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

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*Project funded by La Generalitat Valencia, through IVACE*
*Ref: IMAMCA/2024/1*



# RISK OF SHORTAGE OF PRIMARY RAW MATERIALS

## Co




- Considered a Critical raw material (CRM) by de European Commission since 2011
- 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
- Huge fluctuation in price

## Cu



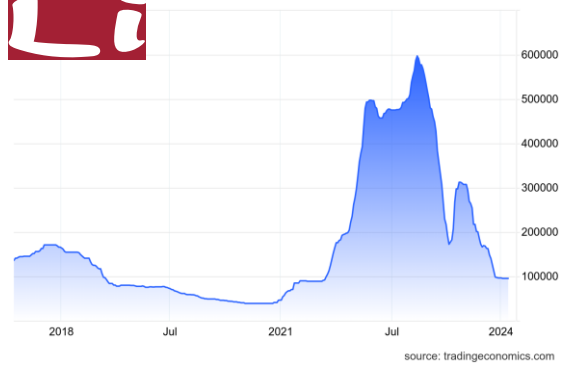

- Increase in price over time
- Use in batteries at current collector in the anode
- Considered as Strategic Raw Material by the European Commission since 2023

## Ni



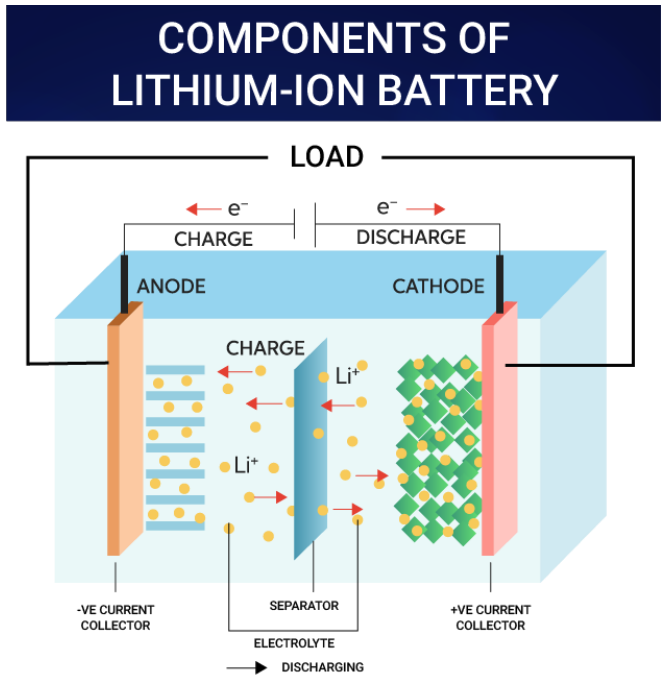

- Nickel production concentrated in Indonesia, Philippines, and Russia
- Increasing demand due to its use in rechargeable batteries
- Considered as Strategic Raw Material by the European Commission since 2023

## 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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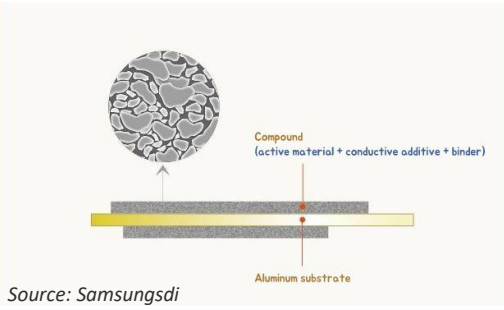

*Source: Esmito*

**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)

**During discharge**

Anode: $C_6Li \longrightarrow 6C + xLi^+ + xe^-$

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow LiCoO_2$

- *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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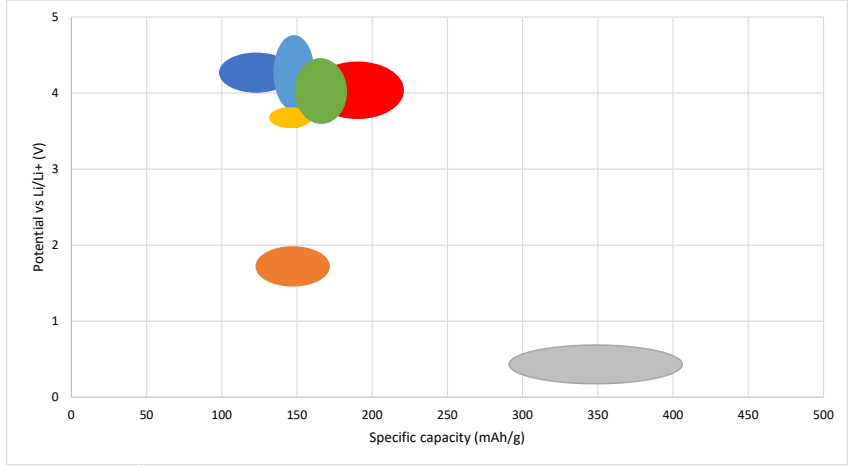
## Cathode active materials

- Lithium Cobalt Oxide (LCO) ($LiCoO_2$)
- Lithium-nickel-cobalt-aluminium (NCA) ($LiNiCoAlO_2$)
- Lithium-nickel-manganese-cobalt (NMC) ($LiNi_xMn_yCo_zO_2$)
- Lithium-nickel-spinel (LMO) ($LiMn_2O_4$)
- Lithium tithanate (LTO) ($Li_2TiO_3$)
- Lithium-iron-phospahte (LFP) ($LiFePO_4$)
- Blends

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

## Anode materials

- Lithiated coke
- Lithiated graphitic carbon
- Lithium tithanate (LTO) ($Li_2TiO_3$)
- C/Sn and C/Si composites



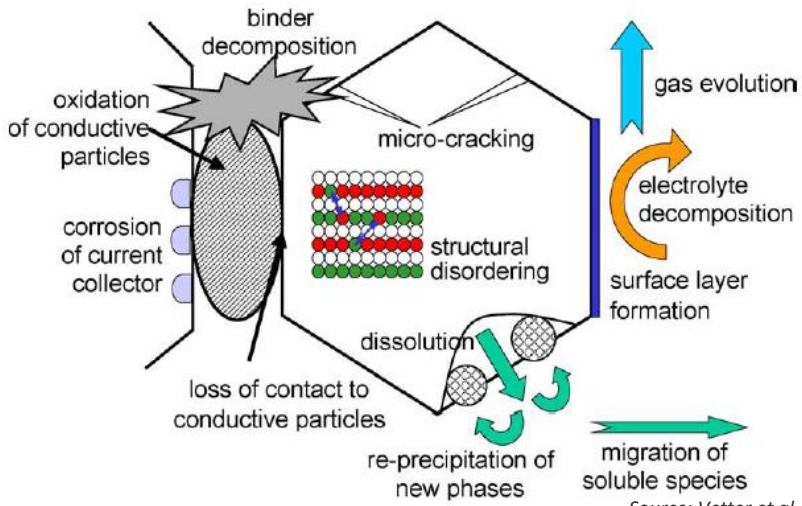

- *Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J. and Pandey, B.D. (2013) 'Recovery of lithium and cobalt from waste lithium ion batteries', Waste Management, Vol. 33, pp. 1890 – 1897*
- *Battery University, BU-205: Types of Lithium-ion [on line] https://batteryuniversity.com/index.php/learn/article/types_of_lithium_ion*
- Wang, R-C., Lin, Y-C. and Wu, S-H. (2009) 'A novel recovery of metal values from the cathode active materials of the lithium-ion secondary batteries', *Hydrometallurgy*, Vol. 99, pp. 194 – 201
- Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H. and Fan, S. (2015) 'Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries', *Waste Management*, Vol. 38, pp. 349 - 356

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## Degradation and unwanted side reactions in the LIB‘s

- *Transition metal dissolution and formation of spinel structure over the particle surface*
- Particle craking
- *Loss of active lithium*
- Contact loss of active material and current collector
- Electrolyte degradation

**Cathode degradation**

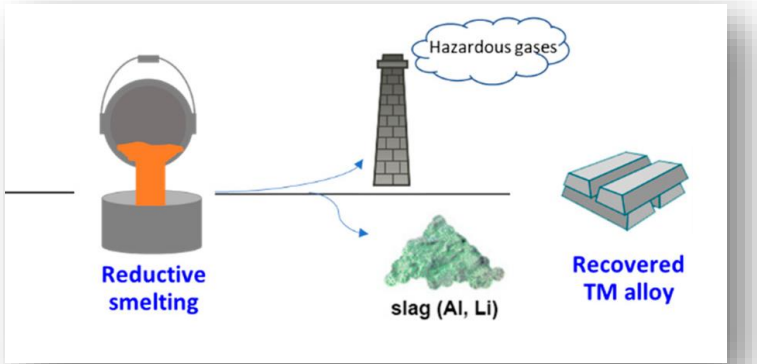



*Source: Vetter et al., 2005*

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## Recycling technologies

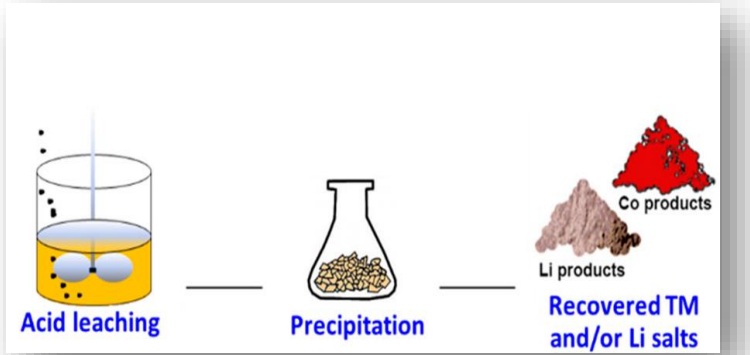
### Pyrometallurgical




*Source: Baum et al., 2022*

| PROS | CONS |
|---|---|
| • No pre-treatment needed<br>• Flexible regarding chemical composition | • High $CO_2$ emissions<br>• High energy consumption<br>• Lithium not recovered |

### Hydrometallurgical




*Source: Baum et al., 2022*

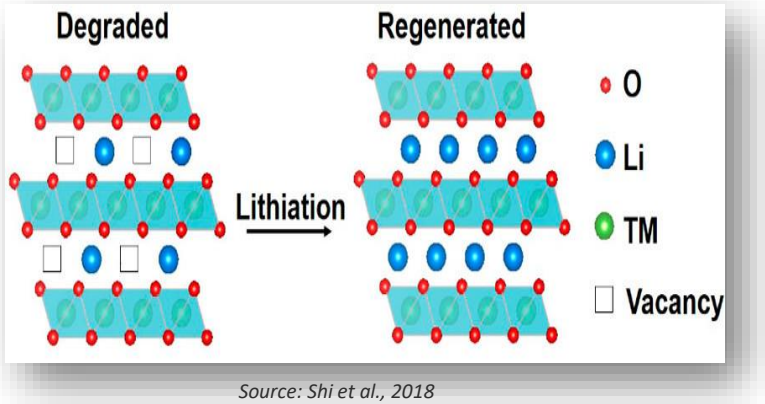
| PROS | CONS |
|---|---|
| • Moderate energy consumption<br>• High efficiency | • High water consumption<br>• Release of toxic gasses due to the use of chemicals<br>• Release of Green House Gasses |

Destruction of the cathode structure

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## Recycling technologies

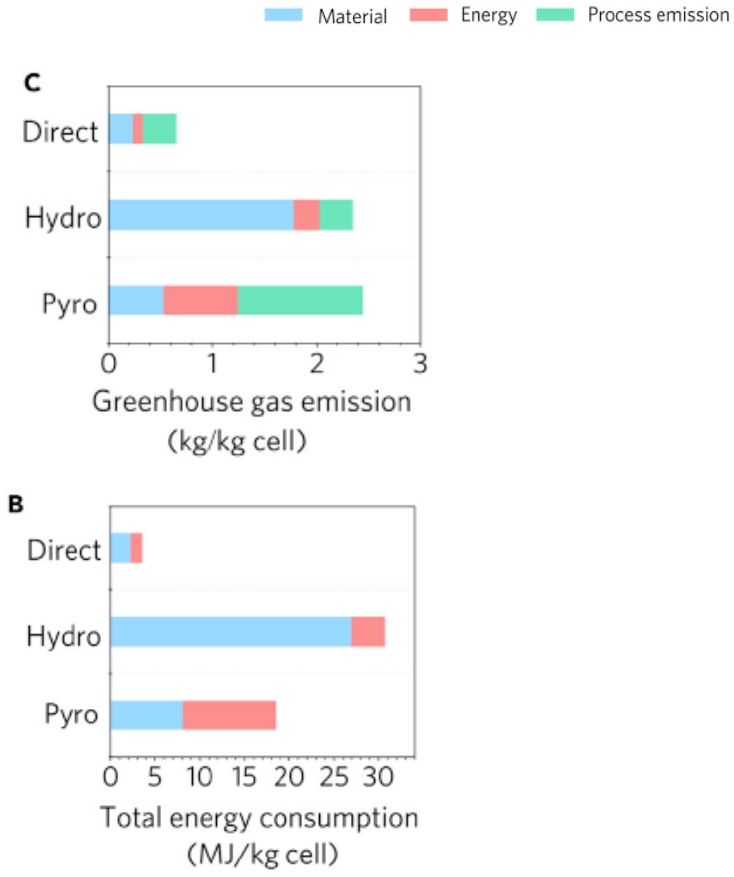
### Direct regeneration




*Source: Shi et al., 2018*

| PROS | CONS |
|---|---|
| • Low energy consumption<br>• Low $CO_2$ emissions<br>• Active material can be directly reused after regeneration<br>• REGENERATION OF THE CATHODE STRUCTURE | • Rigorous sorting process and no universal regeneration procedure for all chemistries |

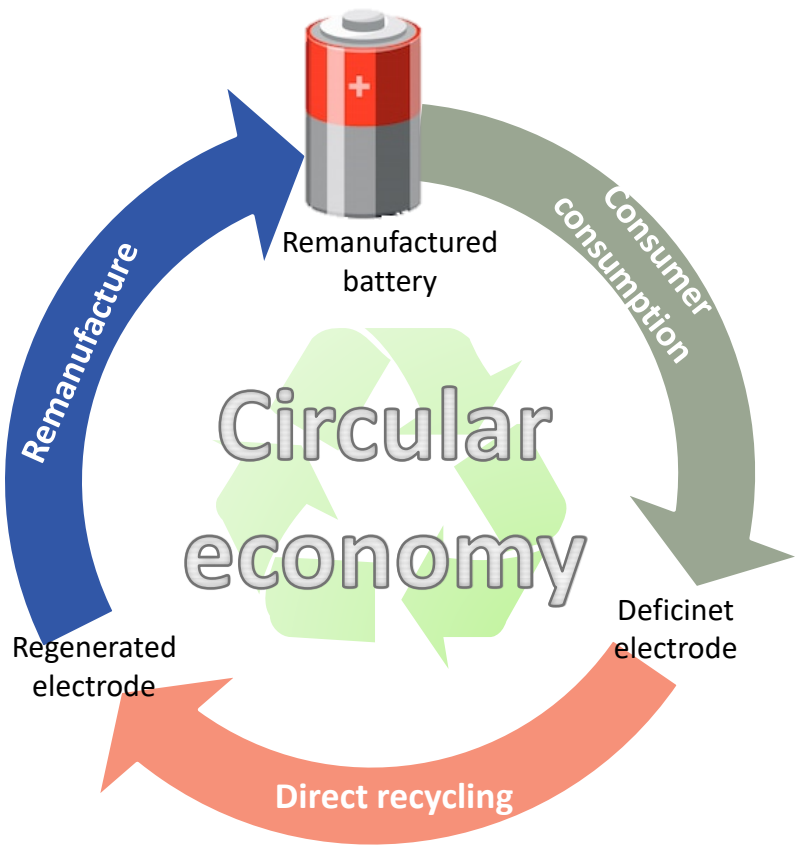
## Comparative




*Source: Xu et al., 2020*

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# OBJECTIVE




## GENERAL

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

## SPECIFIC

1. Chemical and physical characterization of different separated cathodes
2. Separation process of the different components of the battery
3. Design of a regeneration treatment for direct recovery for each cathode chemistry
4. Validation of the developed method

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**DEVELOPMENT**

# DESIGN OF THE SEPARATION PROCESS

PRELIMINARY STUDY AT LABORATORY SCALE

DESIGN OF A PILOT PLANT



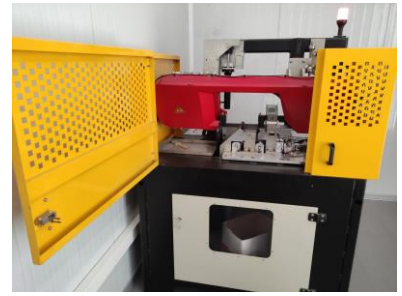




1

2

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

**Spent battery**

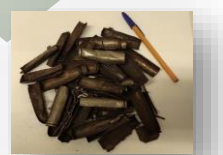


- **Plastic + Electronic**
  - **Plastic**

    
  - **By-product 1 (5%)**

    
- **“Cells” (basic unit)**

  
  - **Shell**
    - **By-product 2 (15%)**

      $Ni^0$ – 60%
      $Fe^0$ – 40%
    - $Co_2O_3$– 17,4%
      NiO– 44,6%
      MnO – 14,2%
      CuO – 2,6%
      $Al_2O_3$ – 1,5
      $Fe_2O_3$ – 0,3%
      $P_2O_5$ – 0,5%
  - **Electrodes (anode and cathode foils)**
    - *Treatment I*
      - **Fraction 1**
        - *Treatment II*
          - **Cathode (20%)**

            $Co_2O_3$– 74,5%
            CuO– 3,8%
            MnO – 1,9%
            NiO – 1,8%
            $Al_2O_3$ – 1,1
            $Fe_2O_3$ – 1,5%
            $P_2O_5$ – 1,6%
      - **Fraction 2**
        - *Treatment II*
          - **Mainly Al and Cu foils**

            
            - **By-product 3 (22%)**

              $Cu^0$ – 50%
              $Al^0$ – 26%
              Mn – 8%
              Co – 2%
              Ni – 14%

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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** |

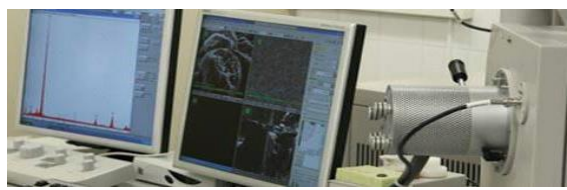


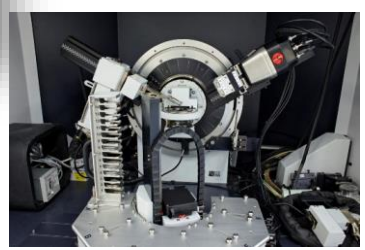










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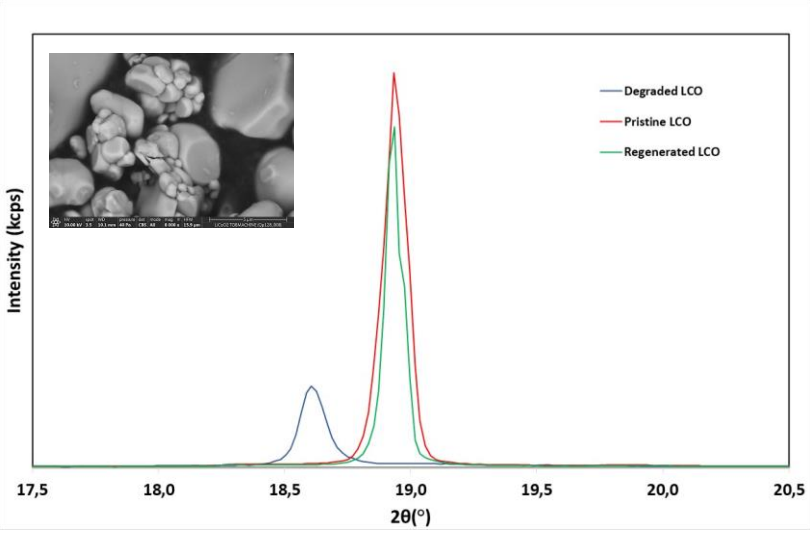
# CHEMISTRY OF ACTIVE MATERIAL IN SPENT Li-ION BATTERIES

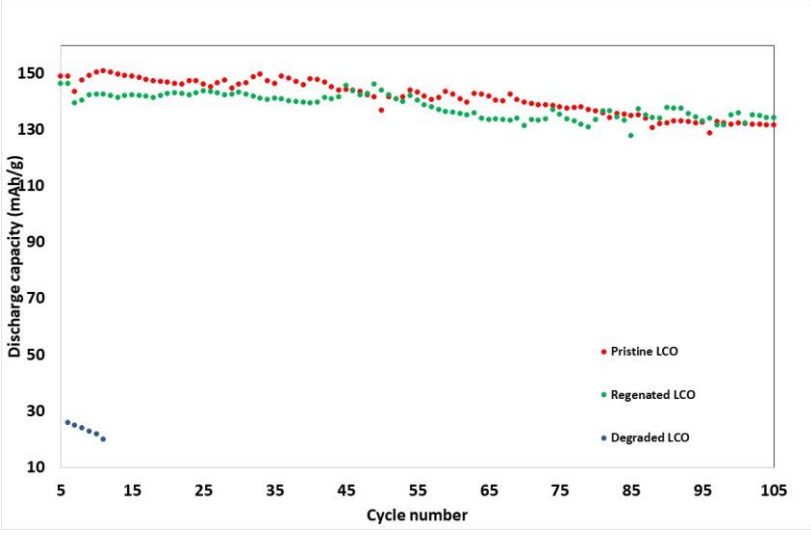
| |  |  |  |
|---|---|---|---|
| **Co (%)** | 69,6 | 13,6 | 22,7 |
| **Ni (%)** | 3,99 | 37,6 | 24,3 |
| **Mn (%)** | 2,55 | 11,9 | 13,0 |
| **Li (%)** | 5,3 | 3,9 | 4,5 |
| **Average weight of recovered cathode active material (g)** | **63** | **300** | **1000** |

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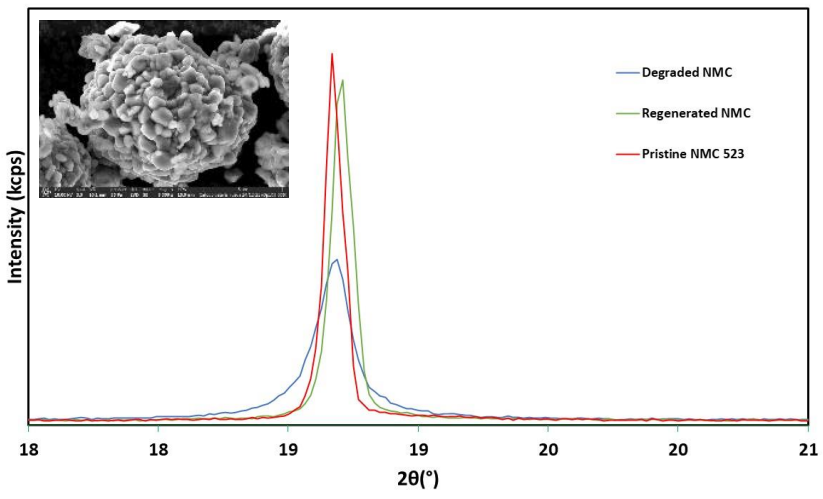
# CHARACTERIZATION OF THE RELITHIATED CATHODE

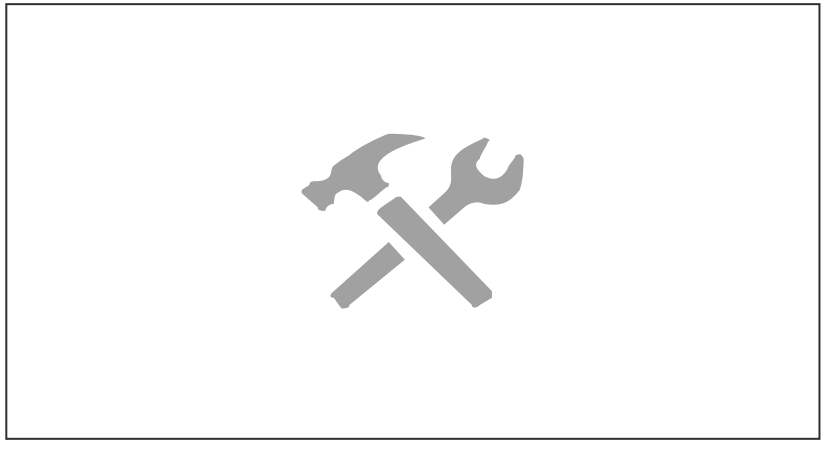
## LCO




## NMC



*Gazulla, M.F.; Rodrigo, M.; Ventura, M.J.; Mallol, J.G.; Gómez, M.P.; Gilabert, J. Direct Recycling of Lithium-Ion Cathode: A Green Solution (Applied To Laptop Batteries). Journal of the Electrochemical Society, 170 (8), 080528, 2023.*

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# Thank you

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*Project funded by:*

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