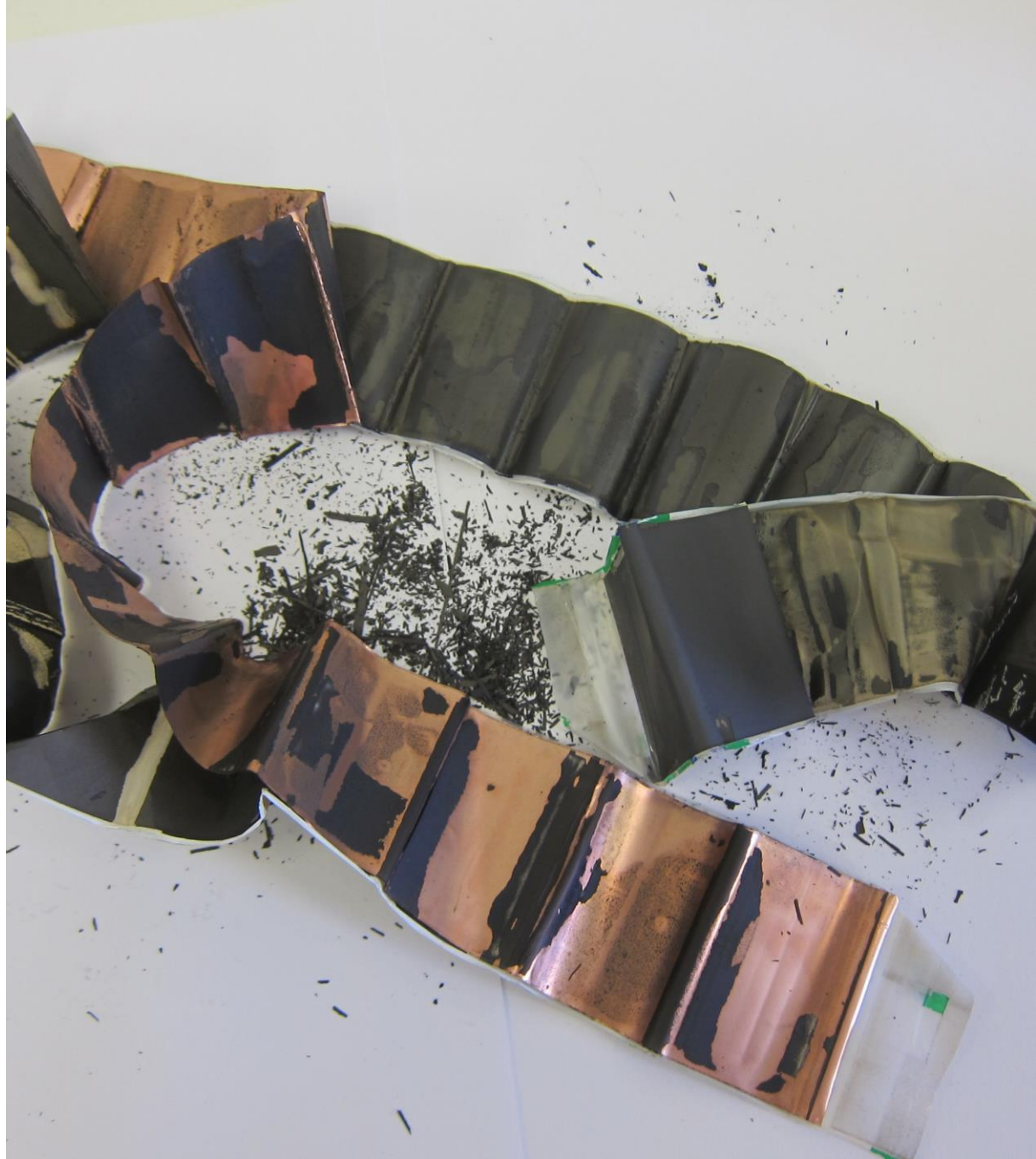
Direct recovery of degraded cathode material from spent lithium-ion batteries. A green solution

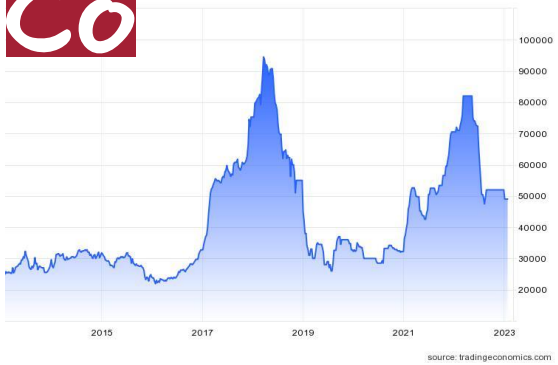
Dr. María Fernanda Gazulla Barreda

Project funded by La Generalitat Valencia, through IVACE
Ref: IMAMCA/2023/1



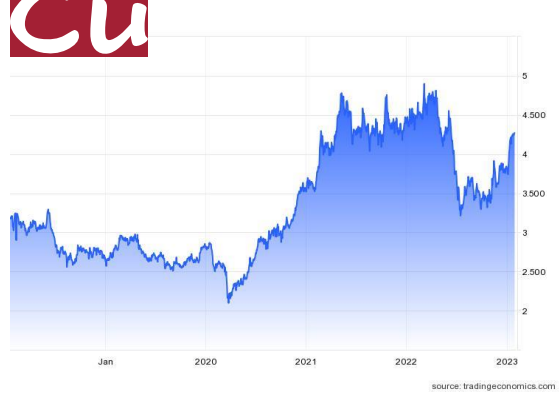
RISK OF SHORTAGE OF PRIMARY RAW MATERIALS

Co



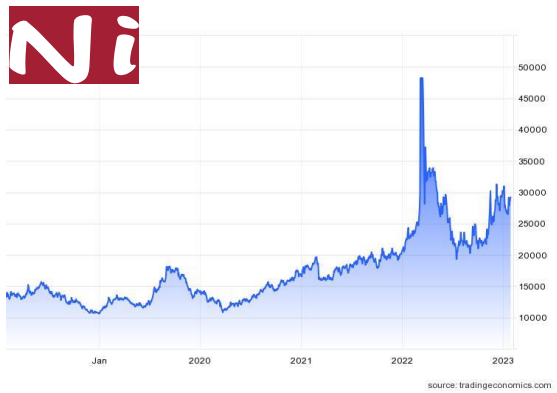
- Considered a Critical raw material (CRM) by de European Commission
- 70% of the global supply is originated in the Democratic Republic of the Congo (DRC) – Supplier dependence
- Increasing demand due to its use in rechargeable batteries

Cu



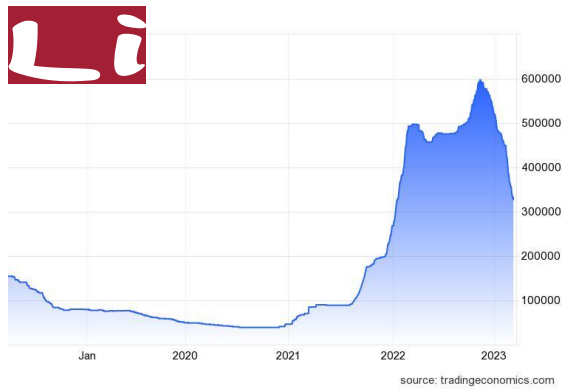
- Increase in price over time
- Use in batteries at current collector in the anode

Ni



- Nickel production concentrated in Indonesia, Philippines, and Russia
- Increasing demand due to its use in rechargeable batteries

Li



- Criticality due to geostrategic, economic, and environmental reasons:
  - 80% of the reserves and production concentrated in Australia and Latin America
  - CO_2-intensive and water consuming mining process

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RECYCLING OF ELECTRONIC DEVICES



Increase of electrical and electronic waste

Need for recycling for environmental protection, favouring the circular economy

New European Regulations

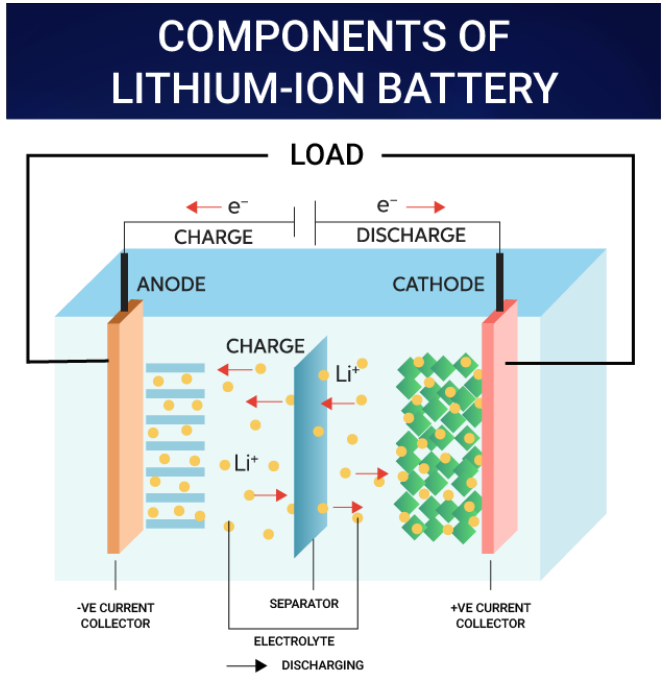
New European directives will demand recycling processes of this type of materials to reach a minimum efficiency of 50%

Source of secondary raw material

Electronic devices, such as Li-ion batteries, present valuables metals that can be introduced in the productive process if properly recovered

Active cathode materials can be directly recovered and used in the manufacturing of new lithium-ion batteries after proper regeneration

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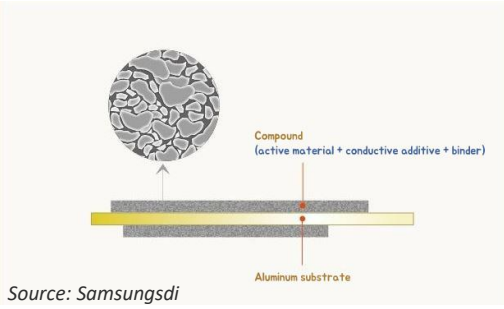
Source: Esmito

Anode

Copper plate coated with a mixture of graphite, electric conductor, binder, and solvent

Cathode

Aluminium plate coated with a mixture of the active cathode material, electric conductor, binder (PVDF), and solvent (NMP)



Source: Samsungsdi

Electrolyte

Medium that is ionic conductor and electron insulator. Most common: $LiPF_6$ dissolved in a polar solvent (ethyl carbonate, dimethyl carbonate, or diethyl carbonate)

Separator

Permable membrane to separate anode and cathode and prevent shortcuits (PE or PP)

"More than 50% of the battery cost is due to the cathode"

- *Battery University, BU-205: Types of Lithium-ion [on line] https://batteryuniversity.com/index.php/learn/article/types_of_lithium_ion*
- *Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J. and Pandey, B.D. (2013) 'Recovery of lithium and cobalt from waste lithium ion batteries', Waste Management, Vol. 33, pp. 1890 – 1897*
- *Zhang, T., He, Y., Ge, L., Fu, R., Zhang, X. and Huang, Y. (2013) 'Characteristics of wet and dry crushing methods in the recycling process of spent lithium-ion batteries', Journal of Power Sources, Vol. 240, pp. 766 - 771*

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Cathode degradation

- Li^+ is not able to return to the original structure
- Formation of spinel structure over the particle surface

Recycling technologies

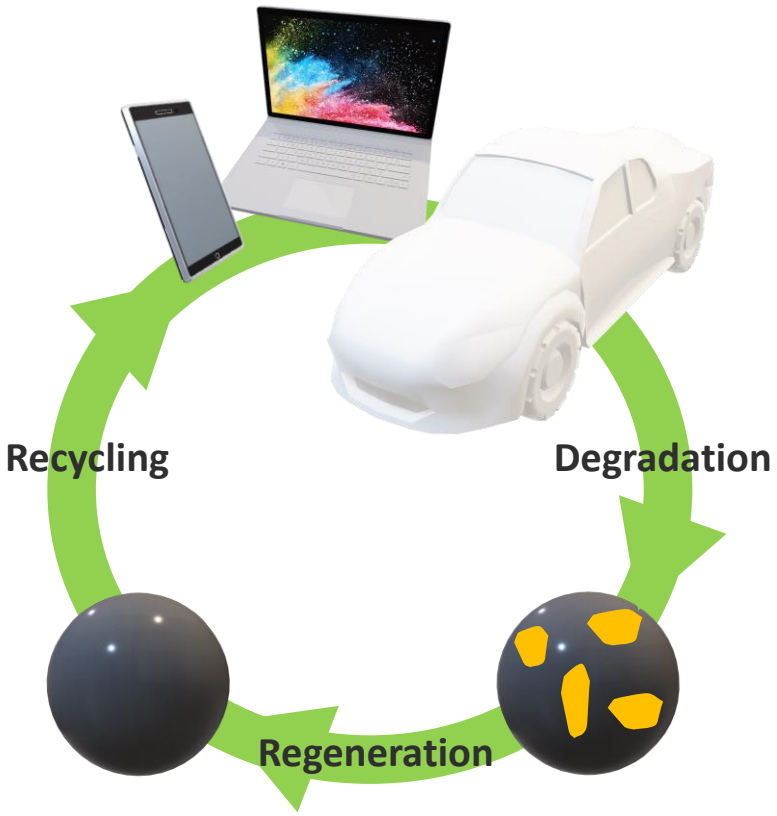
1. Hydrometallurgical process
2. Pirometallurgical process

→ Destruction of the structure

3. Direct recycling process → Regeneration of the structure

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OBJECTIVE



GENERAL

Direct recovery of degraded cathode material from spent lithium-ion batteries

SPECIFIC

1. Chemical characterization of different lithium-ion batteries
2. Design of a physical separation process of the components
3. Design of a regeneration treatment for direct recovery
4. Validation of the developed method

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DEVELOPMENT

DESIGN OF THE SEPARATION PROCESS







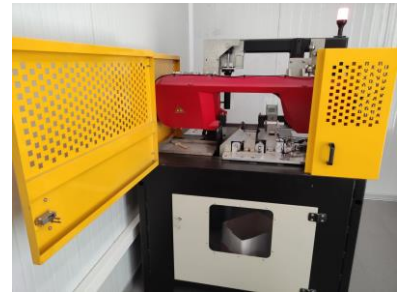
PRELIMINARY STUDY AT LABORATORY SCALE

1

2

DESIGN OF A PILOT PLANT

3





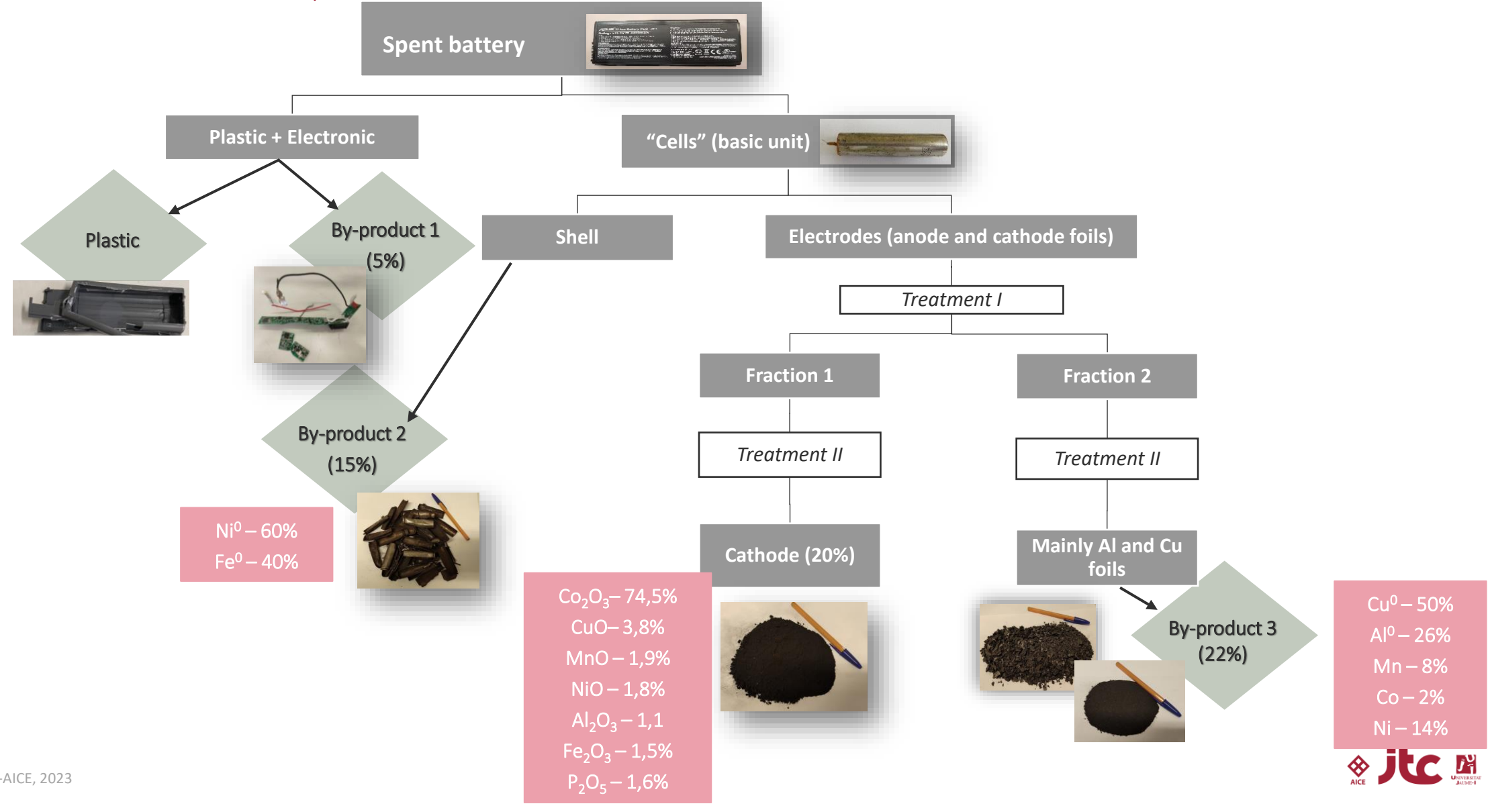
DESIGN OF AN AUTOMATIC SEPARATION PROCESS

***Patent ES2924113A1** METHOD FOR THE RECOVERY OF ACTIVE CATHODE MATERIAL FROM SPENT LITHIUM-ION RECHARGEABLE BATTERIES*

- Zhang, T.; He, Y.; Wang, F.; Ge, L.; Zhu, X.; Li, H. (2014) Chemical and process mineralogical characterizations of spent lithium-ion batteries: an approach by multi-analytical techniques. *Waste Manage.*, Vol. 34, pp. 1051-1058
- Zhang, L.; Xu, Z. (2016) A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *J. Cleaner Prod.,* Vol. 127, 2016, pp. 19-36
- Jha, M.K.; Kumari, A.; Jha, A.K.; Kumar, V.; Hait, J.; Pandey, B.D. (2013) Recovery of lithium and cobalt from waste lithium ion batteries. *Waste Manage., Vol. 33, pp. 1890-1897*

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BY-PRODUCTS OBTAINED IN THE SEPARATION PROCESS



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CHARACTERIZATION OF THE FRACTIONS OBTAINED

Physico-chemical characterization

Inductively coupled plasma optical emission spectrometry (ICP-OES)	Selective electrode	Wavelength dispersive X-ray fluorescence (WD-XRF)	Combustion and IR detection	Thermal treatment in electrode furnace and IR detection	X-ray Difraction	Scanning electron microscopy (SEM)
Li	F	Co, Al, Fe, Ni, Cu, Mn, P, Si, etc.	C	O	Crystalline phases	Morphology Particle size

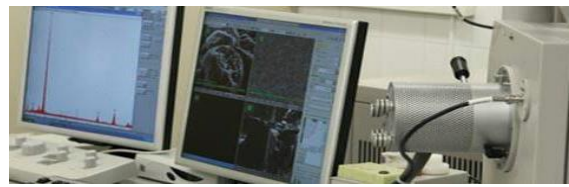


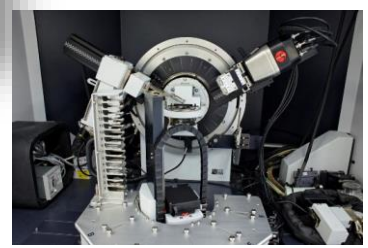












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DEVELOPMENT | DIRECT RECOVERY

Savings in primary raw materials consumption:

- **100%** in Co, Ni, Mn
- **± 50%** in Li







Laptop / Automotive batteries







Separation process

Patent ES2924113A1 METHOD FOR THE RECOVERY OF ACTIVE CATHODE MATERIAL FROM SPENT LITHIUM-ION RECHARGEABLE BATTERIES



Ni recovery



Cu recovery



Relithiated LCO or NMC cathode

Relithiation

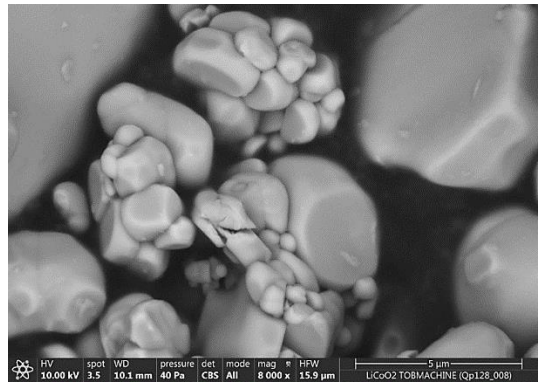


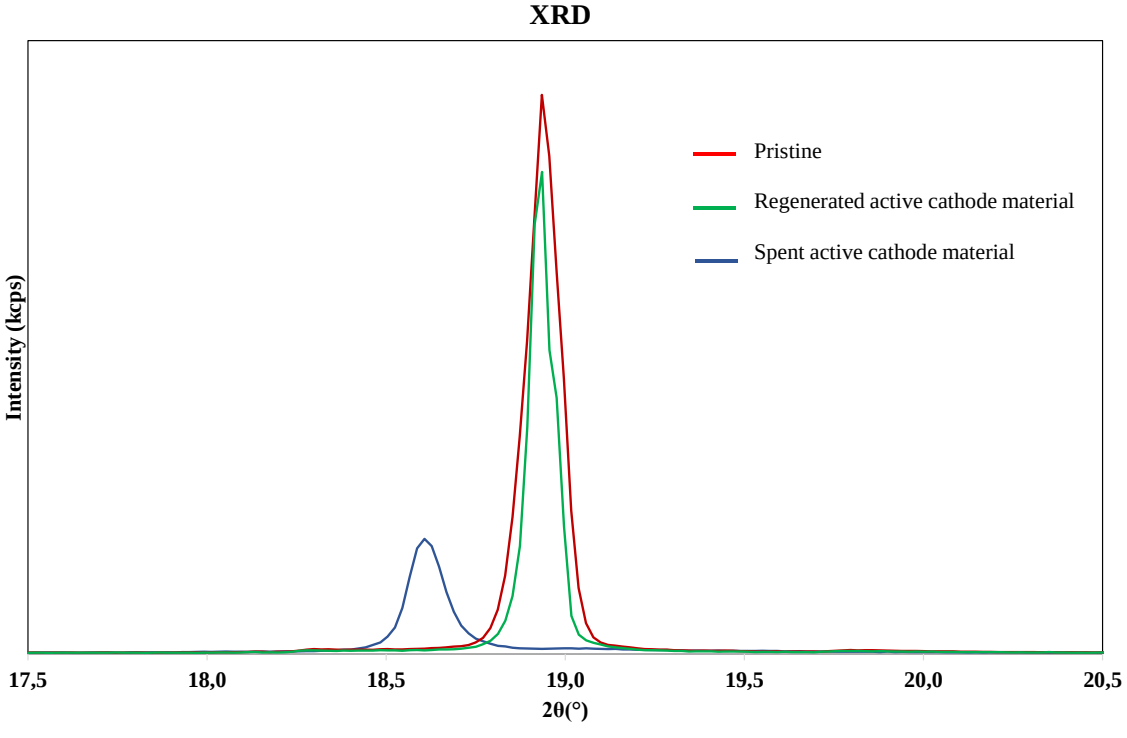
Degraded LCO or NMC cathode

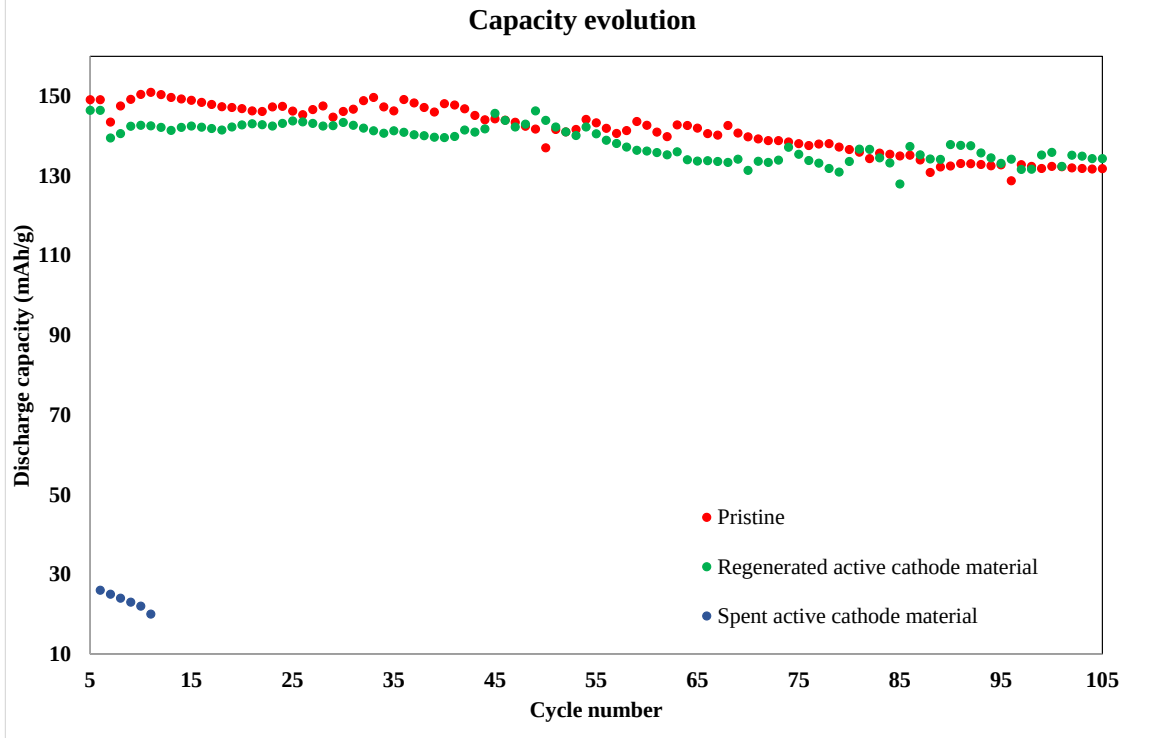
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RESULTS

CHARACTERIZATION OF THE RELITHIATED CATHODE







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Thank you

Dr. Mª Fernanda Gazulla Barreda

Head of the Area for the Analyses and Tests

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Project funded by:

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