Sustainable recycling and regeneration of LCO and NMC cathodes from spent Li-ion batteries (BateCat Project)

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GENERALITAT VALENCIANA

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Instituto de Tecnología Cerámica

Electrochemical Laboratory

BateCat project

The main goal is to provide the battery industry with a cathode regeneration methodology based on direct recycling with feseability for being up-scaled

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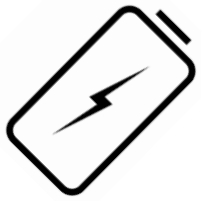
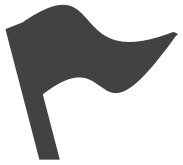
Introduction

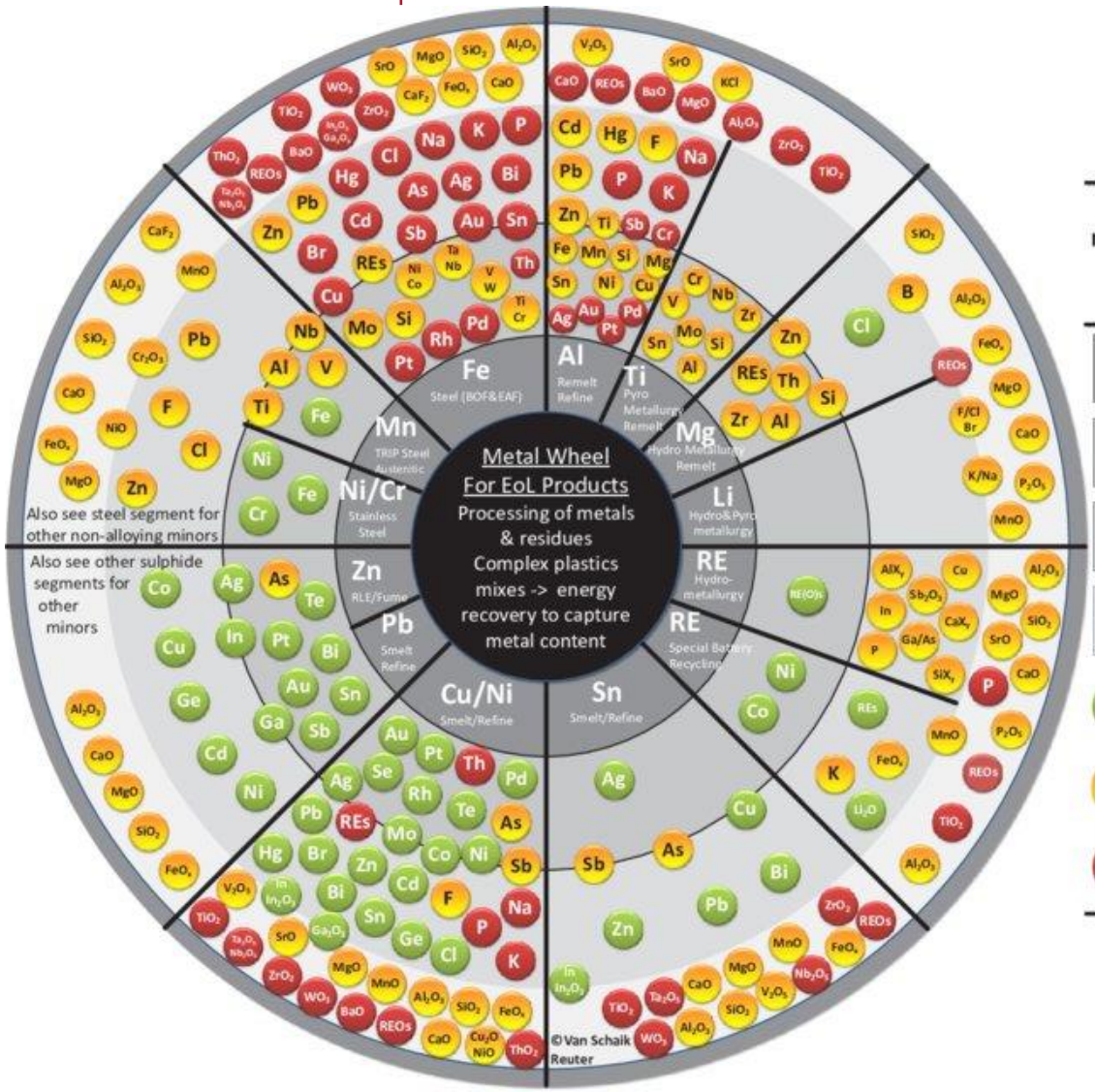


Experimental

Results



Conclusions



Economically viable destinations of complex EoL designed functional material combinations, scrap, residues etc. to metallurgical processing infrastructure (each segment) to produce refined metal, compounds and alloys in best available technology

Circular Economy's carrier metals processing infrastructure
Extractive Metallurgy's Backbone, the enablers of a Circular Economy (CE) as it also recovers technology elements used e.g. in renewable energy infrastructure, IoT, eMobility etc.

Dissolves mainly in carrier metal if metallic (mainly pyrometallurgy)
Valuable elements recovered from these or (dissipative) lost (metallic, speiss, compounds, alloy in EoL also determines destination as also the metallurgical conditions in flowsheet).

Compounds mainly to dust, slime, speiss (mainly hydrometallurgy)
Collector of valuable minor elements as oxides/sulphates/chlorides etc. and mainly recovered in appropriate metallurgical infrastructure if economical.

Mainly to benign lower value building material products
Relatively lower value but inevitable part of society and materials processing. A sink for metals and loss from the CE system as oxides/ compounds. Dissipative losses.

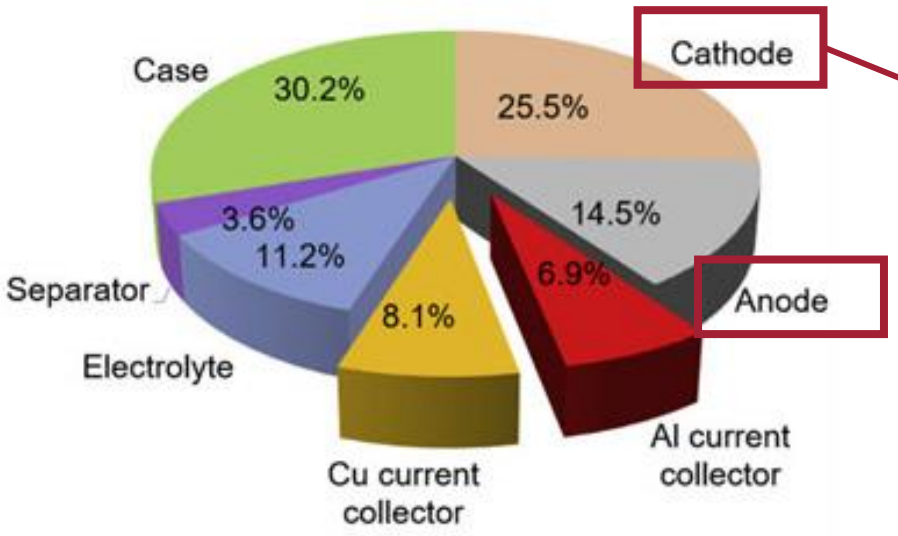
A **Mainly recovered element**
Compatible with Carrier Metal as alloying Element or can be recovered in subsequent Processing.

B **Mainly element in alloy/compound, lost if in incorrect stream/scrap/module**
With possible functionality, not detrimental to Carrier Metal or product (if refractory metals in EoL product report to slag / slag also intermediate product for cement etc.).

C **Mainly element lost, not always compatible with carrier metal or product**
Detrimental to properties and cannot be economically recovered e.g. Au dissolved in steel or aluminium will be lost.

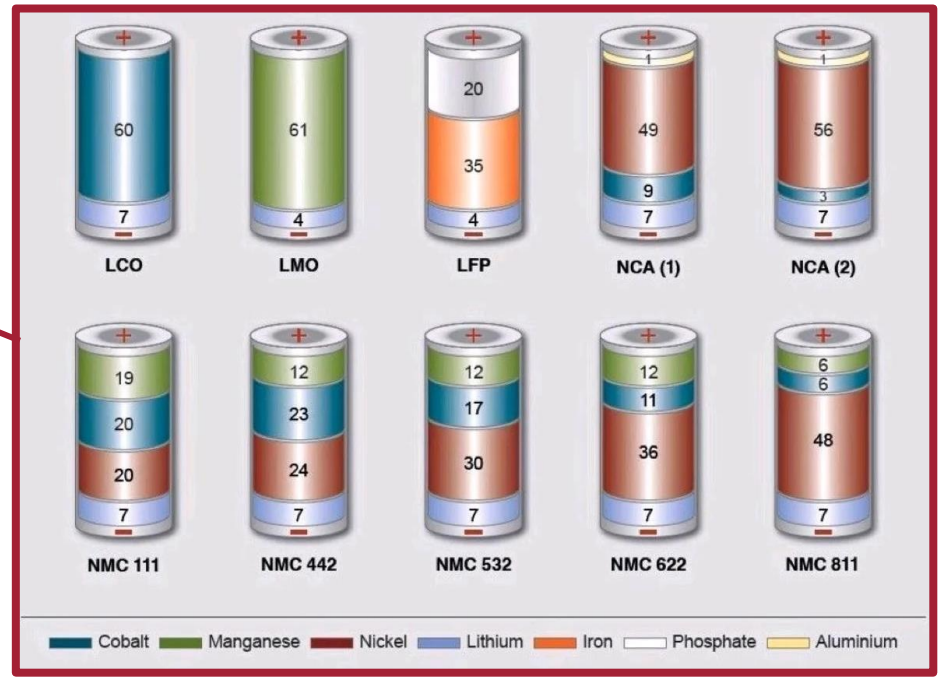
Reuter, M.A.; van Schaik, A.; Ballester, M. (2018): Limits of the circular economy: fairphone modular design pushing the limits. World of Metallurgy, 71(2), 68-79.

Generic composition of Li-ion cells



Source: Suny Group

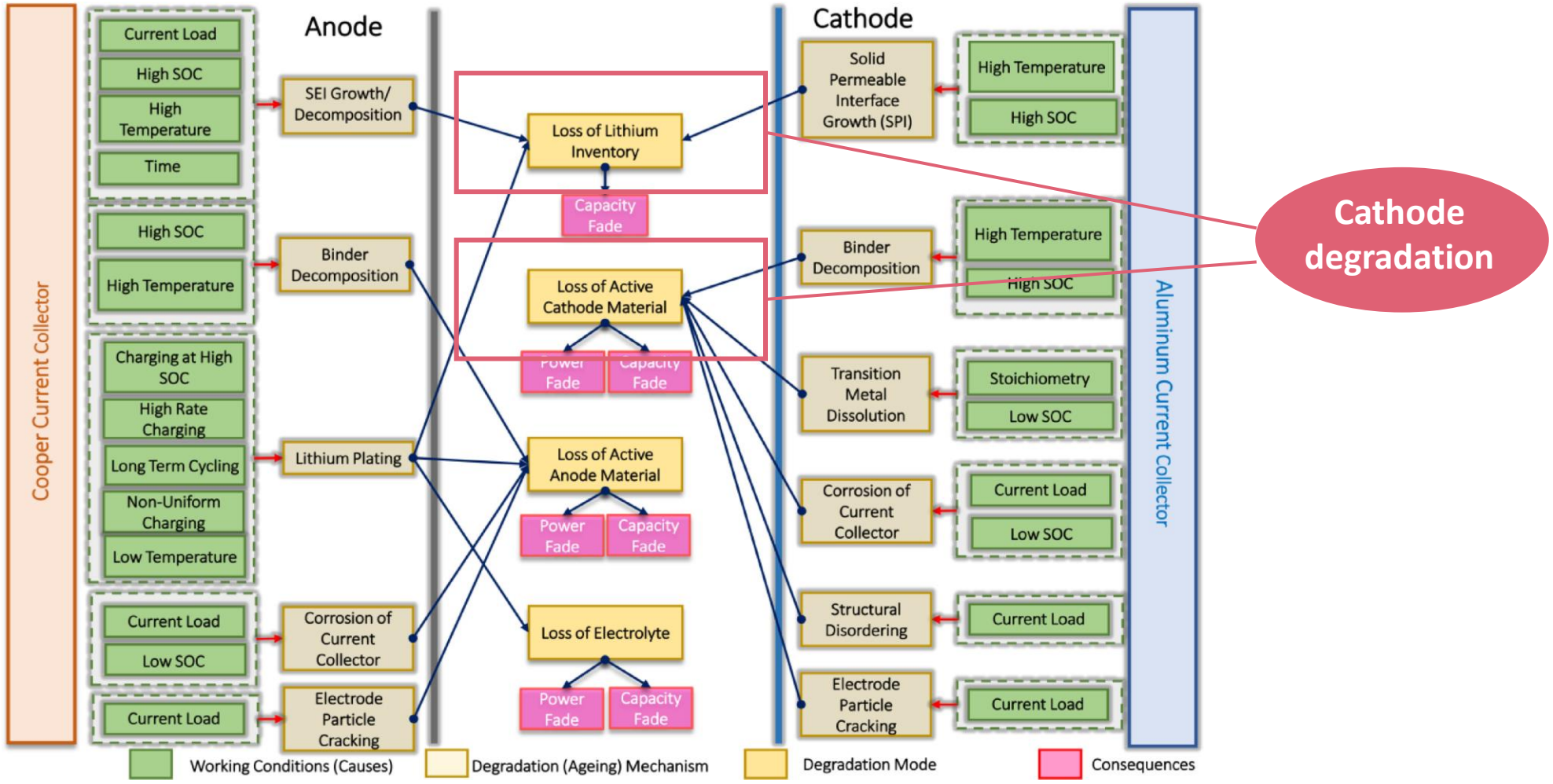
Type of cathode active material



CRMs used in LIB manufacturing

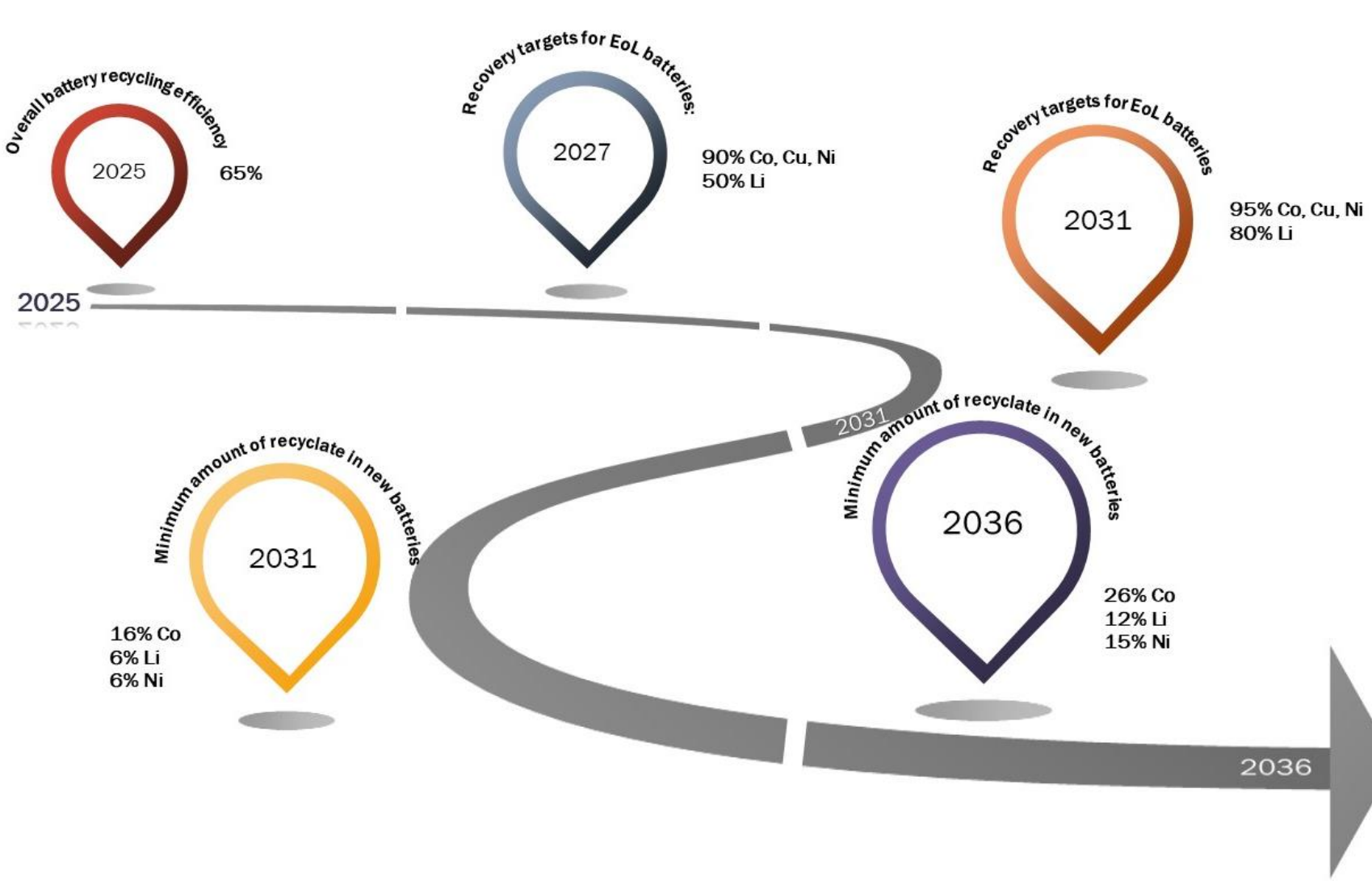
Li	C	Mn	Co	Ni
3	6	25	27	28

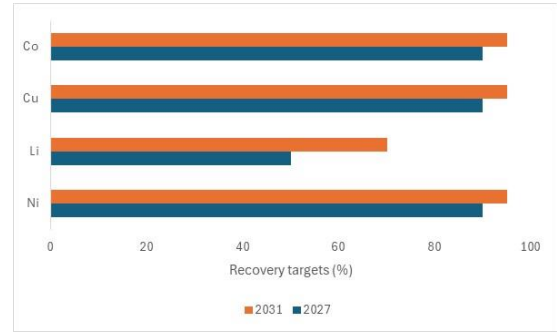
Degradation modes and aging mechanisms

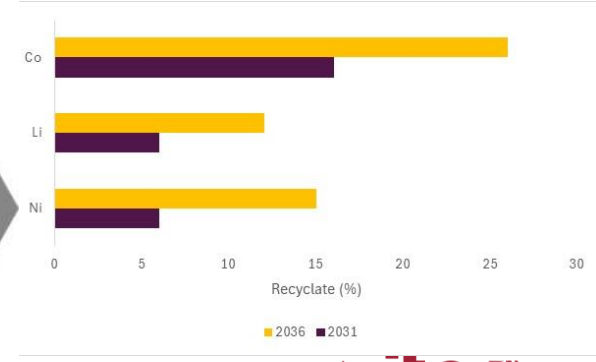


Source: Lin et al. , 2021

European Battery Regulation

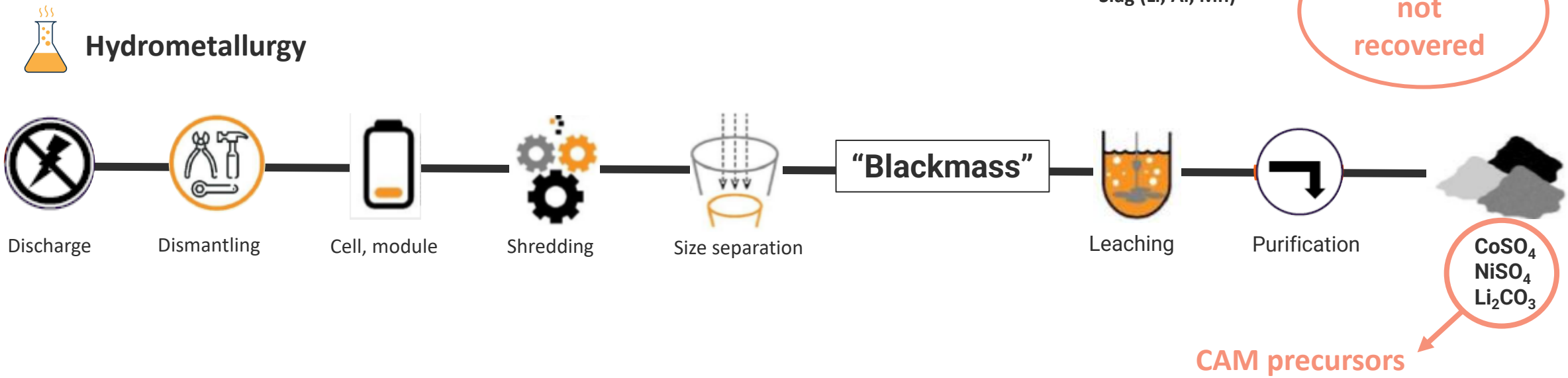




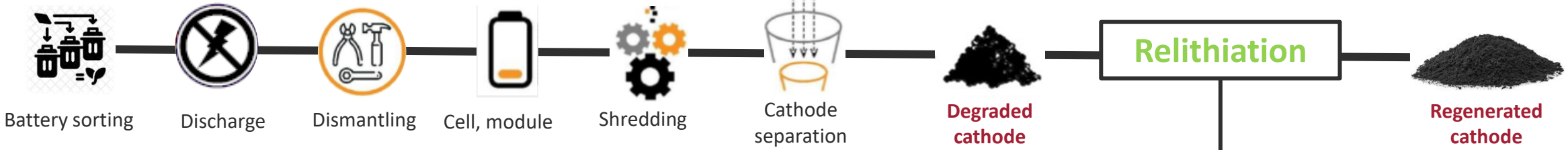


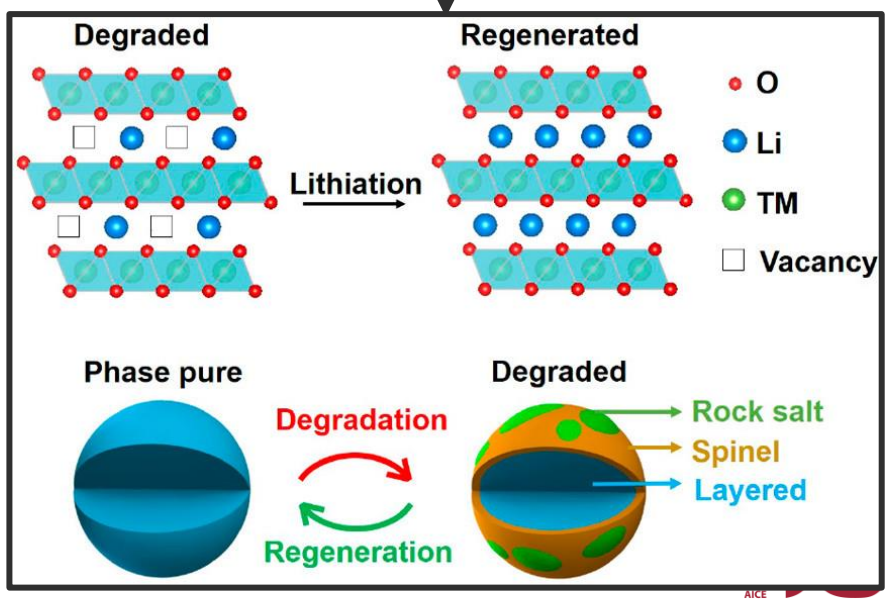
Pyrometallurgy

Hydrometallurgy

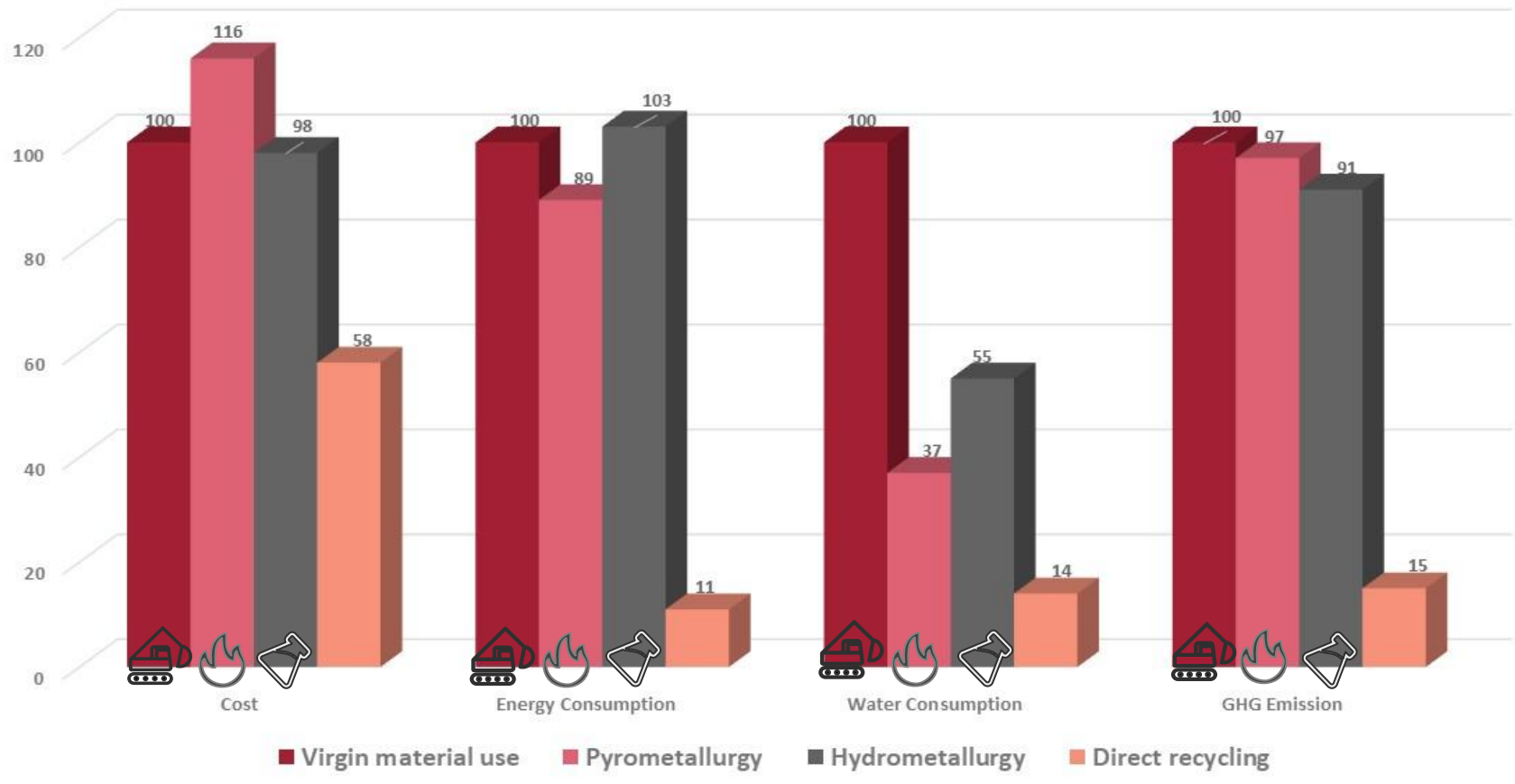


Direct recycling





Source: Shi et al. , 2018

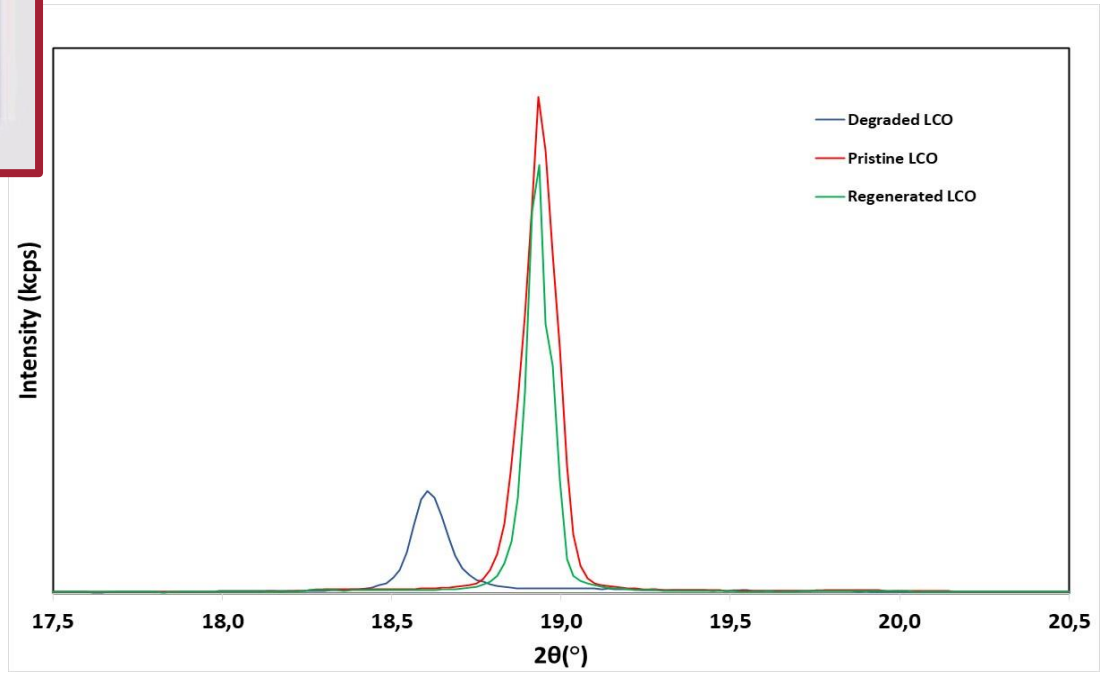


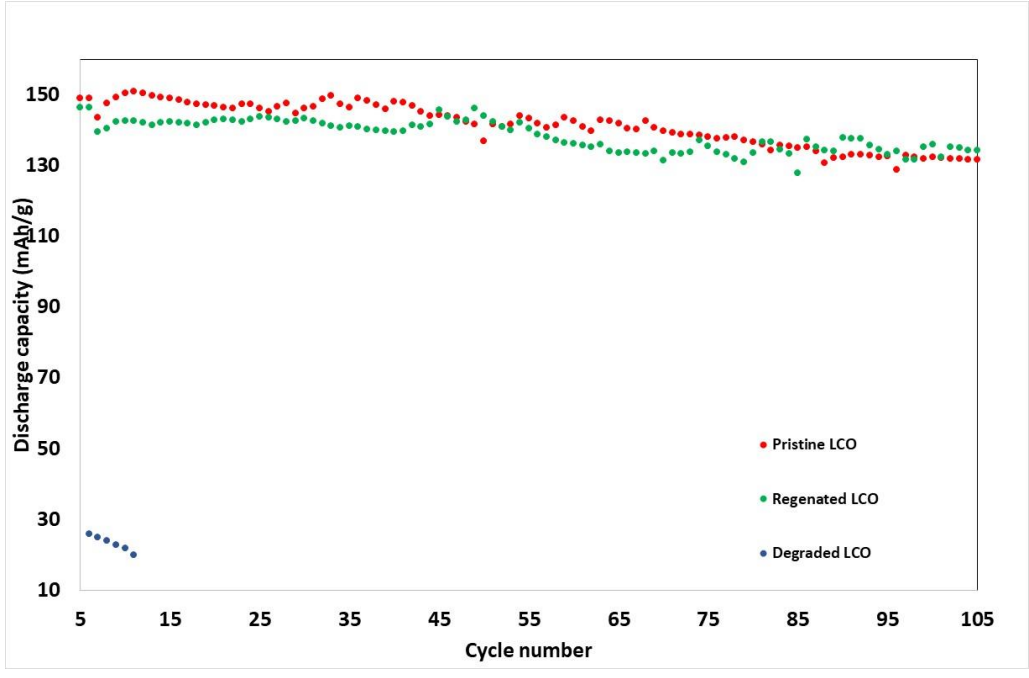
Source: WRI India

Direct recycling has the lowest cost and impacts on the environment in all categories

Experimental

Previous work





Properties of the regenerated cathode

- Recovery of the crystalline structure
- Initial capacity: 147 $mAh \cdot g^{-1}$
- SOH (after 100 cycles): 90%

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

Method for the recovery of the active cathode material from rechargeable spent lithium-ion batteries

Experimental

Characterisation of the EoL battery

Li-ion battery degraded in real conditions

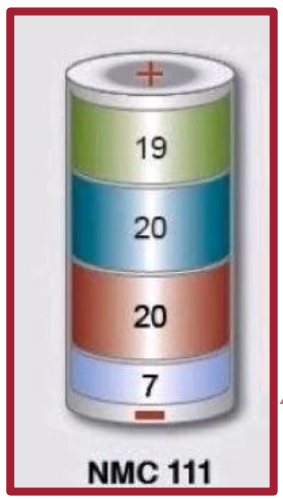
Cell

Cathode foil

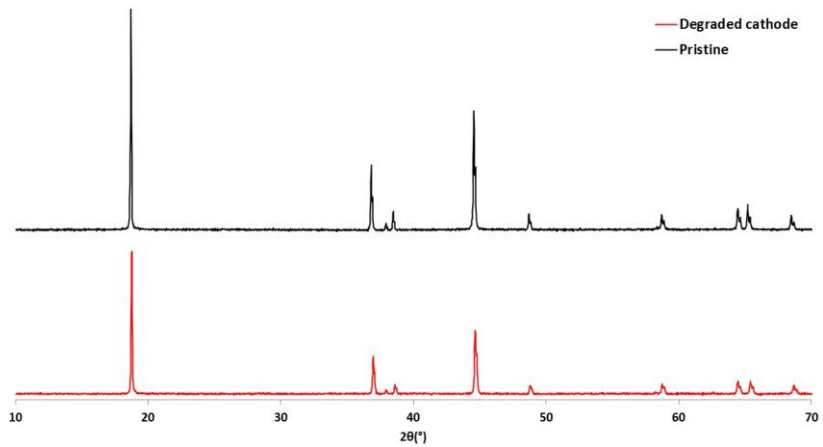
Degraded active cathode material

Chemical composition

Co (%)	Ni (%)	Mn (%)	Li (%)
20.5	20.1	19.0	4.8



Phase identification



Experimental | Characterisation of the EoL battery

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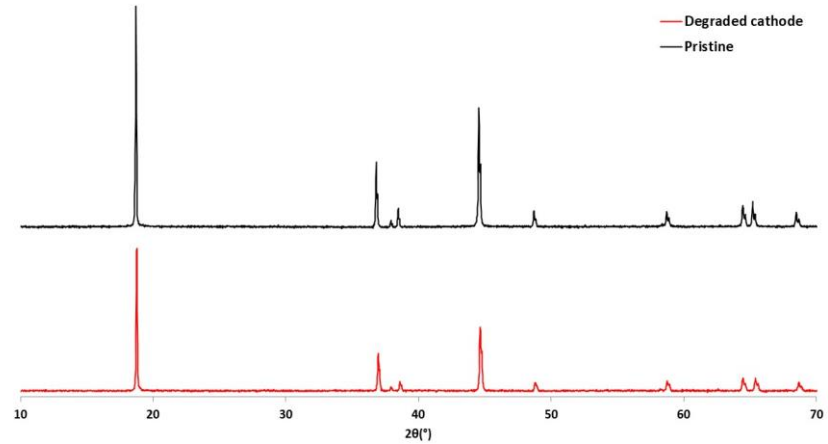
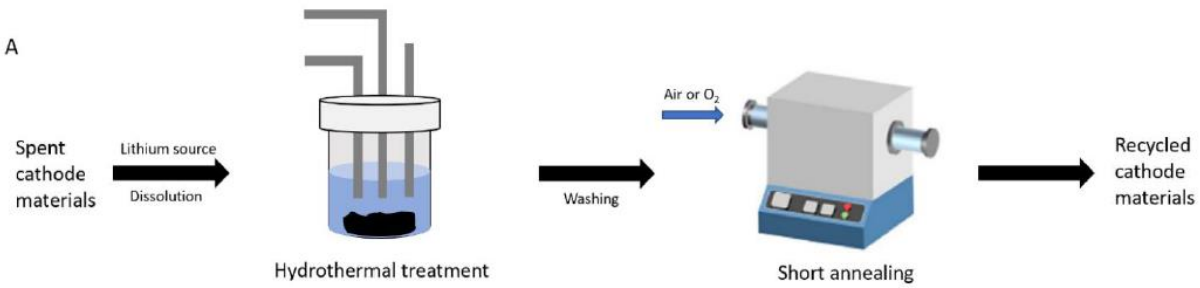


Experimental | Relithiation

Solid sintering

LCO

Hydrothermal



LCO, NMC

- *Shi, Y.; Chen, G.; Liu, F.; Yue, X.; Chen, Z. Resolving the compositional and structural defects of degraded $LiNi_xCo_yMn_zO_2$ particles to directly regenerate high-performance lithium-ion battery cathodes. ACS Energy Lett. 2018,3, 1683*
- *Zhao, Y.; Yuan, X.; Jiang, L.; Wen, J.; Wang, H.; Guan, R.; Zhang,J.; Zeng, G. Regeneration and reutilization of cathode materials from spent lithium-ion batteries. Chem. Eng. J. 2020, 383, 123089*
- *Wang, T.; Luo, H.; Fam, J.; Thaaliya, B.P.; Bai, Y.; Belharouak, I.; Dai, S. Flux upcycling of spent NMC 111 to nickel-rich NMC cathodes in reciprocal ternary molten salts. iScience 2022, 25, 103801*
- *Qin, Z.; Zhnag, Y.; Luo, W.; Zhang, T.; Wang, T.; Ni, L.; Wang, H.; Zhang, N.; Liu, X.; Zhou, J.; Chen, G. A universal molten salt method for direct upcycling of spent Ni-rich cathode towards single-crystalline Li-rich cathode. Angew. Chem. Int. De. 2023, 62, e202218672*

Experimental

Validation

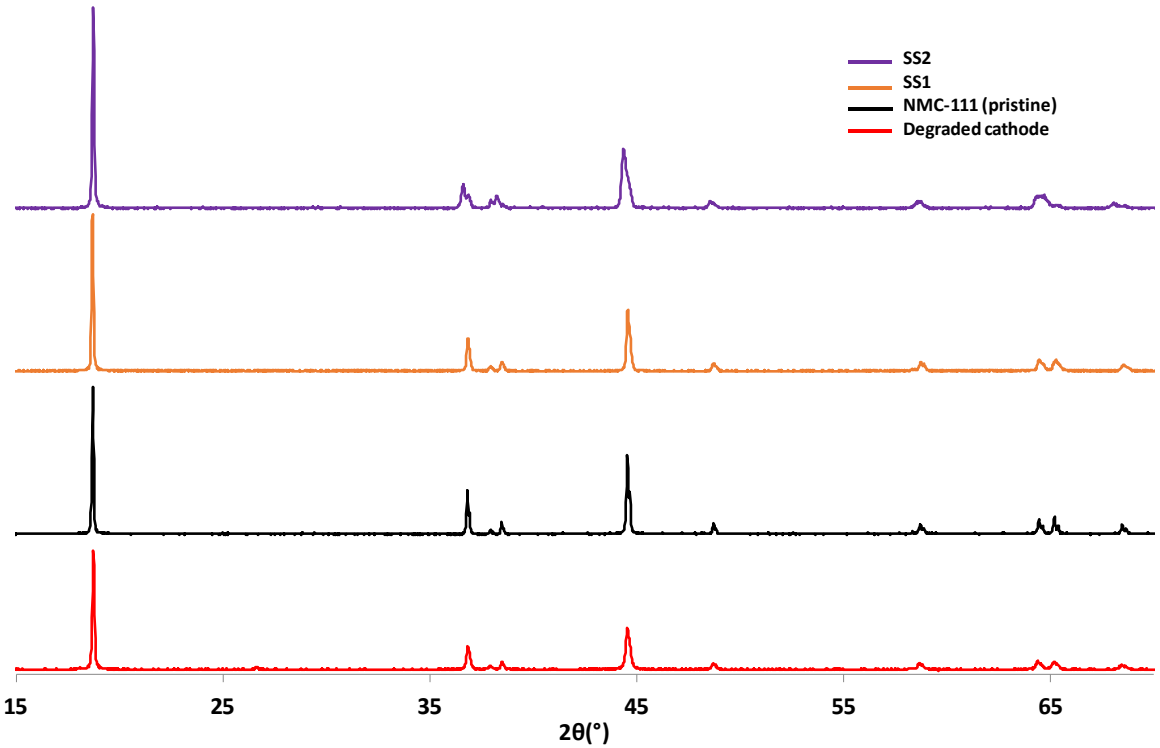
Li concentration

Phase identification

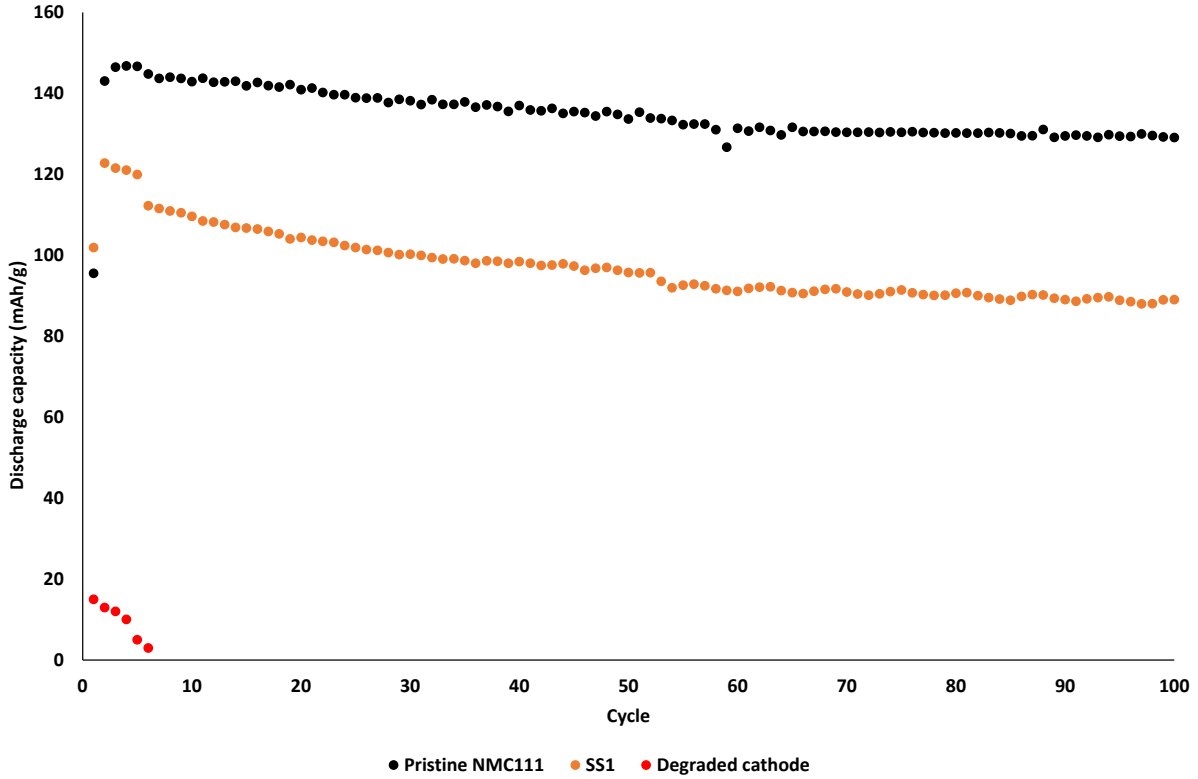
Electrochemical performance

Results

Phase identification

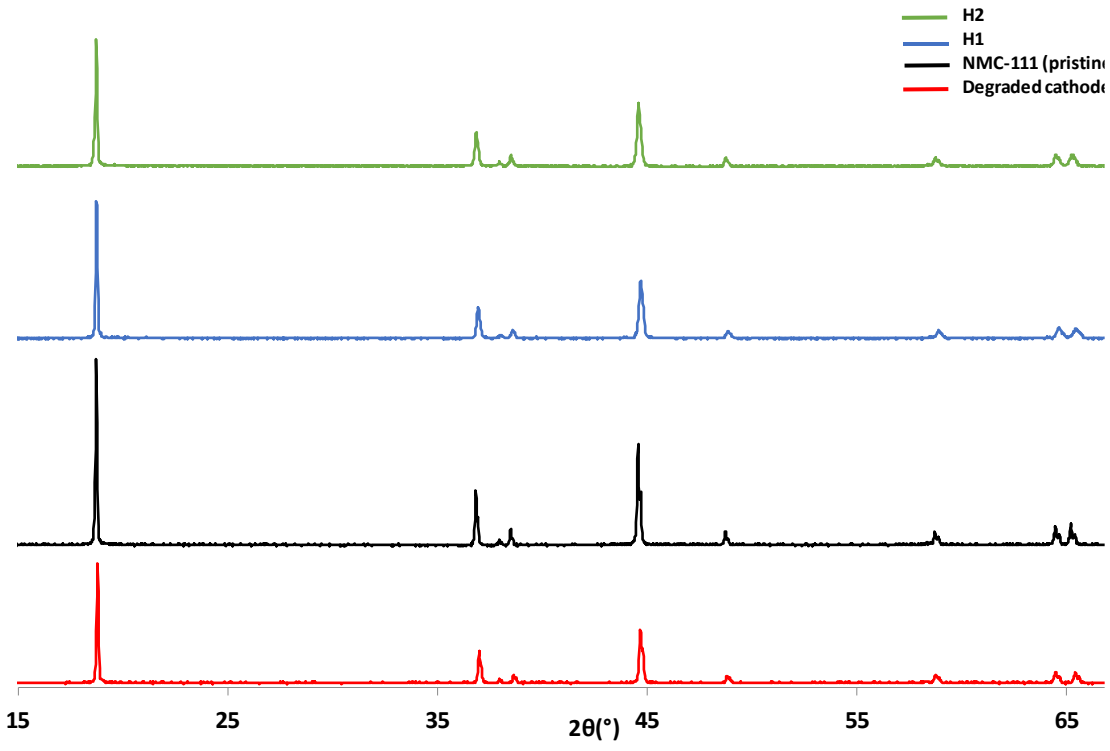


Electrochemical performance



Results

Phase identification



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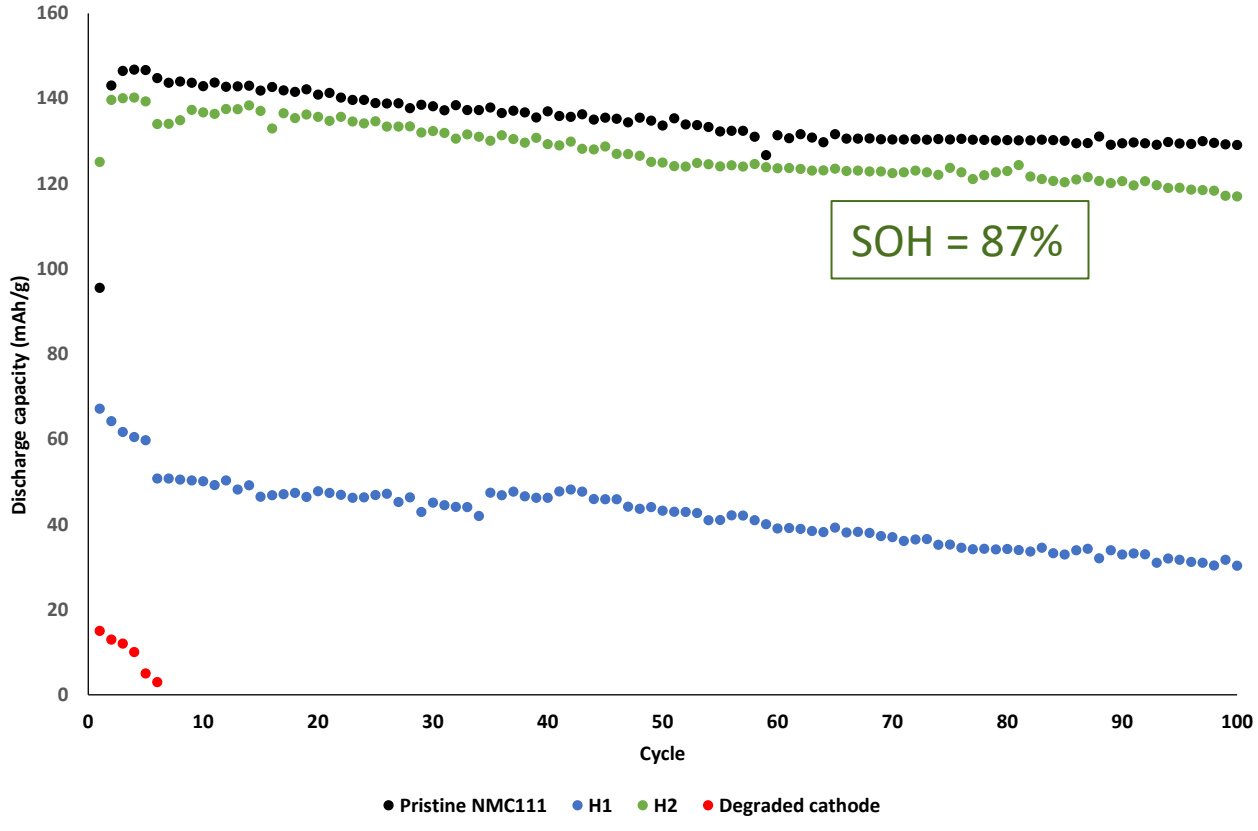

Conclusions

- ITC has a patented method for the separation of the valuable metals that form part of LIBs:
  - Active cathode material
  - By-product riched in Ni
  - By-product riched in Cu
- Chemical analysis and phase identification are crucial for the determination of the cathode chemistry and selection of the most suitable regeneration process
- Various solid-sintering and hydrothermal procedures were tested in order to design the proper regeneration method for NMC 111 cathodes
- The regeneration processes were assessed by the determination of Li content, phase identification,and determination of the electrochemical behaviour
- A degraded cathode after being used in real conditions was regenerated using a hydrothermal method and coin cells manufactured with this regenerated active material showed appropiate capacity and state of health after 100 cycles of charge/discharge

Mª Fernanda Gazulla

Laura Montañes

Jéssica Gilabert

Marta Rodrigo

Thank you

Marta Rodrigo Edo

Head of the Electrochemical Laboratory

Battery Recycling

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