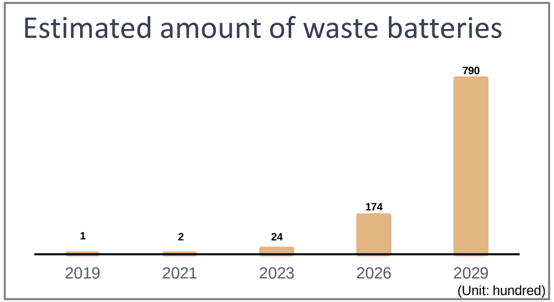
Battery Recycling

Korea’s Battery Recycling Industry

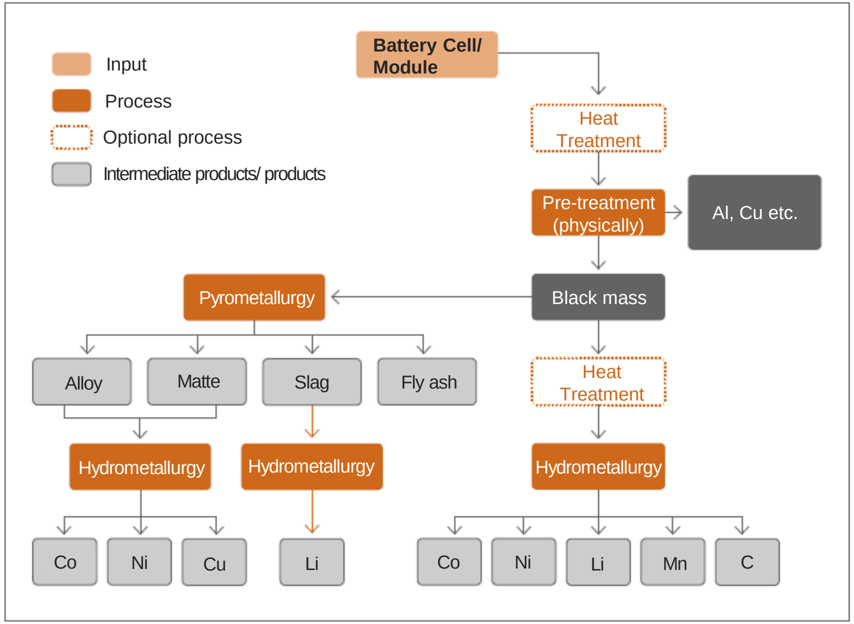
The size of the South Korean battery recycling market was $170 million in 2020, and it is expected to grow at a compound annual rate of 6.1% until 2025, reaching $220 million. Accordingly, the disposal of used electric vehicle batteries is estimated to increase from 100 units in 2019 to 79,000 units in 2029.

Battery Market Forecast





Flow sheet for Battery recycling



Battery Recycling

Comparison of Large and Small Battery Recycling Processes

EV BATTERY RECYCLING

Large spent LIBs recycling process

EV Battery → Dismantle → Valuation → Classification → Discharge → Crushing → Metal/Non-Metal sorting → Refining

SMALL BATTERY RECYCLING

Small spent LIBs recycling process

Small IT device → Fire/explosion prevention type crusher → Metal/Non-Metal sorting → Refining process

Fire/explosion prevention type crusher → Black Powder

Metal/Non-Metal sorting → Plastic

Li-ion Battery Recycling R&D

LIBs Recycling R&D

Research on Pre-treatment for Small Electrical Appliances(on-going)

Development of technology for stable dismantling of small waste electrical and electronic products including lithium-ion batteries and the optimal separation process for plastic-metal materials

WHY?

Explosion and fire problems during pre–treatment

HOW?

Development of fire/explosion prevention type crusher

Establishment of customized pretreatment system for future waste

LIBs Recycling R&D

Experimental part 1: Development of Stable Shredding Technology

✓ **Battery shredding**

✓ **Causes of fire and explosion**

Fire	• Combustion of organic materials/electrolyte by sparks caused by short circuit • Heat generated by thermit reaction by Al separation film and cathodic oxide-white smoke • During charging and discharging, unconverted energy generates heat and burns
Explosion	• By burning oil vapor • By thermit reaction – explosive • Pressure increase due to oil vapor combustion • Increased pressure due to gas generation by oxide and carbon reaction

LIBs Recycling R&D

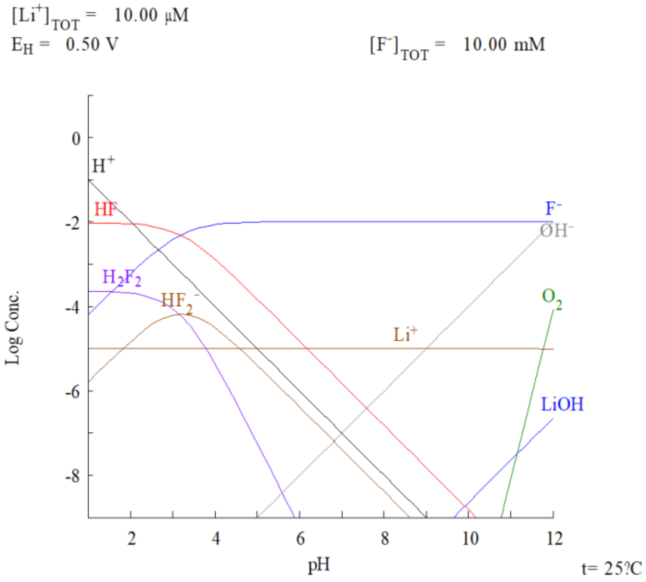
Experimental part 1: Development of Stable Shredding Technology

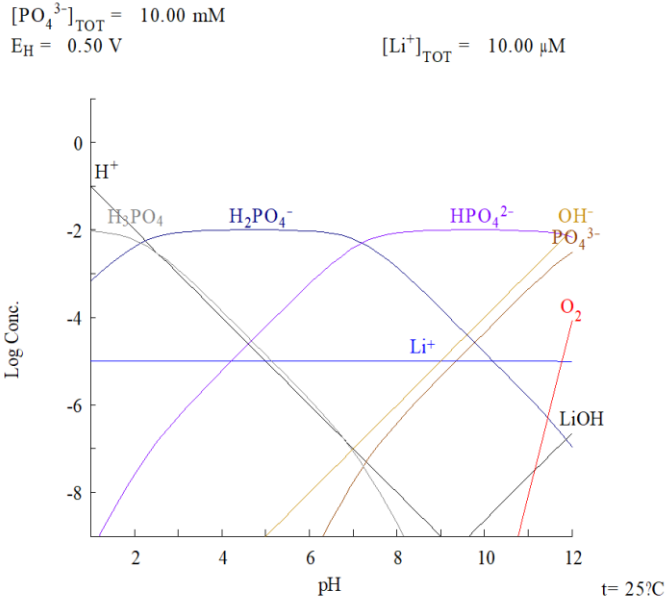
✓ **Stable shredder development**

LIBs Recycling R&D

Experimental part 1: Development of Stable Shredding Technology

✓ **Log C-pH Diagram**





$LiPF_6 + H_2O \rightarrow LiF \cdot HF + HF\uparrow + POF_3\uparrow$

$POF_3 + H_2O \rightarrow H[PO_2F_2]$

$H[PO_2F_2] + H_2O \rightarrow H[PO_3F] + HF\uparrow$

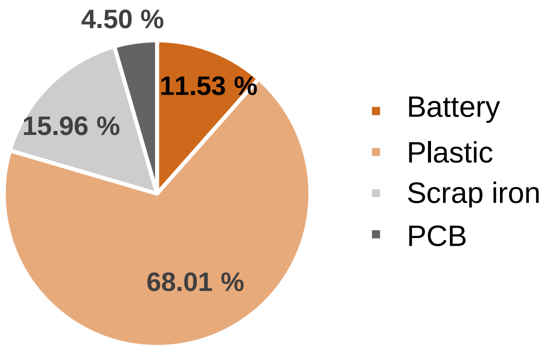
$H_2[PO_3F] + H_2O \rightarrow H_3[POF] + HF\uparrow$

LIBs Recycling R&D

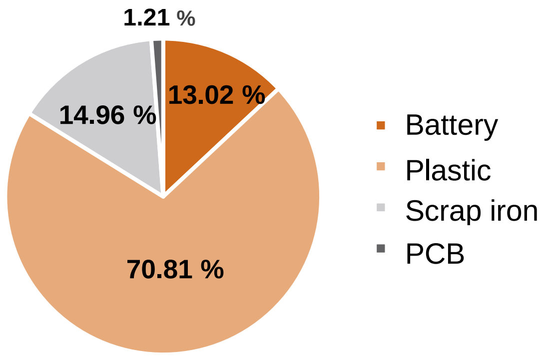
Experimental part 1: Development of Stable Shredding Technology

✓ **Samples information**

No	Robot Vacuum					Handheld Vacuum				
	Weight(g)				Total	Weight(g)				Total
	Battery	Plastic	Ferrous	PCB		Battery	Plastic	Ferrous	PCB	
1	0.199	2.375	0.857	0.146	3.577	0.778	2.037	0.163	0.037	3.015
2	0.198	2.742	0.321	0.099	3.360	0.405	1.817	0.314	-	2.536
3	0.672	1.531	0.243	0.192	2.638	0.586	2.440	1.234	0.037	4.297
4	0.201	1.934	0.383	0.115	2.633	0.460	2.431	0.310	0.036	3.237
5	0.218	2.086	0.415	0.164	2.883	0.265	2.210	0.164	0.030	2.669
6	0.199	1.616	0.332	0.033	2.180	0.105	2.346	0.250	0.087	2.788
7	0.428	2.522	0.428	0.145	3.523	0.251	2.522	0.402	0.046	3.221
8	0.213	2.087	0.399	0.170	2.869	0.382	2.506	0.346	0.054	3.288
9	0.221	2.011	0.532	0.195	2.959	0.242	2.063	0.646	0.033	2.984
10	0.426	2.437	0.862	0.103	3.828	0.270	1.813	0.291	0.016	2.390
11	0.193	2.099	1.446	0.166	3.904	0.243	2.056	0.218	0.025	2.542
12	0.191	1.513	0.410	0.072	2.186	0.562	2.498	1.237	0.016	4.313
13	0.583	1.666	0.362	0.173	2.784	0.283	1.905	0.369	0.012	2.569
14	0.642	1.605	0.171	0.148	2.566	0.705	2.025	0.428	0.055	3.213
15	0.692	2.892	0.141	-	3.725	0.177	0.403	0.191	0.010	0.781
Av.	**0.352**	**2.074**	**0.487**	**0.137**	**3.050**	**0.381**	**2.071**	**0.438**	**0.035**	**2.925**
wt%	**11.53 %**	**68.01 %**	**15.96 %**	**4.50 %**		**13.02 %**	**70.87 %**	**14.96 %**	**1.21 %**	



[Robot Vacuum]



[Handheld Vacuum]

LIBs Recycling R&D

Experimental part 1: Development of Stable Shredding Technology

✓ **Stable shredder development**

- Conducting a shredding experiment with a spent batteries secured after disassembling small waste appliances
- To derive stable crushing conditions in an inert gas

[Separated LIBs]

[Lab scale shredder]

[Gas, Salt water injection system]

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LIBs Recycling R&D

Experimental part 1: Development of Stable Shredding Technology

✓ Experimental Results

Atmosphere	Contents		
	Spark	Fire	Note
Atmospheric	O	X	Spark long time
Nitrogen 85%	X	O	Shredded product fire
Nitrogen 90%	X	O	Shredded product fire
Nitrogen 95%	X	X	-
Carbon dioxide 10%	X	X	-
Carbon dioxide 20%	X	X	-
Carbon dioxide 30%	X	X	-

- Sparks continuously occur for about 30 sec. in atmospheric shredding conditions
- N_2 85%, 90% partial pressure shredding product fire and stable shredding in N_2 95%
- CO_2 atmosphere is possible at all partial pressures (10-30%) for stable shredding

[Atmospheric shredding]

[Nitrogen 85% shredding]

LIBs Recycling R&D

Experimental part 1: Development of Stable Shredding Technology

✓ Compositions of shredded LIBs samples

Name	Chemical composition(%)								
	Li	Ni	Co	Mn	Fe	P	Cu	Al	C
Un-fired sample	3.54	21.6	6.07	6.62	0.41	0.48	0.33	0.20	35.5
Sample on fire	1.95	10.4	3.74	3.28	0.47	2.83	0.80	1.59	-

- The occurrence of fire during the shredding process has an effect on the decrease in the concentration of Co, Ni, and Li
- Therefore, the pretreatment process is reduced through proper atmosphere control without the discharge process

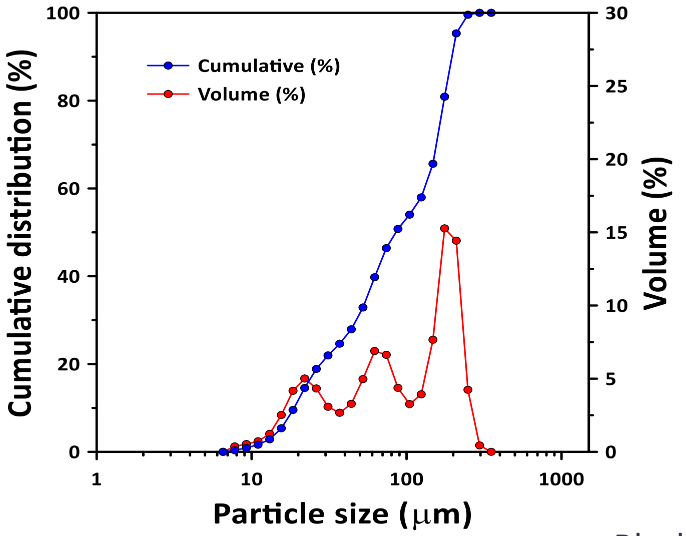
[Atmospheric shredding]

[Nitrogen 85% shredding]

LIBs Recycling R&D

Experimental part 2: Efficient Separation Technology for Electrode Active Materials

✓ Particle size analysis of black powder



✓ Composition of lithium-ion batteries(NCM)

Cathode material (%)			
Ni	Co	Mn	Li
16.55	4.62	5.22	3.05
Other metal and carbon (%)			
Cu	Al	Carbon	
3.25	3.73	30.1	

- Black powder recovered after classification of ground spent LIBs
- Recovered black powder is divided into the cathode material containing Ni, Co, Mn, and Li, and the portion separated into metals or carbon

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LIBs Recycling R&D

Experimental part 2: Efficient Separation Technology for Electrode Active Materials

- Since the material is in a powdered state, no pretreatment process, such as density or electrostatic separation, is performed before flotation

[Denver D12 laboratory flotation machine]

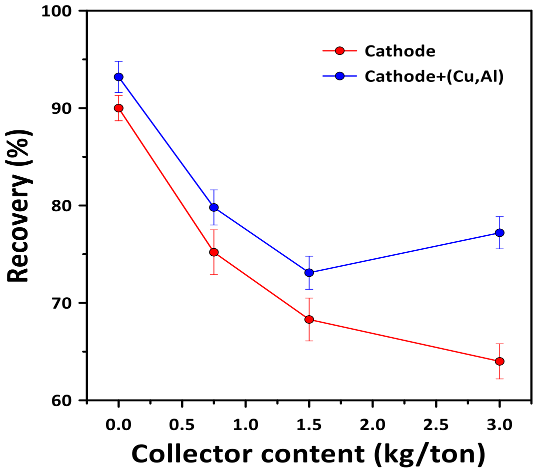
[Experimental conditions]

- Agitation 1500 rpm
- Time 0.5, 1, 2, 4 min
- Pulp density 1% (w/w)
- Flocculant conc. 0, 0.75, 1.5, 3 (kg/ton)
- Foaming agent conc. 1.5 (kg/ton)

Recovery(%) = $\frac{c(f-t)}{f(c-t)} \times 100$; >90%

Impurities ; <2.0%

[Recovery efficiency of metals]



[Composition of carbon after flotation]

Carbon (%)				
Feed	Collector content (kg/ton)			
	0 (natural floatability)	0.75	1.50	3.00
30.1	22.6	8.93	5.74	3.67

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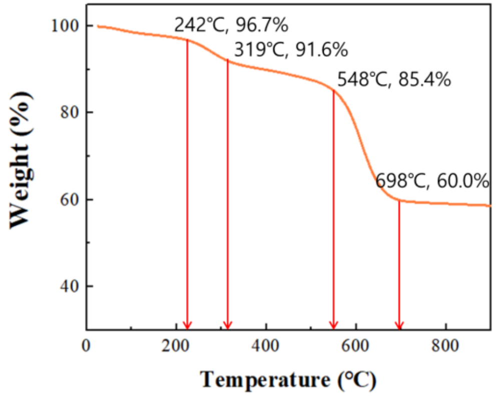
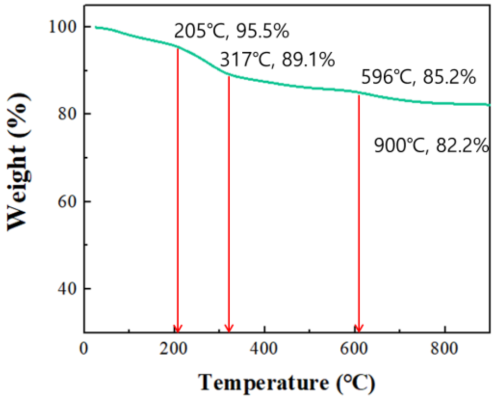
LIBs Recycling R&D

Experimental part 2: Efficient Separation Technology for Electrode Active Materials

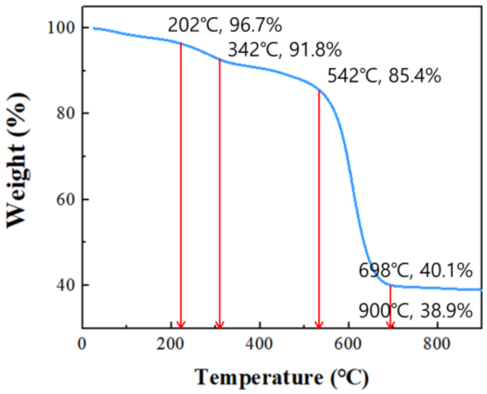
✓ **TGA analysis**



[feed]



[sink]

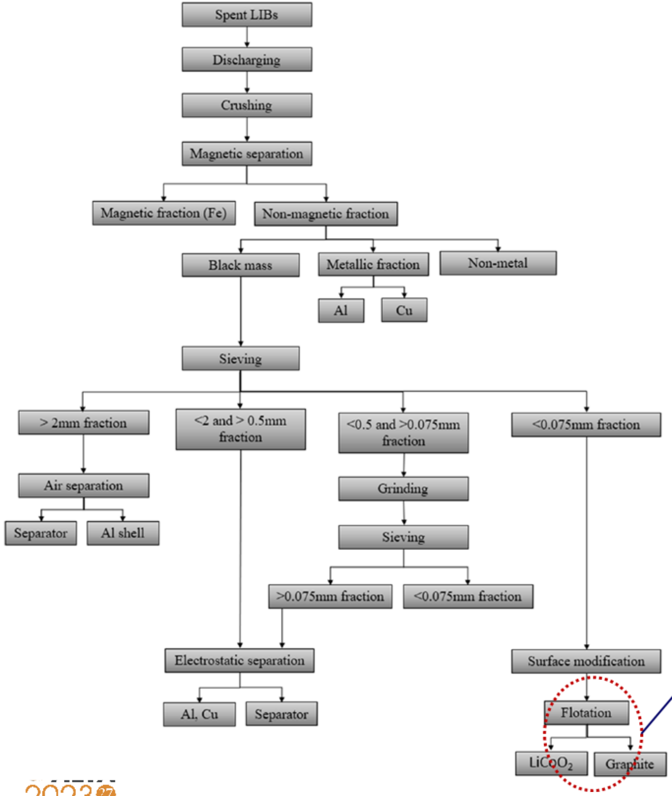


[floating]

- Feed sample contains a relatively high amount of carbon and binder
- Sink samples showed a decrease in carbon and binder content, whereas floating samples showed a significant increase in binder and carbon content

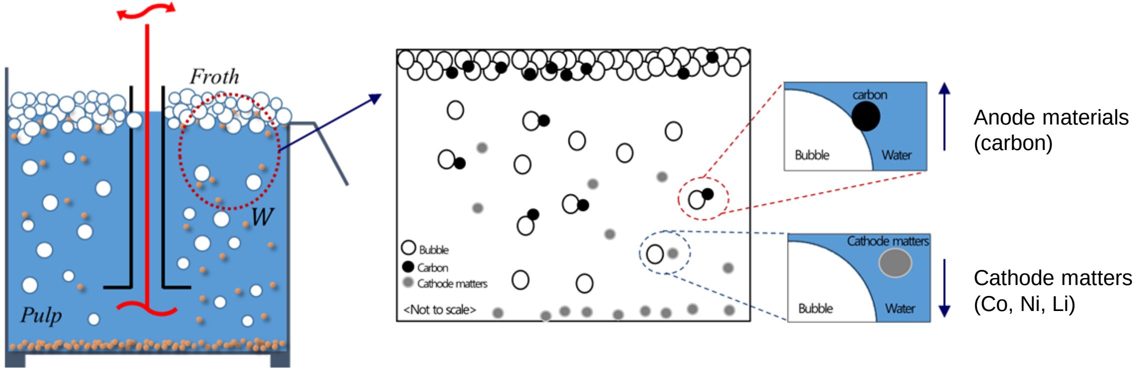
LIBs Recycling R&D

Experimental part 2: Efficient Separation Technology for Electrode Active Materials



- Due to the presence of a significant amount of active material in micro-sized black powder, selective separation based on the surface hydrophobicity characteristics of the particle-bubble is possible

- In some cases, pre-treatment involving specific gravity and electrostatic separation may be necessary, and floatation separation is carried out through reverse floatation process (with the target material sinking and impurities floating)."



Thank you for your attention!