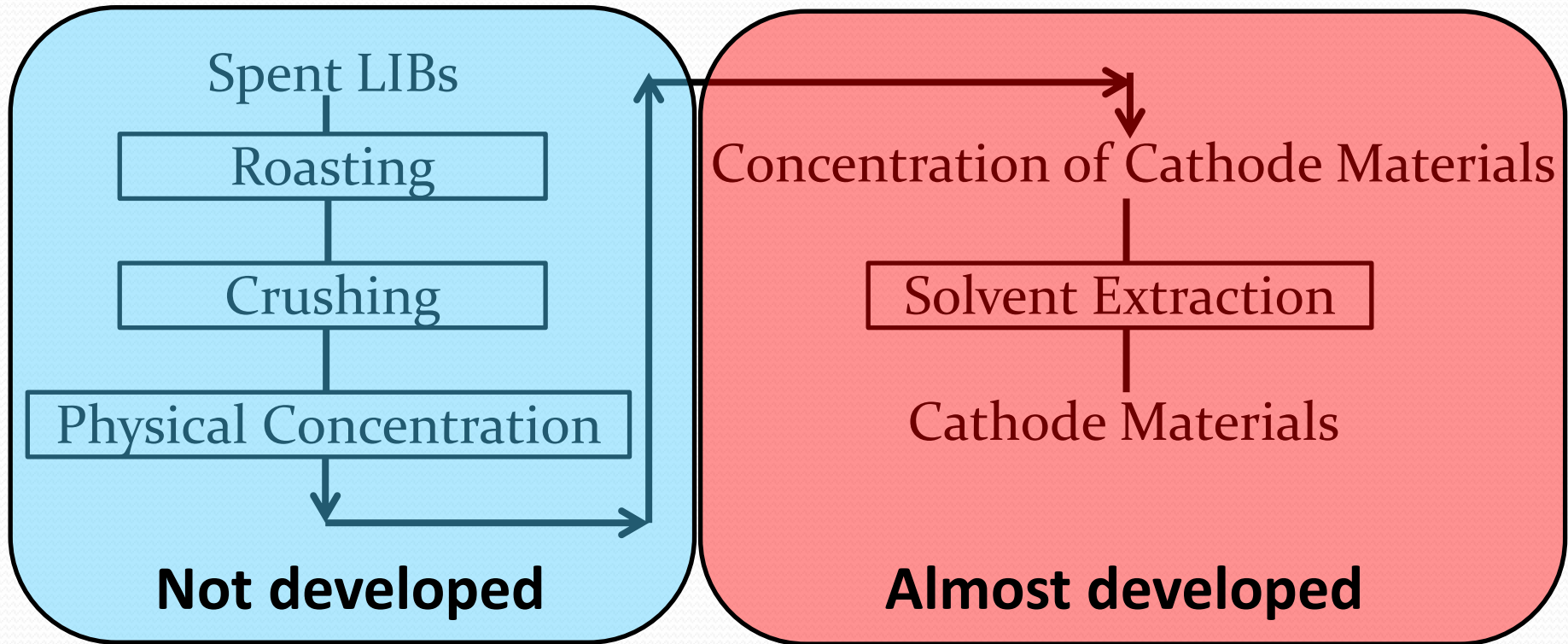


Effect of Phase Transition in Roasting on the Concentration Behavior of Cathode Materials of Spent Lithium Ion Battery

ASEAN⁺⁺2013 : Moving Forward Conferences
November 11-13, 2013, Chiang Mai, Thailand

Toru Ishii, Naoya Santo, Shuji Owada, Chiharu Tokoro (Waseda University)
and Yoshitsugu Miyabayashi (JX Nippon Mining & Metals)

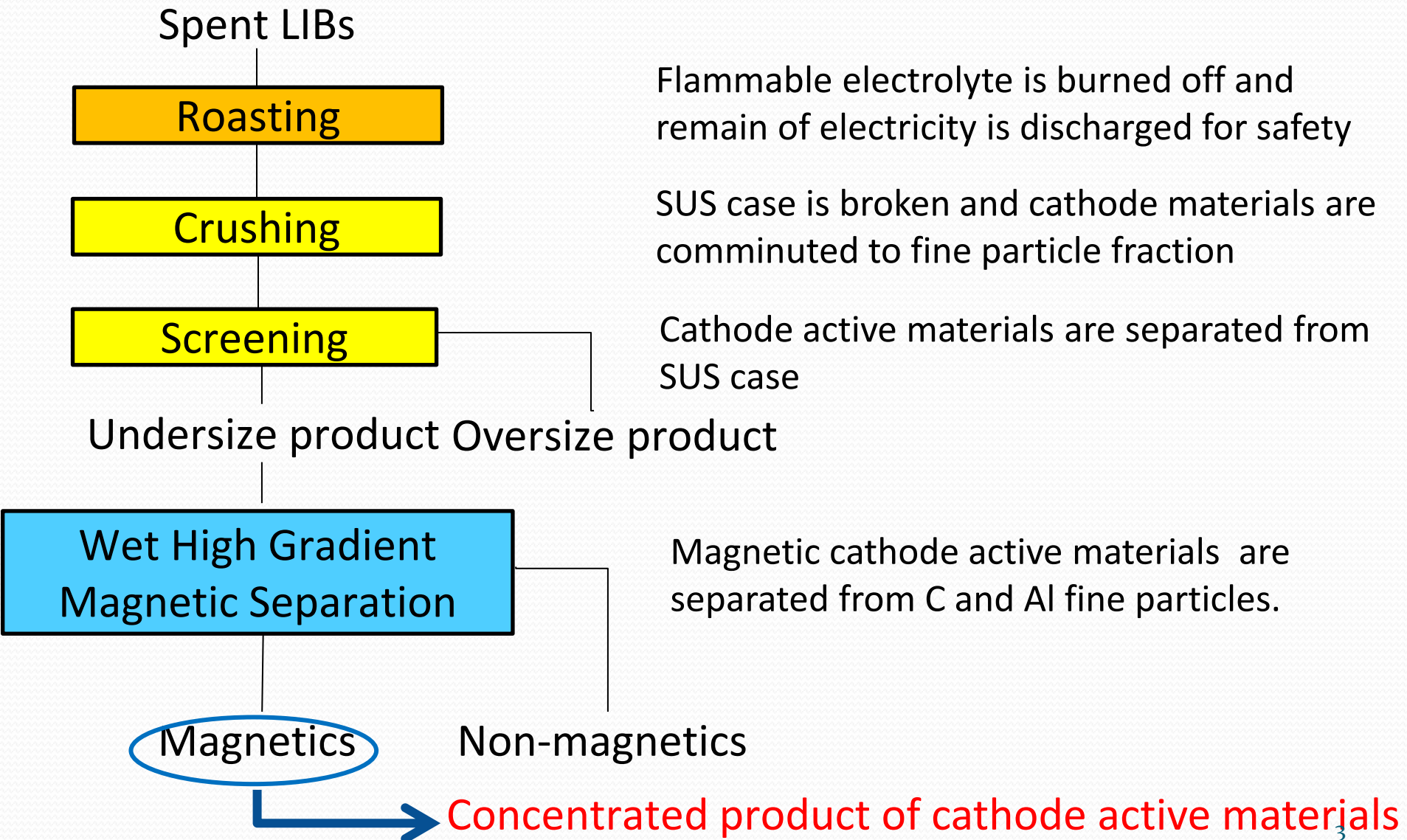
LIB Recycling Process to be Developed



Our purpose is...

To create a new process for concentrating cathode materials from Al and C in spent LIBs by roasting and physical concentration.

Establishment of New LIB Concentrating Process



Roasting Stage

Sample



Spent LIB for electric vehicles

Experimental

- Spent LIBs were roasted to 900 °C by furnace in an air atmosphere with no temperature control.
- Mineral composition of raw and roasted cathode and anode in spent LIB was identified by XRD.

Compositional materials of spent LIB

<Cathode>

LiMO_2 (M=Co, Ni, Mn) ,
Al

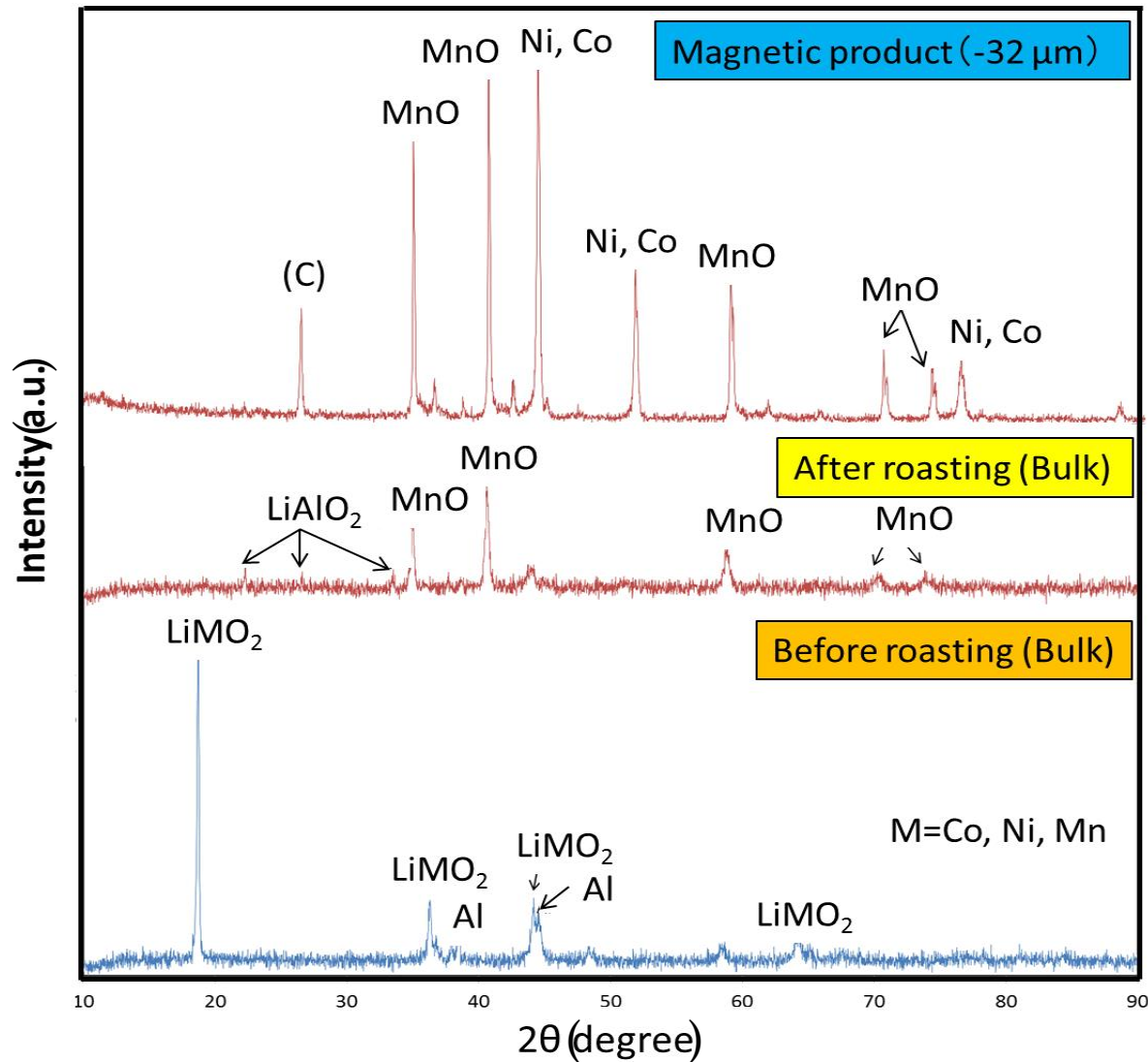
<Anode>

C, Cu

<Case>

SUS430F

XRD Patterns of Cathode before and after Roasting

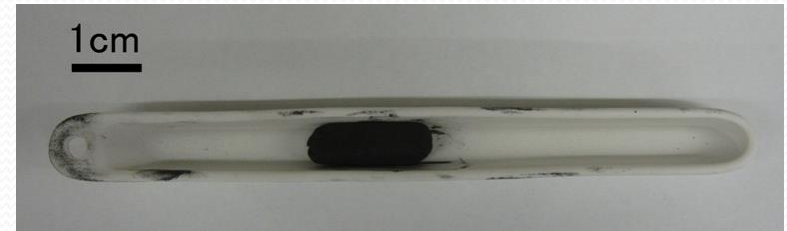


LiAlO₂, MnO, Co and Ni were identified in the cathode after roasting.
→ Phase transition occurred in roasting stage.

Roasting Test in Lab Scale

Sample

Cathode sheet after grinding
(-106 μm particle fraction)

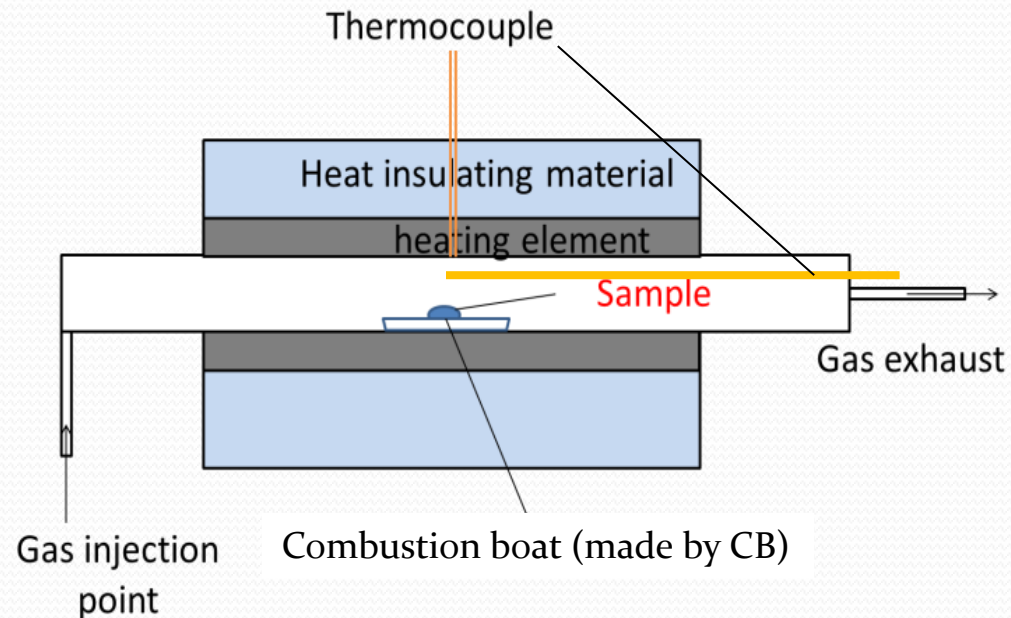


Sample for tube furnace roasting test

Experimental

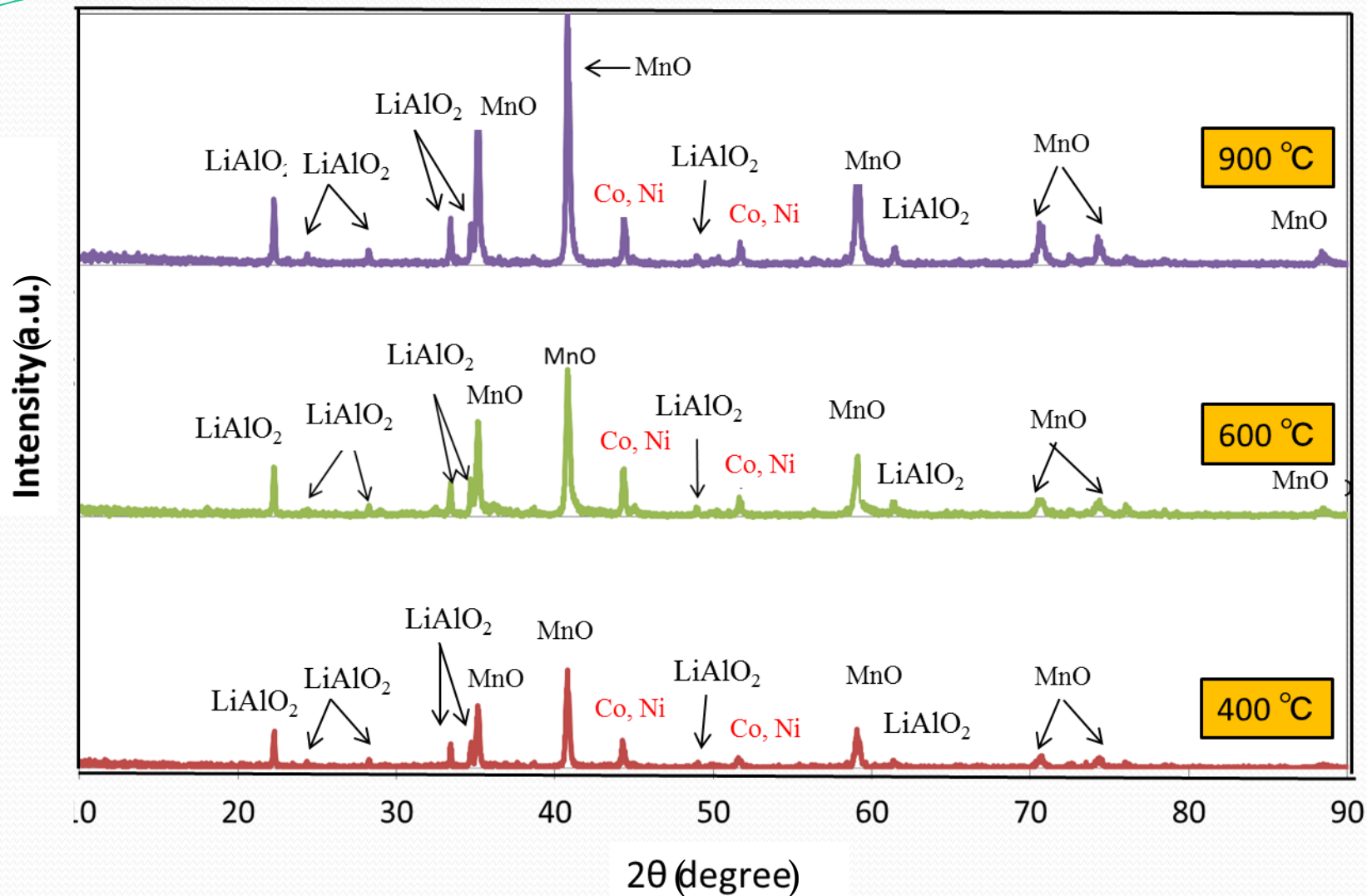


Tube furnace
(YAMADA DENKI, T-740)



Cathode was heated from 20 to 400, 600, 900 $^{\circ}\text{C}$ with a heating rate of 30 $^{\circ}\text{C}/\text{min}$ in Ar atmosphere and XRD was carried out.

XRD Patterns of Roasted Cathode



LiMO₂ (M=Co, Ni, Mn) was transformed into Co and Ni as metal phase by phase transition in roasting exactly.

XANES Measurement

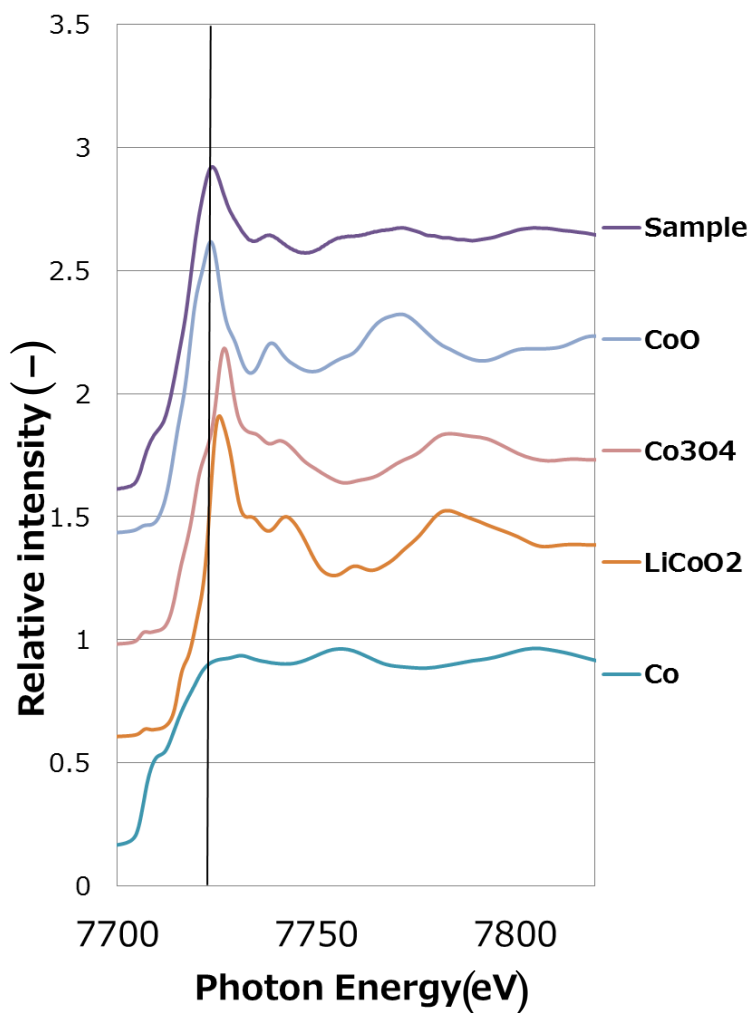
Sample

Roasted and crushed LIBs (-32 μm particle fraction)

Experimental

- X-ray absorption near edge structure (XANES) measurement was performed at Co K absorption edge.
- Analysis software REX2000 Ver2.5 was used for pattern fitting to the spectrum of each Co bearing compounds (Co, LiCoO_2 , CoO , Co_3O_4).

Results of XANES Measurement



XANES spectrum at Co K edge

The ratio of Co bearing compounds

	Co	CoO	LiCoO ₂	R
mol%	39	46	16	0.025

LiCoO₂ was resolved into CoO at over 900 °C as ① and ②. (Antolini, 1994)



$$\Phi = (1-y)(2-y), y < 1$$

Transforming into Co reaction can be represented as ③.



ΔG of this reaction is slightly negative.

Phase transition from LiCoO₂ to Co metal phase occurred in this process.

Crushing and Screening

Sample

Roasted LIBs

Experimental

Sample (40 kg)

Crushing

Single-shaft Crusher

(Motor power:155 kW, 125 rpm)

Screening

-32, 32-63, 63-125, 125-250, 250-500 μm ,
0.5-1, 1-2, 2-4 mm

ICP-AES

4-8, 8-16, +16 mm

XRF

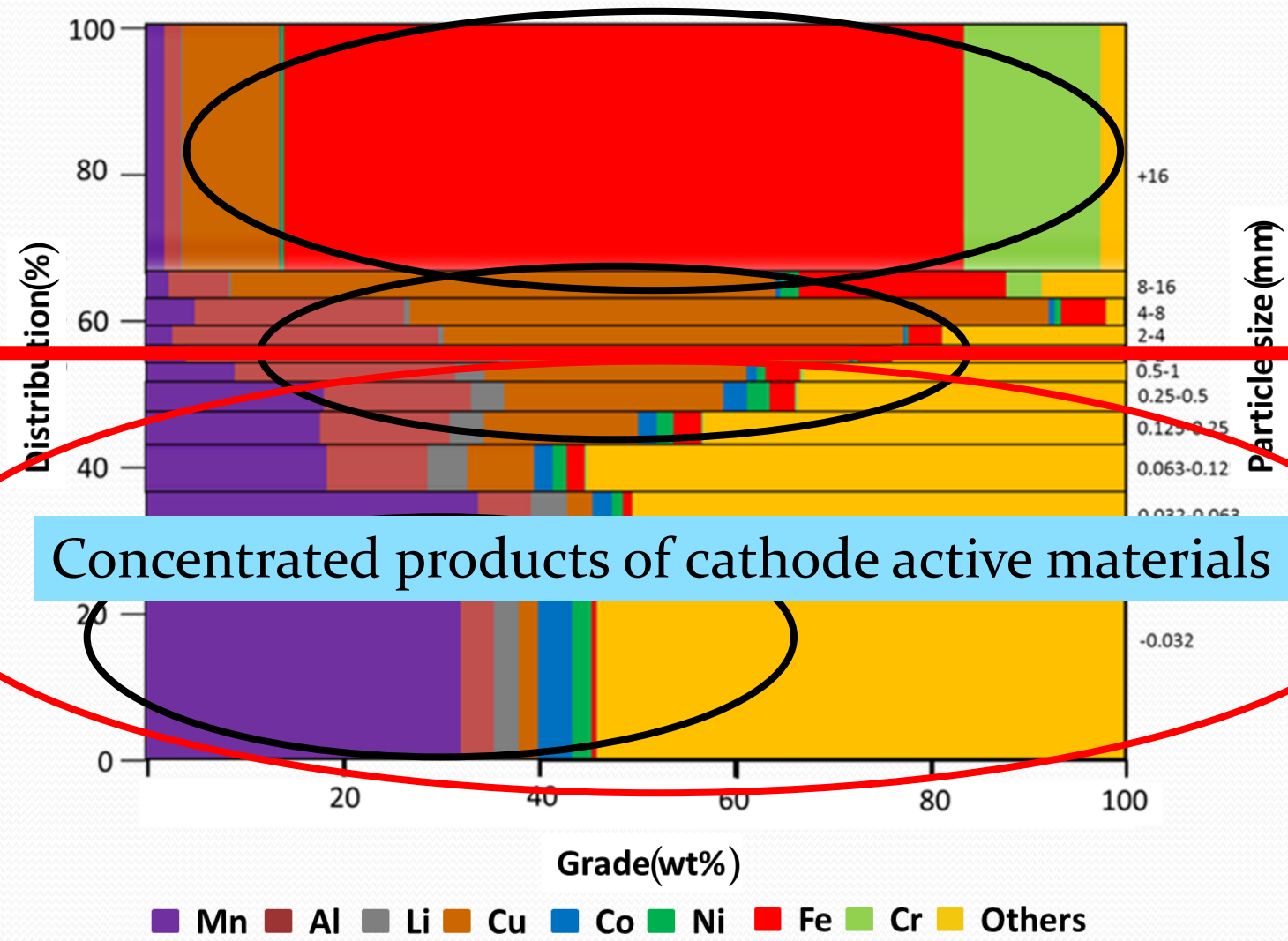


Single-shaft crusher
(MTB, BDR2000BN)



Screen for single-shaft crusher
(Φ 200 mm)

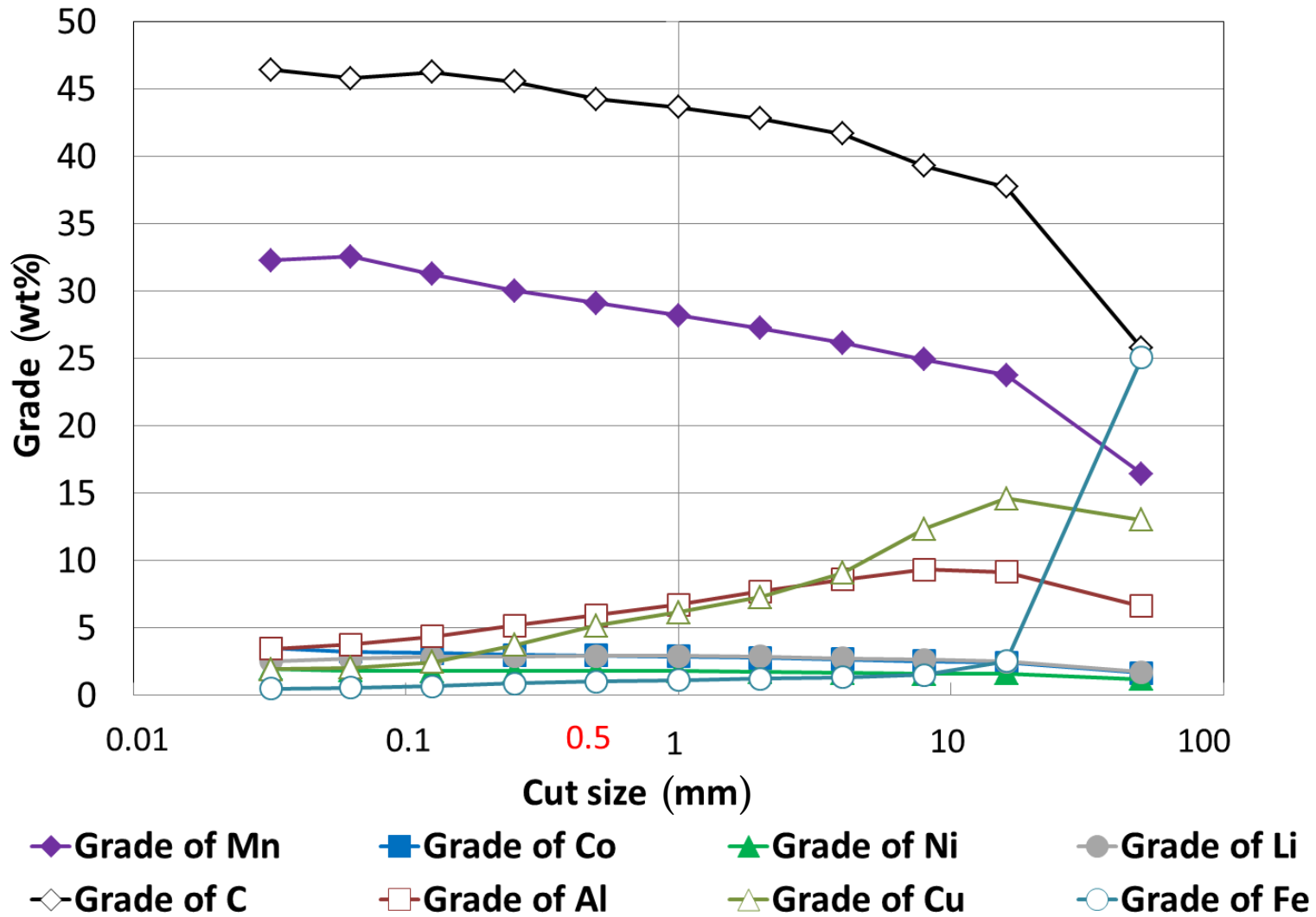
Chemical Composition of Roasted and Crushed Products in Various Size Range



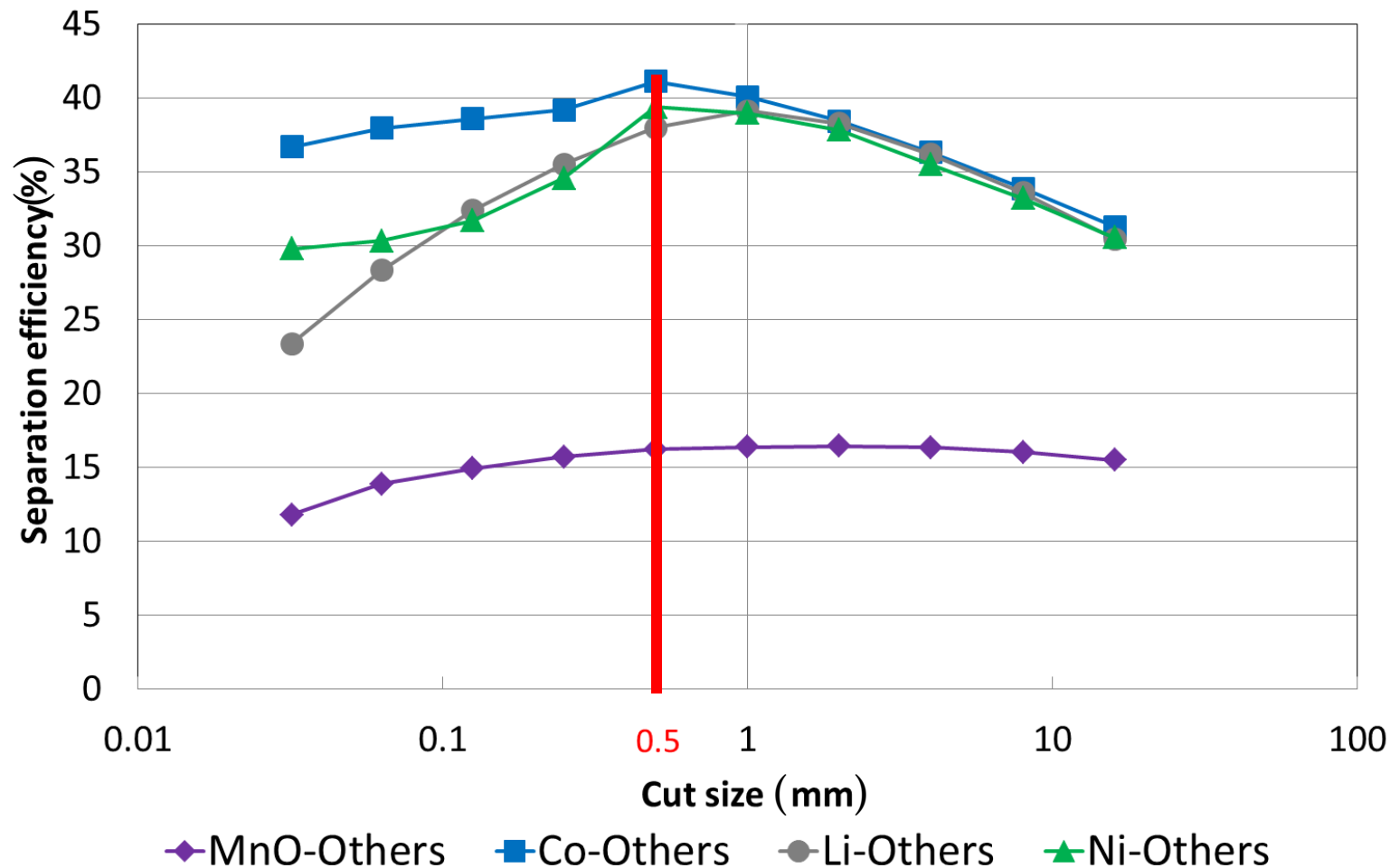
Concentrated products of cathode active materials

Cathode active materials were concentrated in -32 μm fraction.

Grade of Each Element by Cut Size

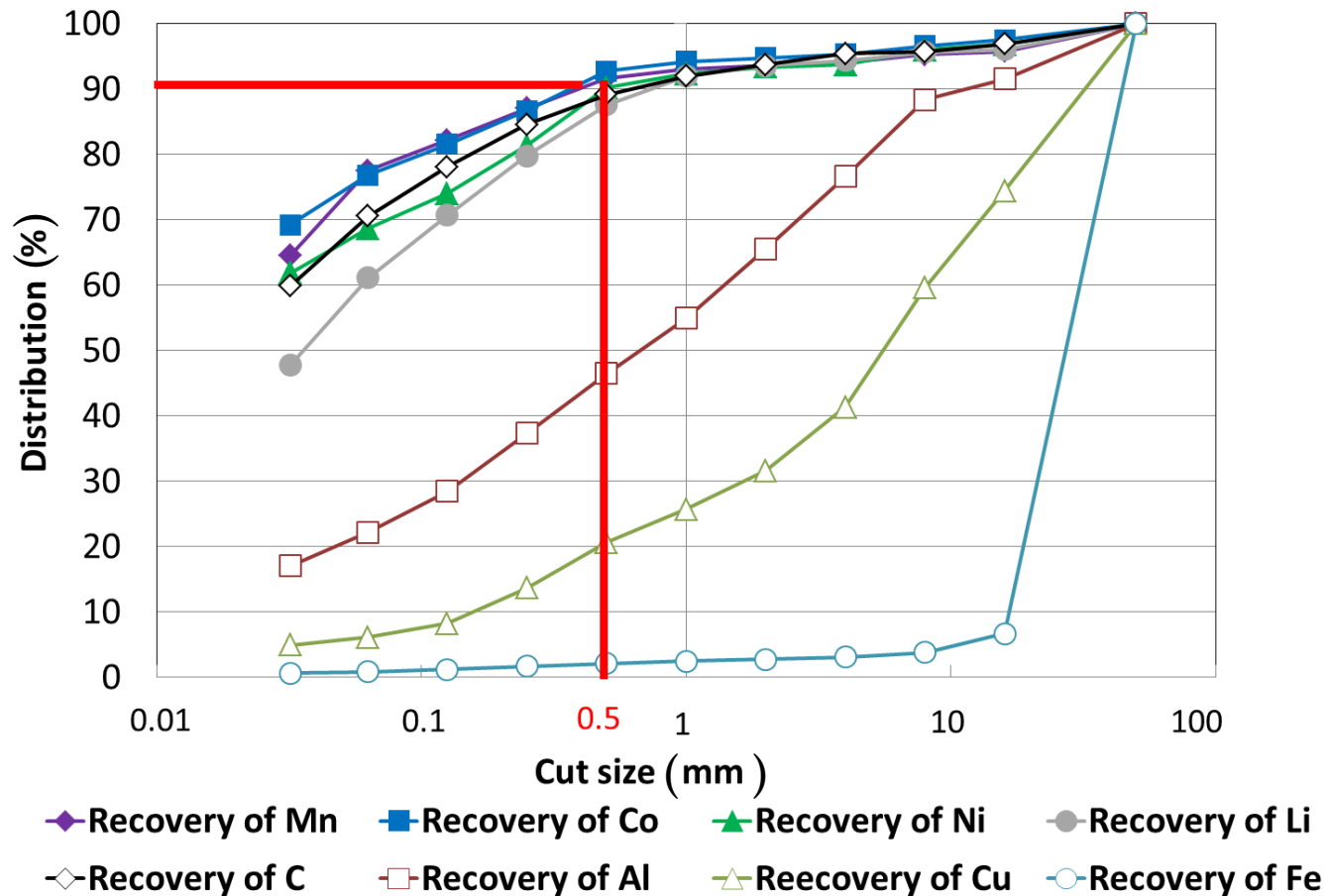


Separation Efficiency of Each Compound from Other Elements by Cut Size



Cathode active materials could be concentrated in -0.5 mm particle fraction most effectively.

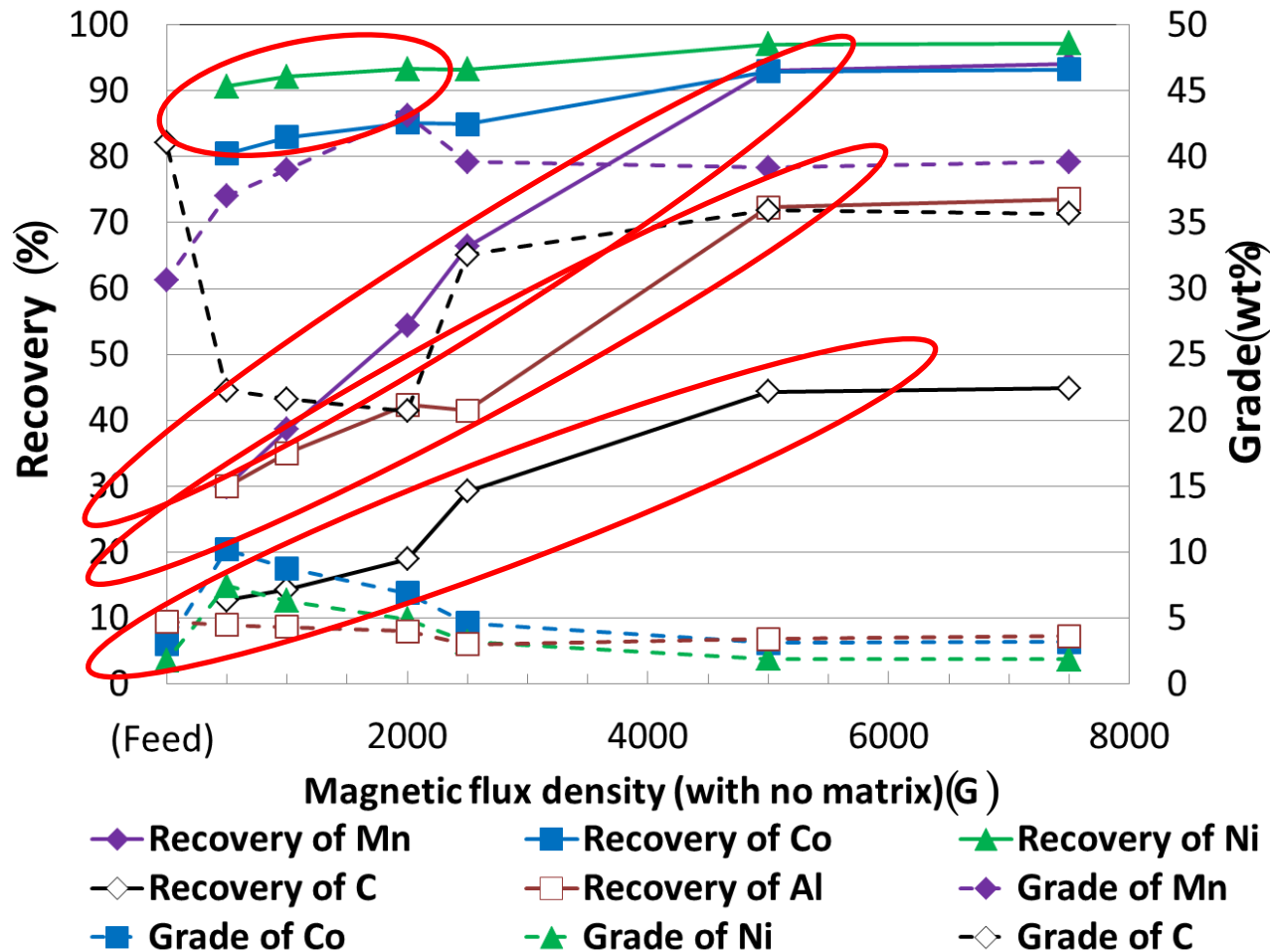
Recovery of Each Element by Cut Size



Cathode active materials in fine particle fraction can be separated from Cu and SUS in coarse particle fraction by screening.

(Co, Ni, Mn, Li, Al and C can be recovered with the recovery of 92.7, 90.2, 91.6, 87.6, 46.5, 89.2 % in -0.5 mm particle fraction.)

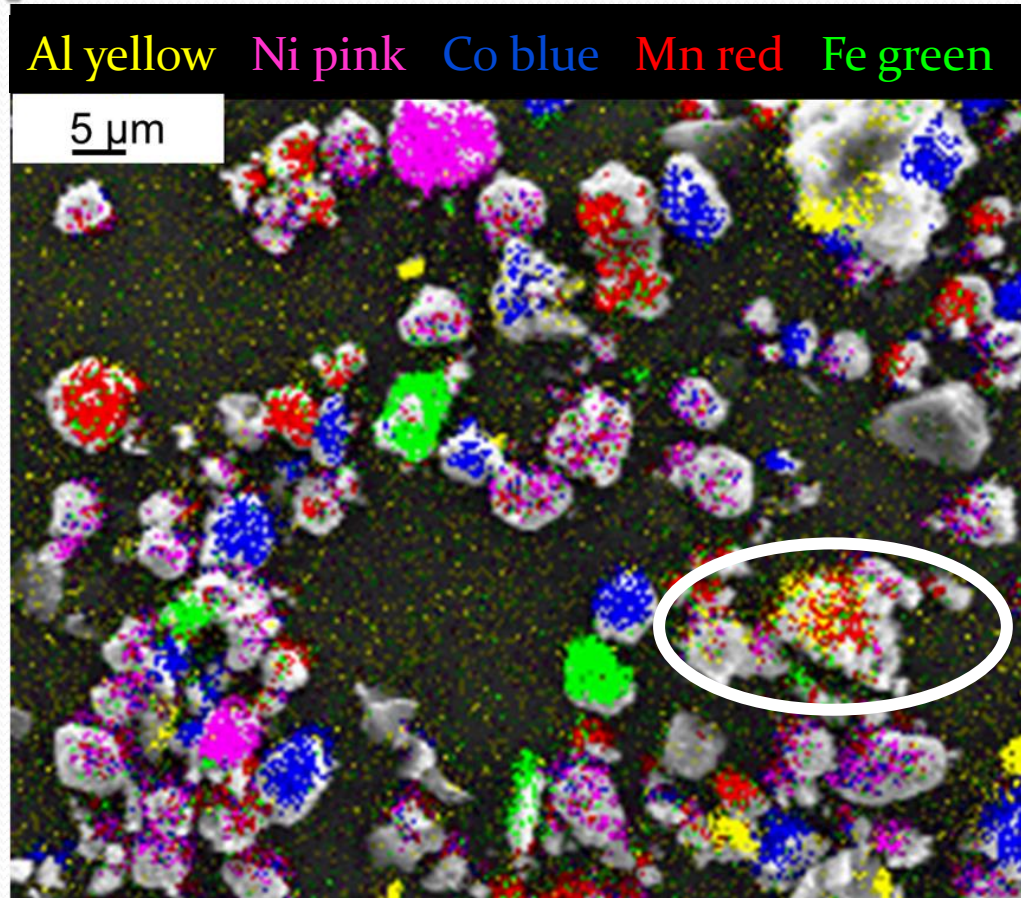
Recovery and Grade of Each Element in Magnetic Products with Various Magnetic Flux Density



High recovery and grade of Ni and Co could be obtained at low magnetic flux density.

→ Because Ni and Co bearing compounds transformed into metal phase.

Elemental Mapping of Magnetic Product by SEM-EDX



Melted Al adhered to the surface of cathode active material particles in the roasting stage.

Conclusion

<Roasting>

LiCoO₂ and LiNiO₂ were transformed into Co and Ni metal phases in roasting stage which have ferromagnetism.

<Crushing and screening>

Cathode active materials could be separated into fine size fractions and Cu & SUS into coarse size fractions by cut size of 0.5 mm in screening stage depending on the differences of their brittleness. Co, Ni, Mn, Li, Al and C can be recovered with the recovery of 92.7, 90.2, 91.6, 87.6, 46.5, 89.2 % in -0.5 mm particle fraction.

<Wet high gradient magnetic separation>

It was possible to concentrate ferromagnetic Co and Ni as metal phase at low magnetic flux density, but separating cathode active materials from Al was difficult because of adhesion of melted Al to their surface in roasting stage.

Concentrated cathode materials of Co, Ni, Mn, Li, Al and C could be recovered with the recovery of 74.6, 81.8, 27.3, 23.2, 13.9, 12.7 % from spent LIBs

Difference of Condition between Al and Cu

Separator



Cathode

Anode

Row sample



Anode
(Cu)

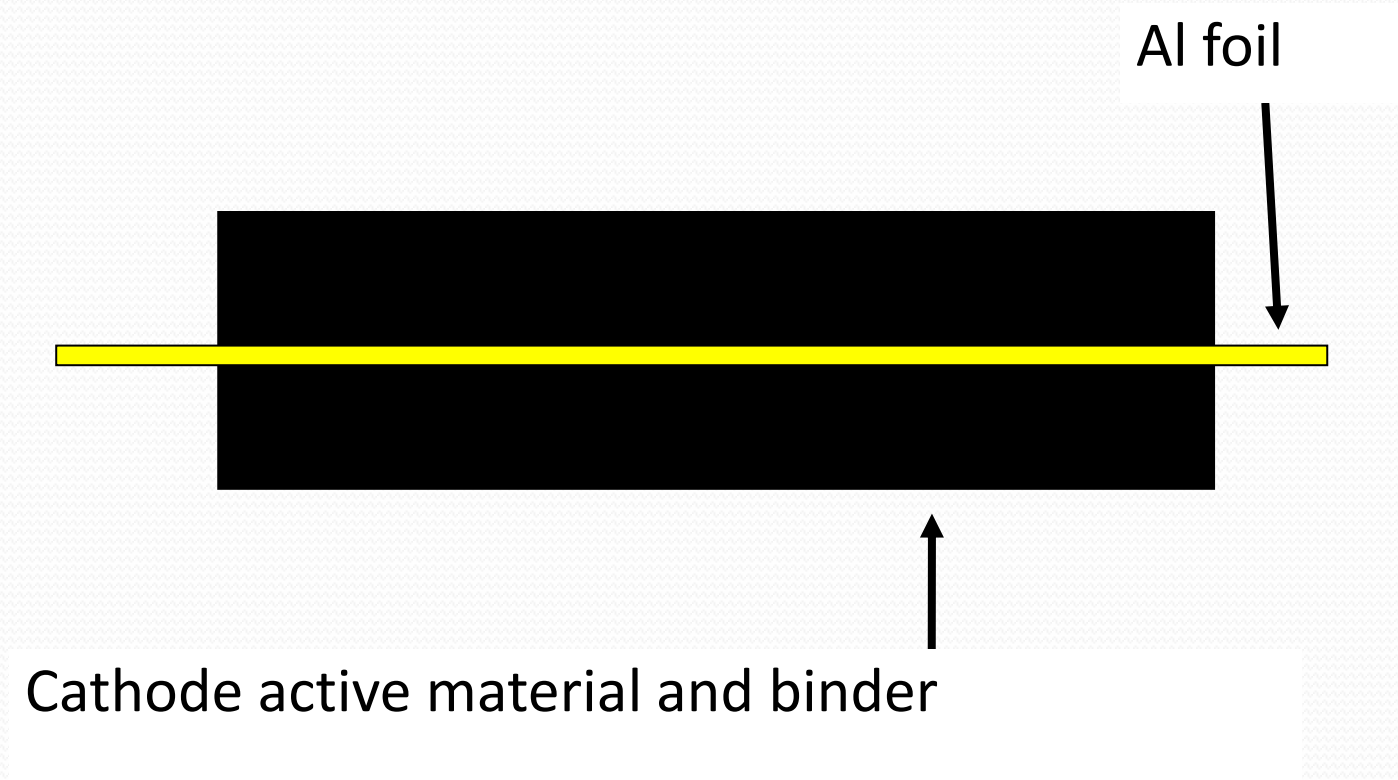
Cathode
(Al)

Roasted sample

Al foil in after roasting cathode gets brittle but Cu foil in after roasting anode does not.

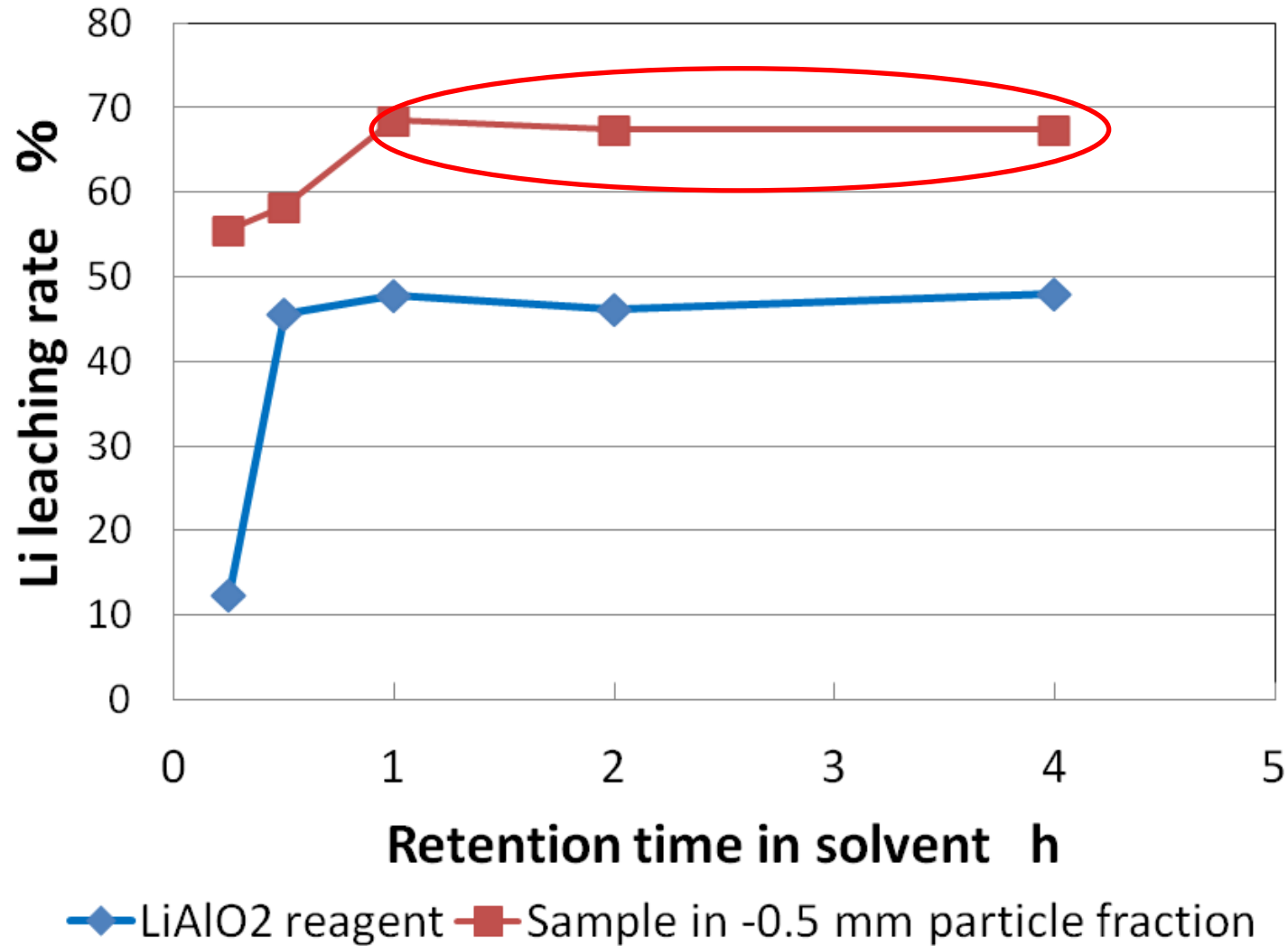
→ This is the reason why Al and Cu are concentrated in different particle fraction.

Structure of Cathode



Melted Al adhered to the surface of cathode active materials selectively because of this structure.

Leaching Behavior of Li



Li leaching rate was saturated at approximately 70 % after 1 hour.

C Particle Trapping



1 cm

500 G



1 cm

7500 G

Inside of separator was filled with magnetic particles as increasing magnetic flux density, and C particles were entrapped by other magnetic particles as this illustration.