Low-temperature carbothermic reduction for recycling of $LiCoO_2$: the crucial role of cellulose

Eleonora Carena, Chiara Ferrara

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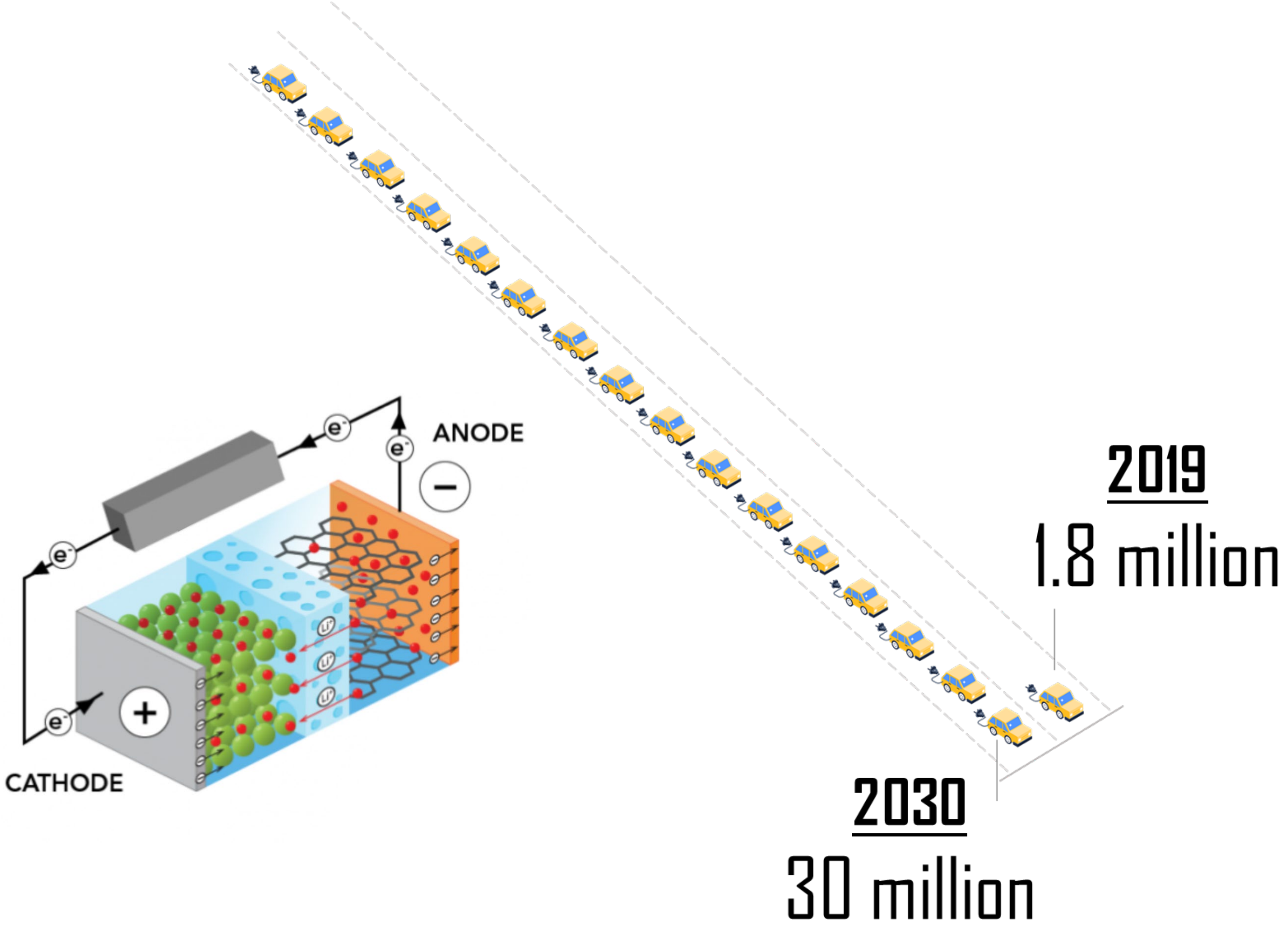
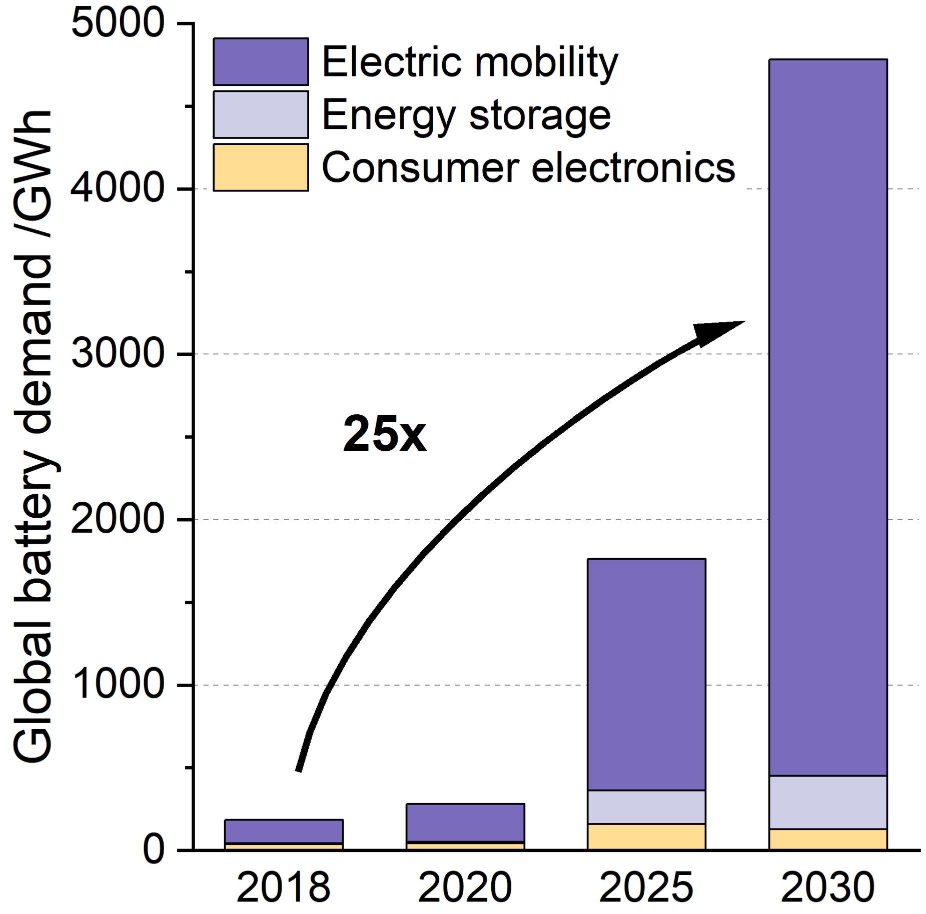
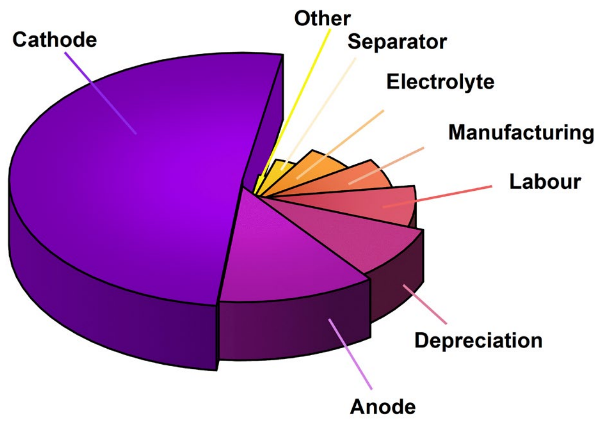
Lithium-Ion Batteries

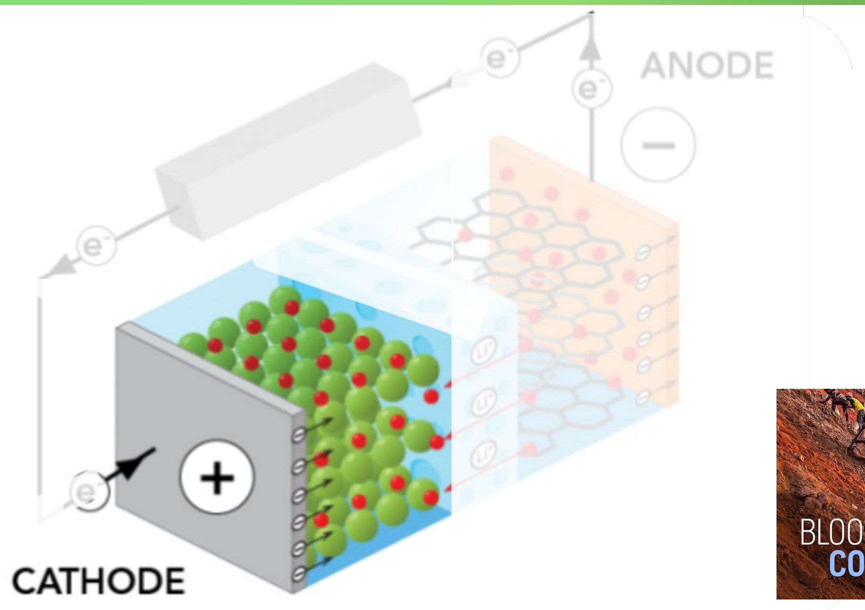


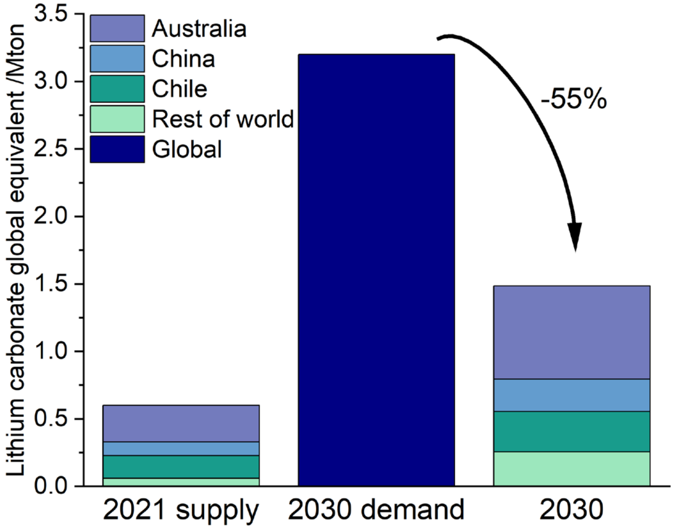


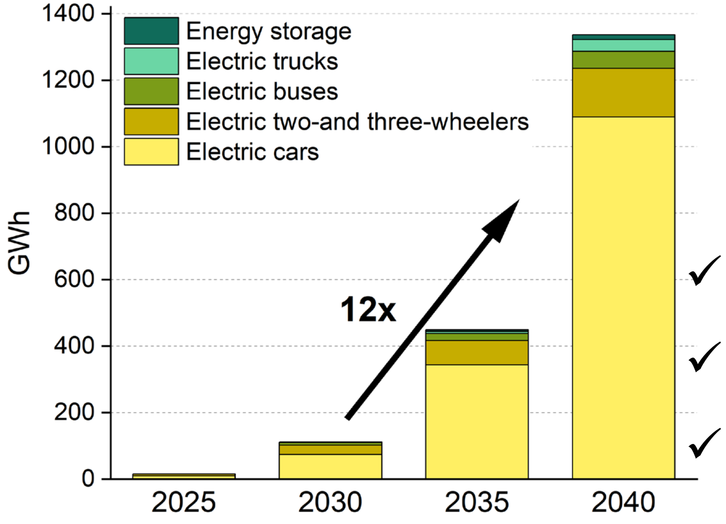
BATTERY 2030+ Roadmap, February 2022

Lithium-Ion Batteries









- ✓ Human price and geographical disruption
- ✓ Short supply of lithium
- ✓ Massive amount of waste LIBs

McKinsey&Company, *Battery 2030: resilient, sustainable, and circular, 2023*

IEA (2023), *Global EV Outlook 2023*

Lithium-Ion Batteries

'Like slave and master': DRC miners toil for 30p an hour to fuel electric cars

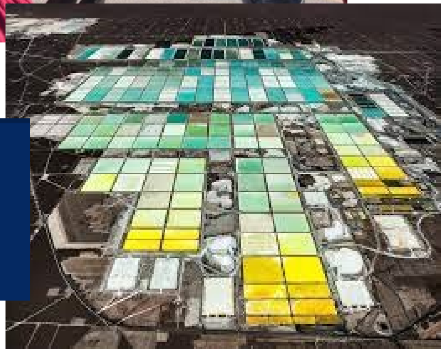
The Guardian

The Washington Post
Democracy Dies in Darkness

CLEAN CARS, HIDDEN TOLL

Despite reforms, mining for EV metals in Congo exacts steep cost on workers

After revelations of child labor and treacherous conditions in many cobalt mines, automakers and mineral



AMNESTY INTERNATIONAL ENGLISH

POWERING CHANGE OR BUSINESS AS USUAL

Forced evictions at industrial cobalt and copper mines in the Democratic Republic of the Congo

Blinded, sexually assaulted, silenced: the war over lithium, Argentina's 'white gold'

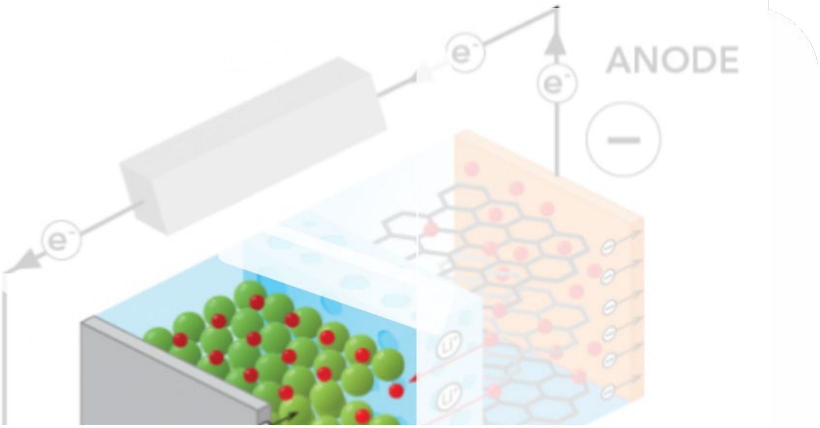
The Guardian

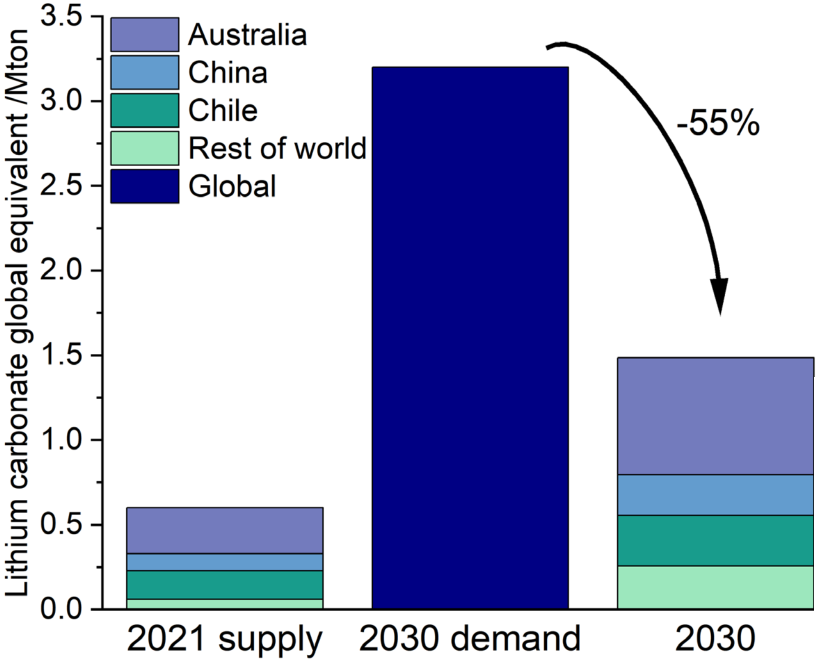
✓ **Human price and geographical disruption**

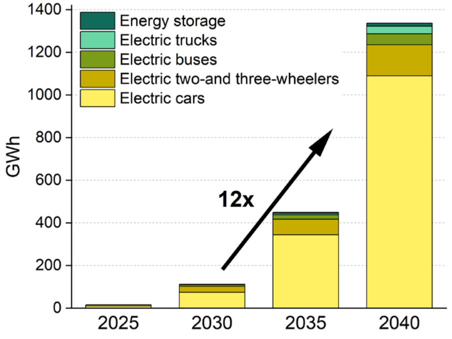
Argentina: la fiebre por el litio amenaza los derechos de los pueblos indígenas en Jujuy

fidh FEDERACIÓN INTERNACIONAL POR LOS DERECHOS HUMANOS

Lithium-Ion Batteries







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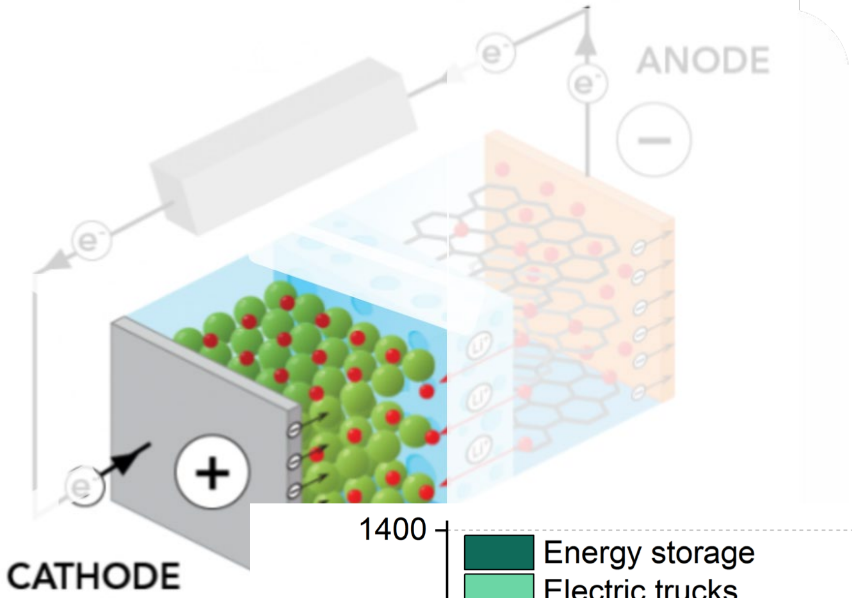
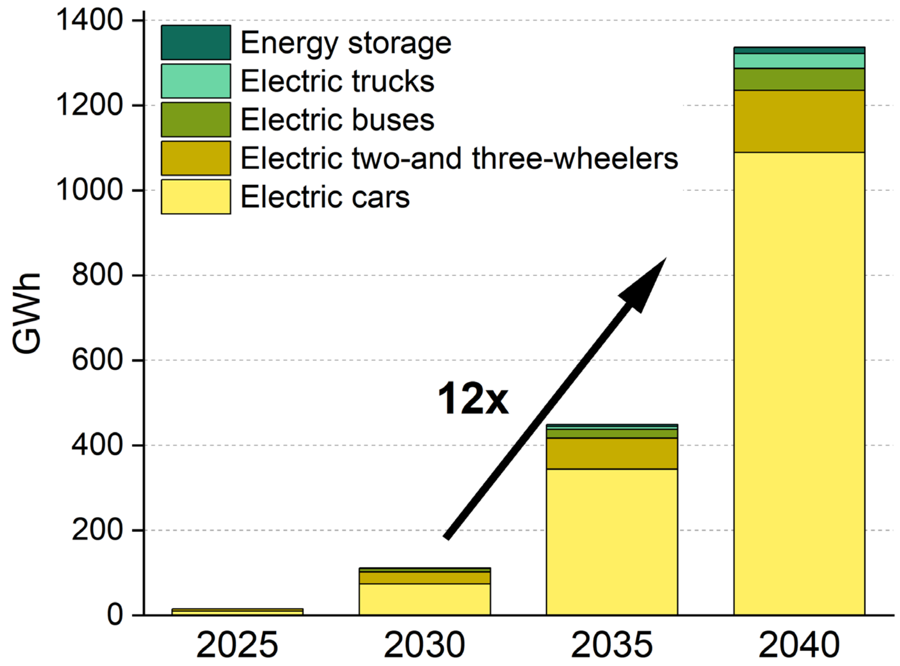
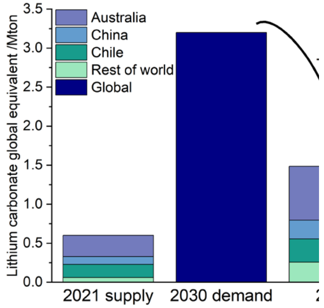
Lithium-Ion Batteries







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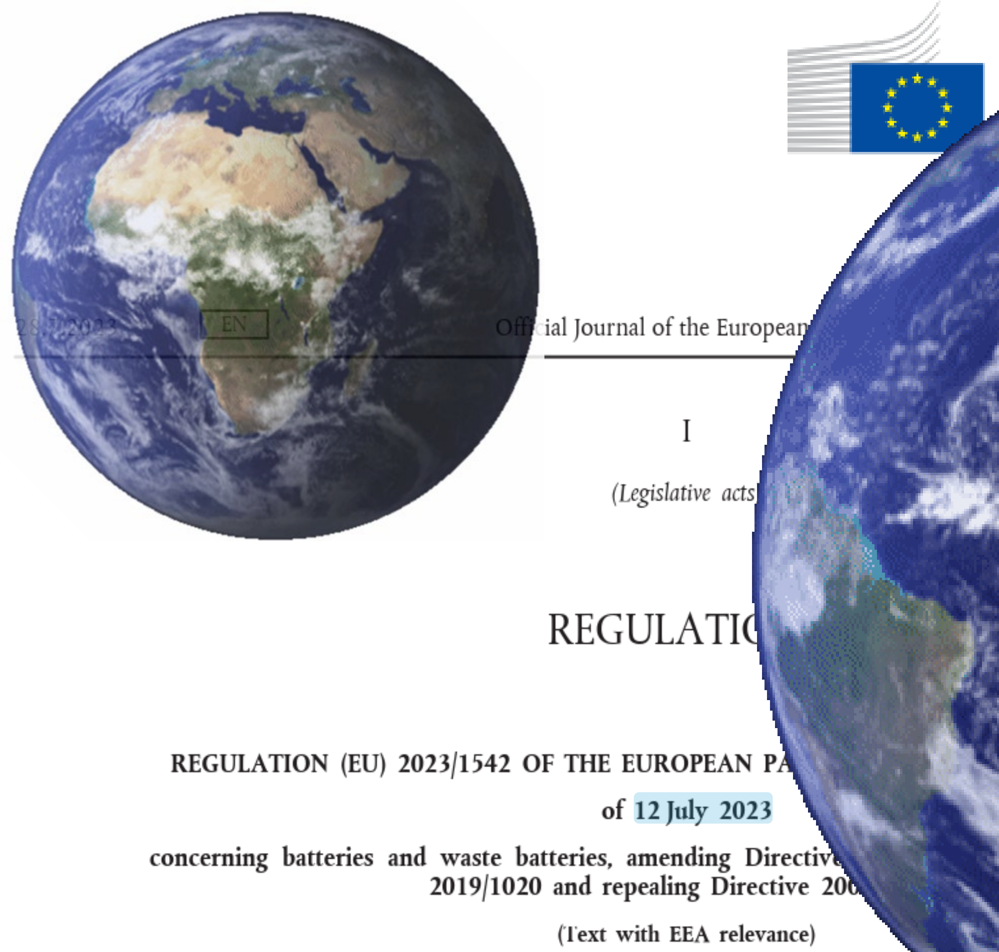
Recycling as a global opportunity – EU Regulations



Official Journal of the European

EN

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(Legislative acts

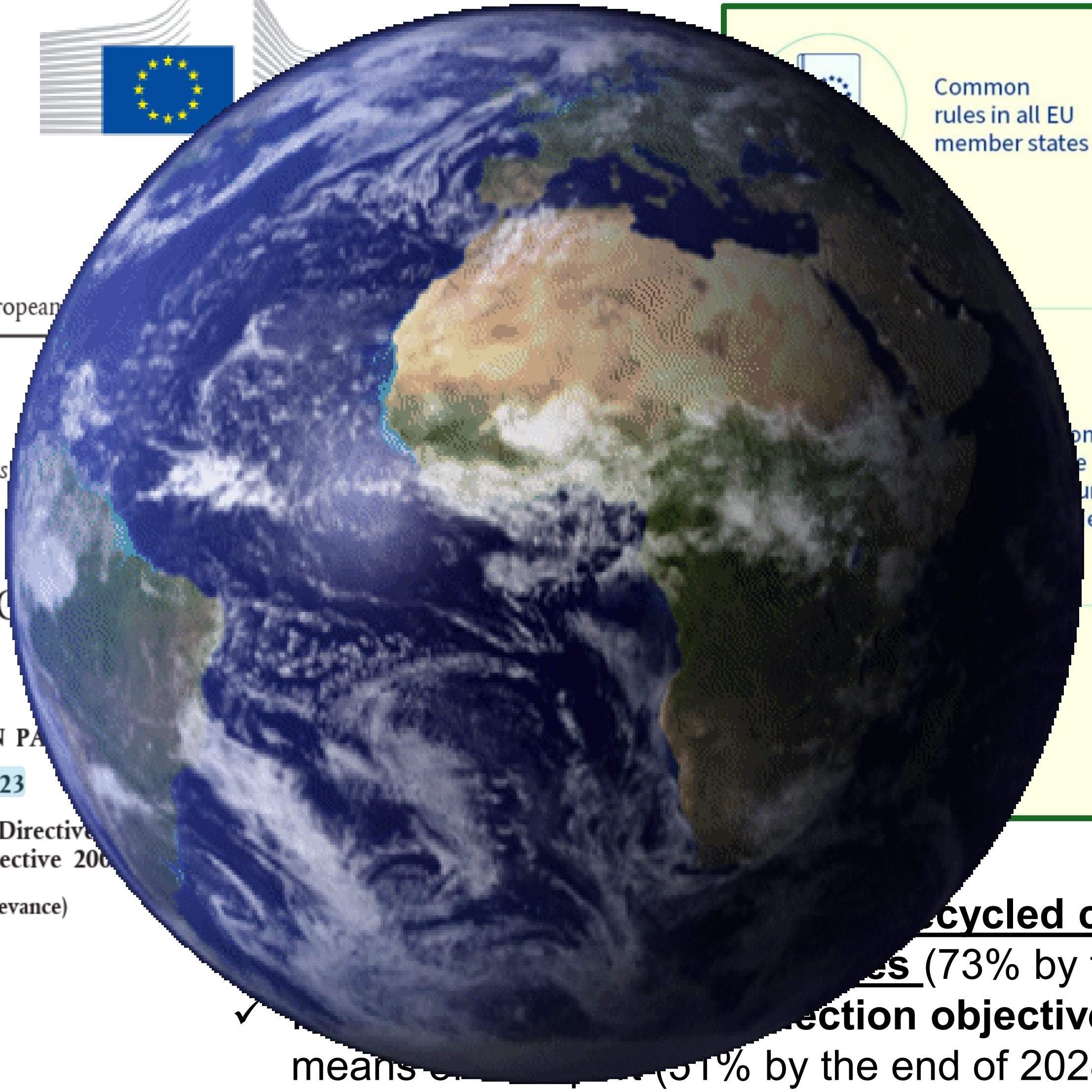
REGULATIO

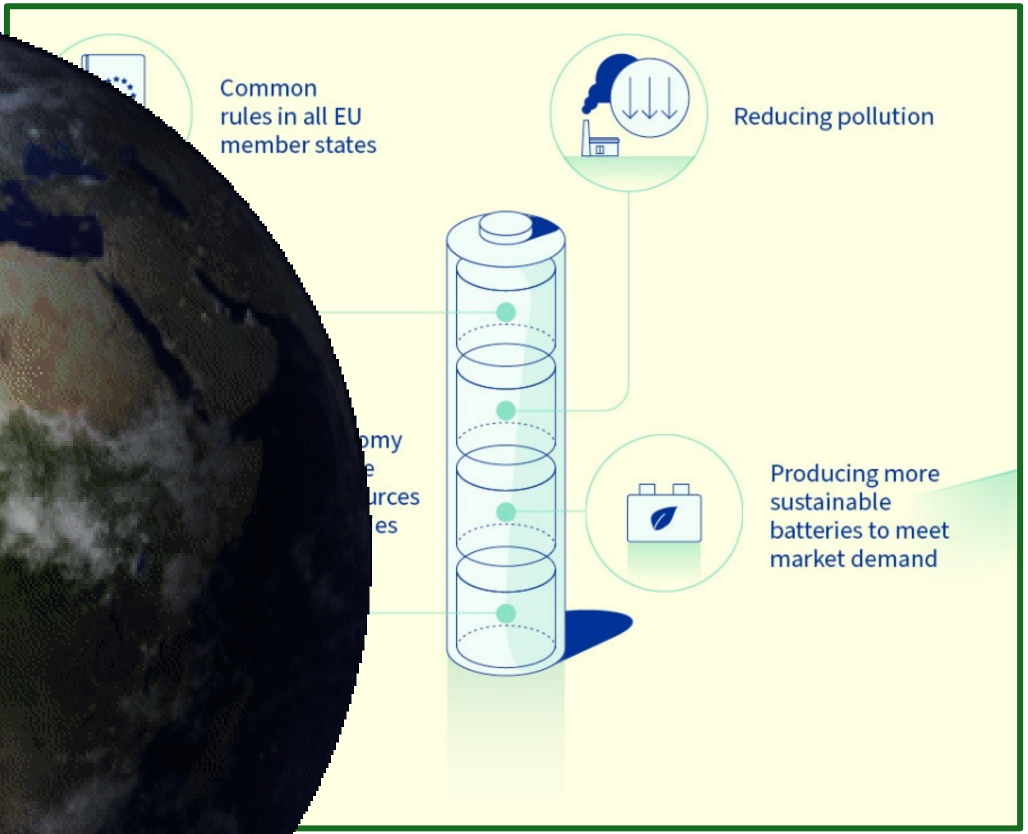
REGULATION (EU) 2023/1542 OF THE EUROPEAN PA

of 12 July 2023

concerning batteries and waste batteries, amending Directive
2019/1020 and repealing Directive 200

(Text with EEA relevance)





cycled content
es (73% by the end of 2030)
- ✓ **ection objective for waste batteries** for light means … 1% by the end of 2028 and 61% by the end of 2031)
- ✓ **Minimum targets for <u>recovery of lithium at 80%</u> by the end of 2031**

Recycling as a global opportunity – US Regulations

US Federal Statutes:

- **Infrastructure Investment and Job Act** (Nov. 2021):
  - $3 billion for battery manufacturing and recycling grant program
  - process for research into reuse of electric vehicle batteries
  - proposes a task force to develop an extended producer responsibility framework
  - guidelines for voluntary battery labelling
  - best practices for battery recycling
- **Resource Conservation and Recovery Act** (Oct. 1976) for the disposal of solid waste and hazardous waste
  - legal framework for the disposal of solid wastes

Memorandum of Understanding (Sep. 2021)

- develop recycling standards for Li-ion batteries to help manufacturers understand what materials and designs will be more recyclable

congress.gov # epa.gov # energy.gov

Bird *The Regulatory Environment for Lithium-Ion Battery Recycling* (2022)

Recycling as a global opportunity

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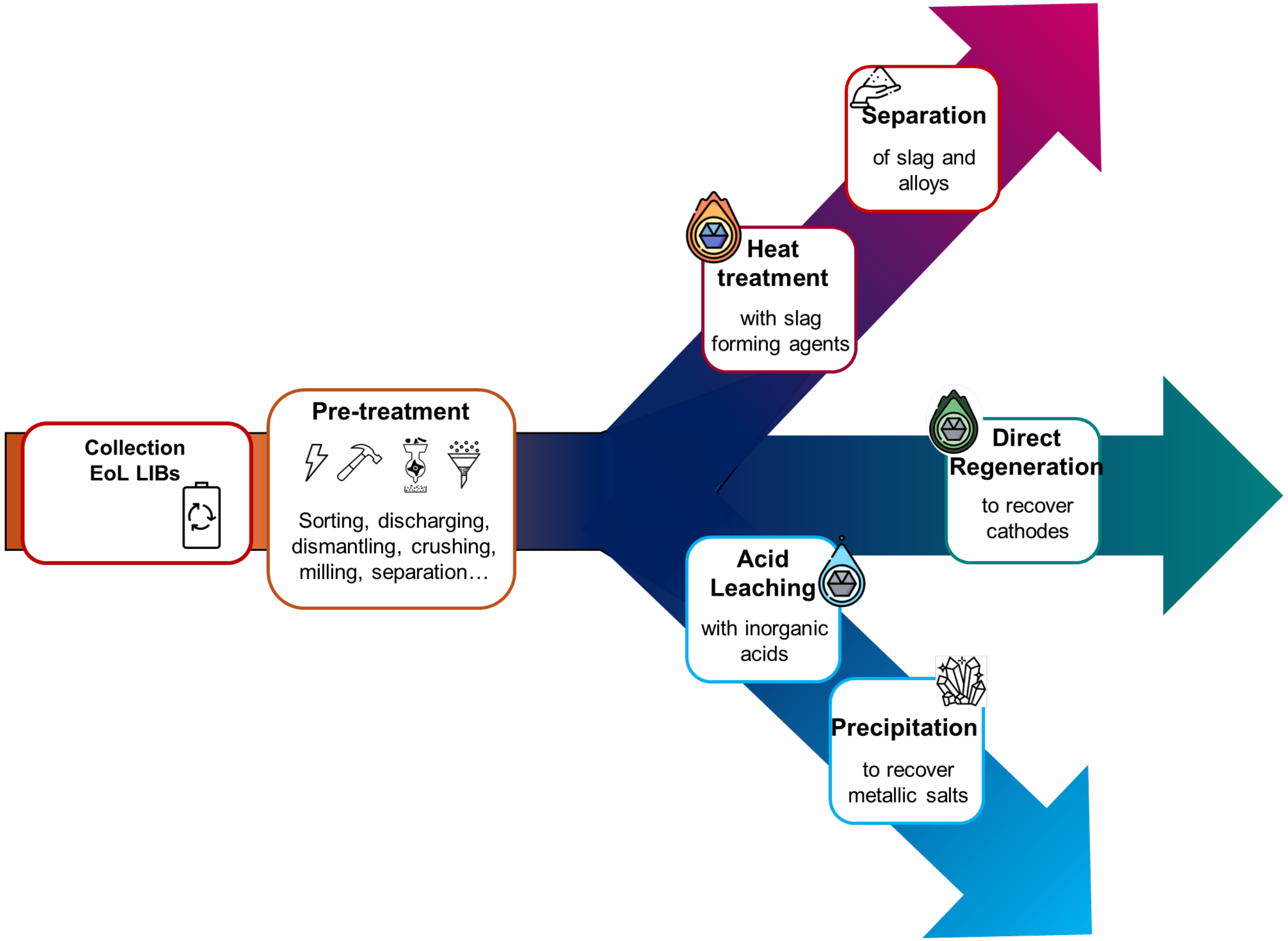
Pyrometallurgy

Direct Recycling

Hydrometallurgy

Recycling as a global opportunity



Industrial level

Pyrometallurgy

- High energy consumption (T> 1500 °C)
- Loss of lithium
- Low purity (metal alloy)
- Emission of polluting gases

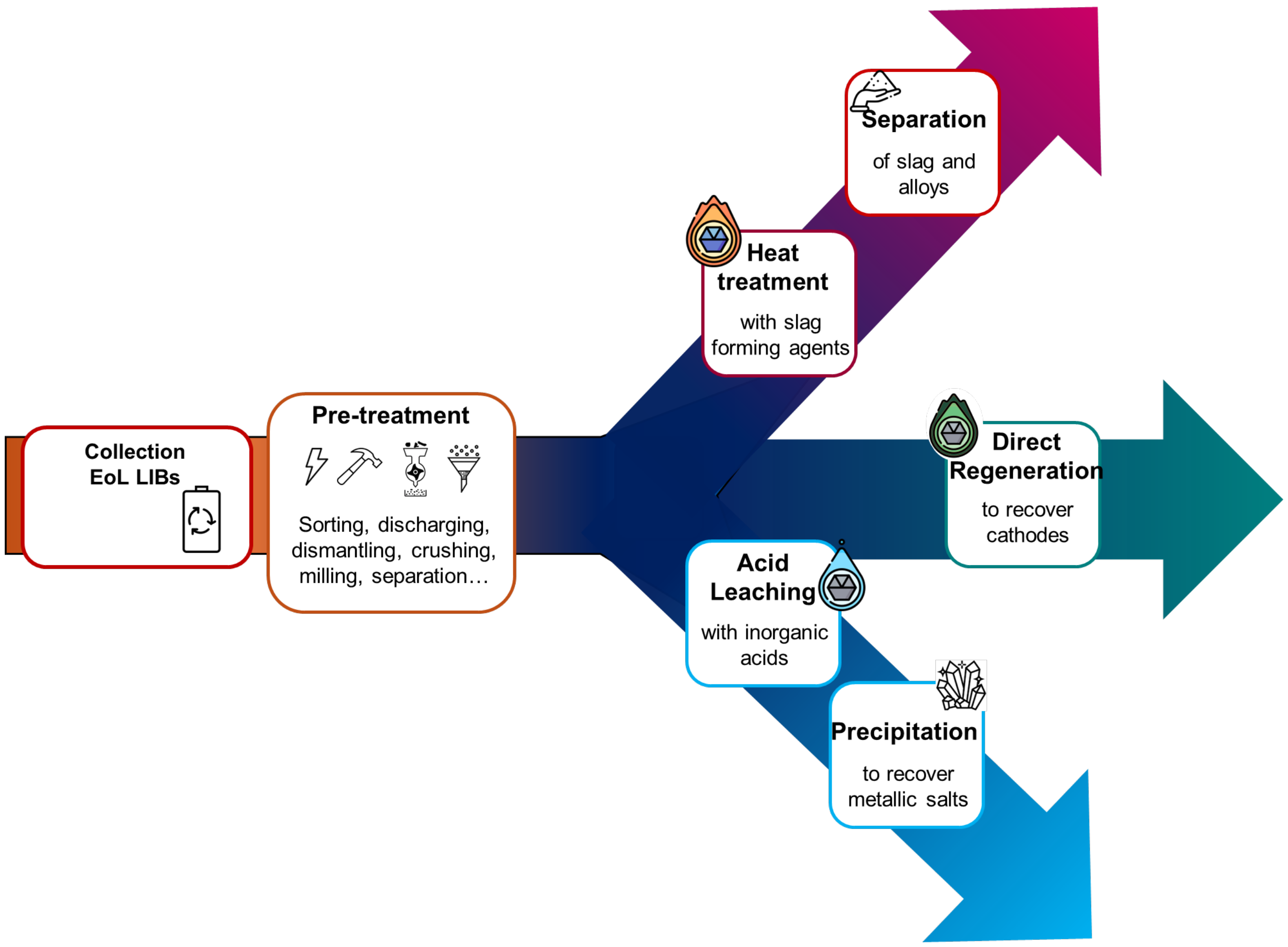
Direct Recycling

- Low impurity tolerance
- High cost of lithium sources and additives
- Safety concerns related to high vapor pressure
- Complicated upscaling

Hydrometallurgy

- High water consumption
- Acidic wastewater neutralization
- Need of separation and purification techniques
- Emission of polluting gases

Recycling as a global opportunity



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Recycling as a global opportunity

Industrial level

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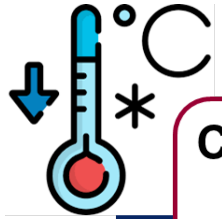
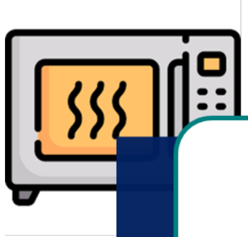
Research level



Carbothermic reduction

with reducing agents or changing the atmosphere



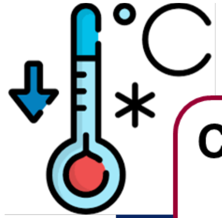
Microwave assisted treatments to lower the time of the treatment

Additive-assisted roasting

to produce metal salts readily soluble in water

Carbothermic reduction @UNIMIB

Research level



Carbothermic reduction

with reducing agents or changing the atmosphere

↓ **operating temperature:**

↓ **energy consumption**

↑ **lithium recovery**

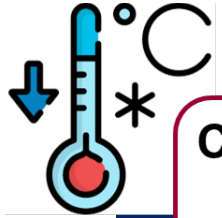
Tunable process

Implementable and scalable process

Low-Temperature Carbothermic Reduction for Recycling $LiCoO_2$ for the Recovery of Critical Raw Materials: The Role of Cellulose *Energy & Fuels (2024)*

Carbothermic reduction @UNIMIB

Research level



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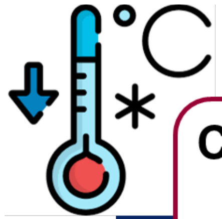

Carbothermic reduction

with reducing agents or changing the atmosphere

$\downarrow$ operating temperature:

$\downarrow$ energy consumption

$\uparrow$ lithium recovery

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Low-Temperature Carbothermic Reduction for Recycling $LiCoO_2$ for the Recovery of Critical Raw Materials: The Role of Cellulose *Energy & Fuels (2024)*

Carbothermic reduction @UNIMIB

Optimization and rationalization of the **thermal process**: identification of the **experimental parameters**

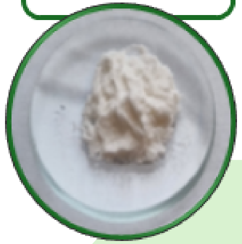
Post-pyrolysis product

Water leaching for easy separation

Recovery of Cobalt and Lithium

Li_2CO_3

CoO/Co



Proof of concept: **resynthesis** and electrochemical test of recovered $LiCoO_2$

Identification of the experimental parameters

Parameters explored:
- ✓ $LiCoO_2$-to-cellulose weight ratio
- ✓ Temperature
- ✓ Holding time

biowaste/carbon source	cathode	experimental conditions	Ni/Mn/Co % recovery	Li % recovery	total cellulose content
pine sawdust	LCO	vacuum pyrolysis 2 h @ 400 °C	97%	94%	~70%
wheat straw	LCO	pyrolysis 40 min @ 1000 °C (not optimized)			50–60%
bamboo sawdust	NMC-111	roasting under N_2 4 h @ 600 °C/800 °C	93–99	86–99	40–55%
macadamia shell	NMC-111	microwave assisted, 30 min @ 500 °C + 25 min @ 750 °C	mixed Ni/Co/Mn as hydroxide	93.4	~60%
bean dregs	NMC-523	pyrolysis 40 min @ 700 °C	93.78%	93.78%	70–80%

Identification of the experimental parameters

Parameters explored:
- ✓ $LiCoO_2$-to-cellulose weight ratio
- ✓ Temperature
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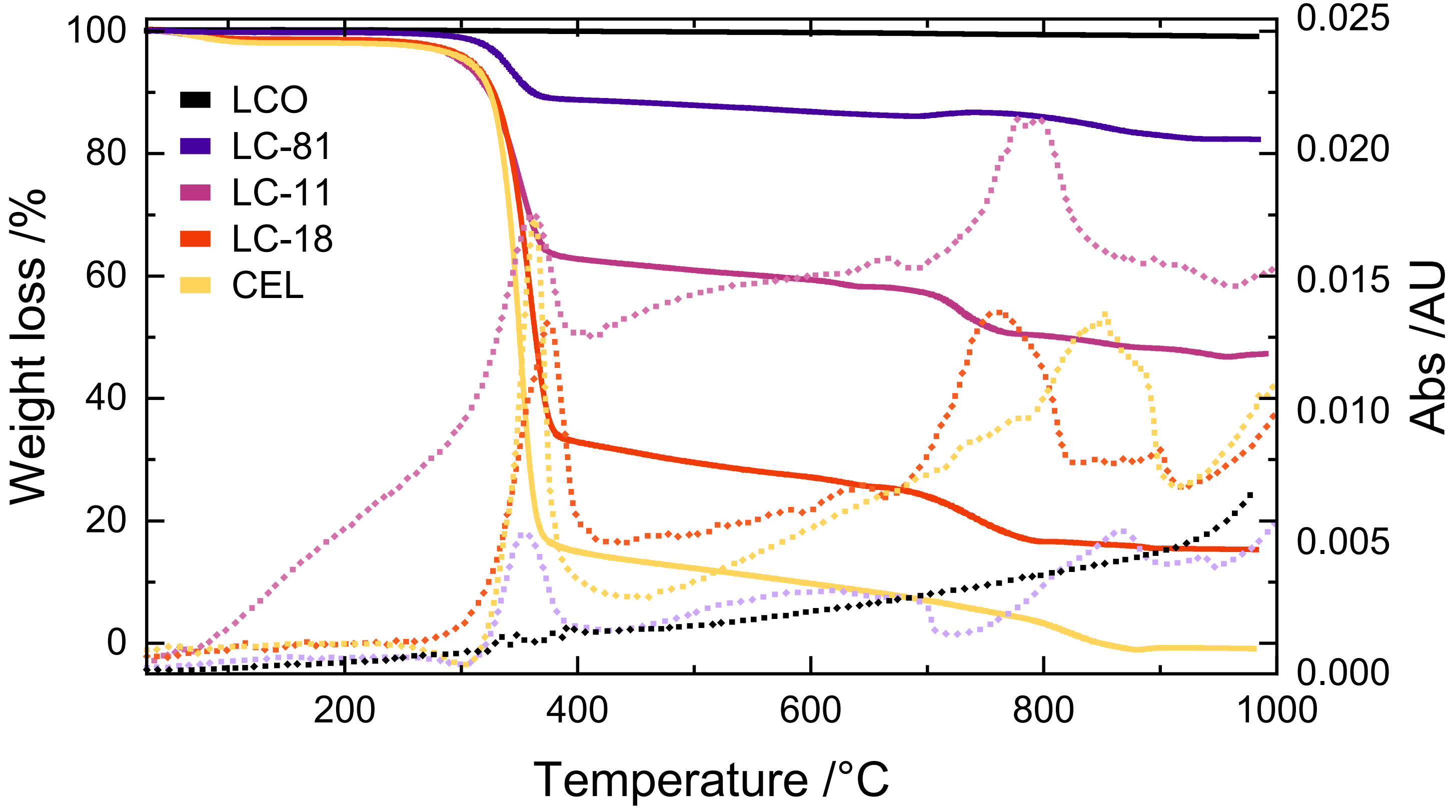

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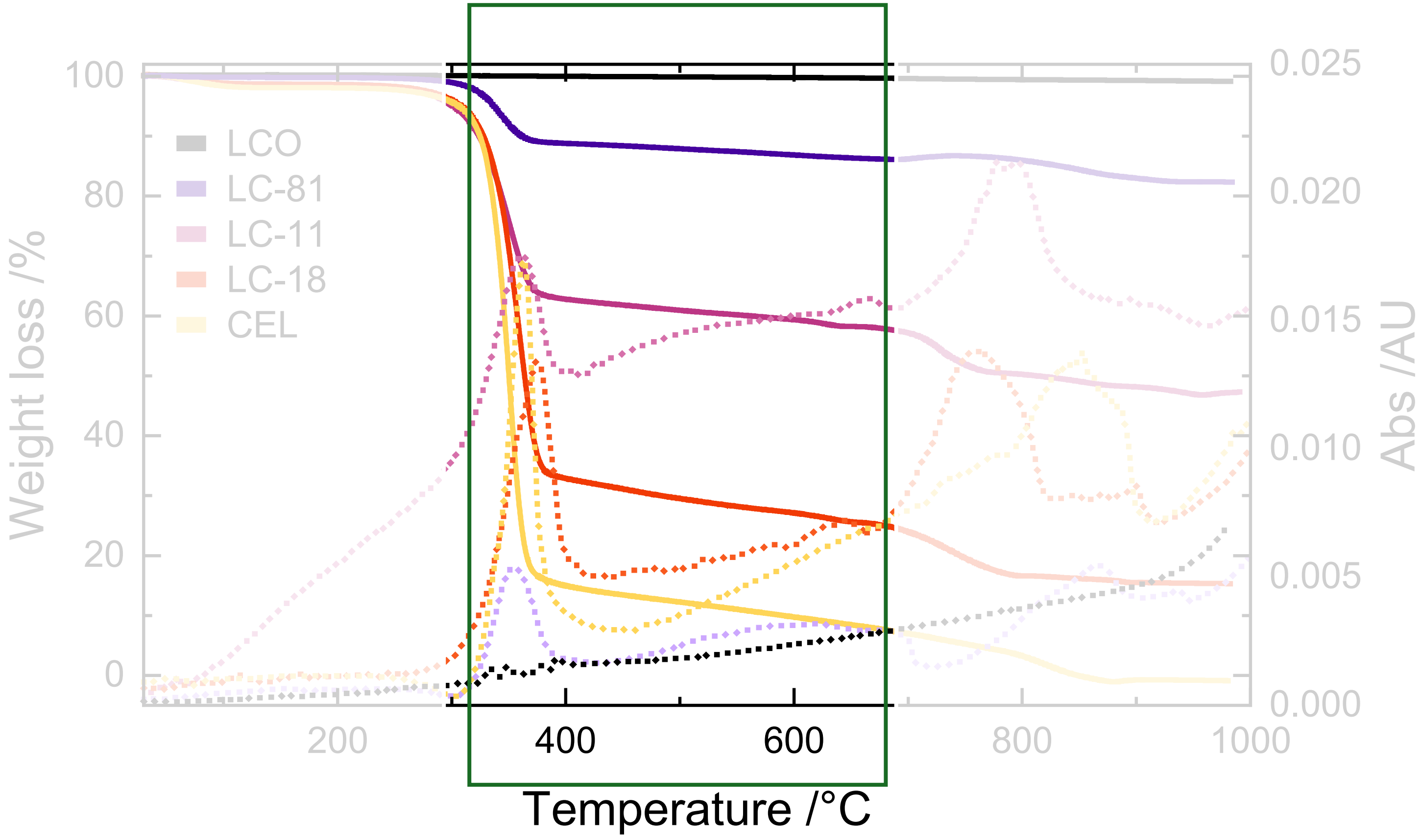
Parameters explored:
- ✓ $LiCoO_2$-to-cellulose weight ratio
- ✓ Temperature
- ✓ Holding time

Carbothermic Reduction Protocol
$LiCoO_2$:Cellulose (1:8 – 8:1 w:w)
T range: 200 °- 800 °C
Isotherm time: 30 min – 24 hours
N_2 flux



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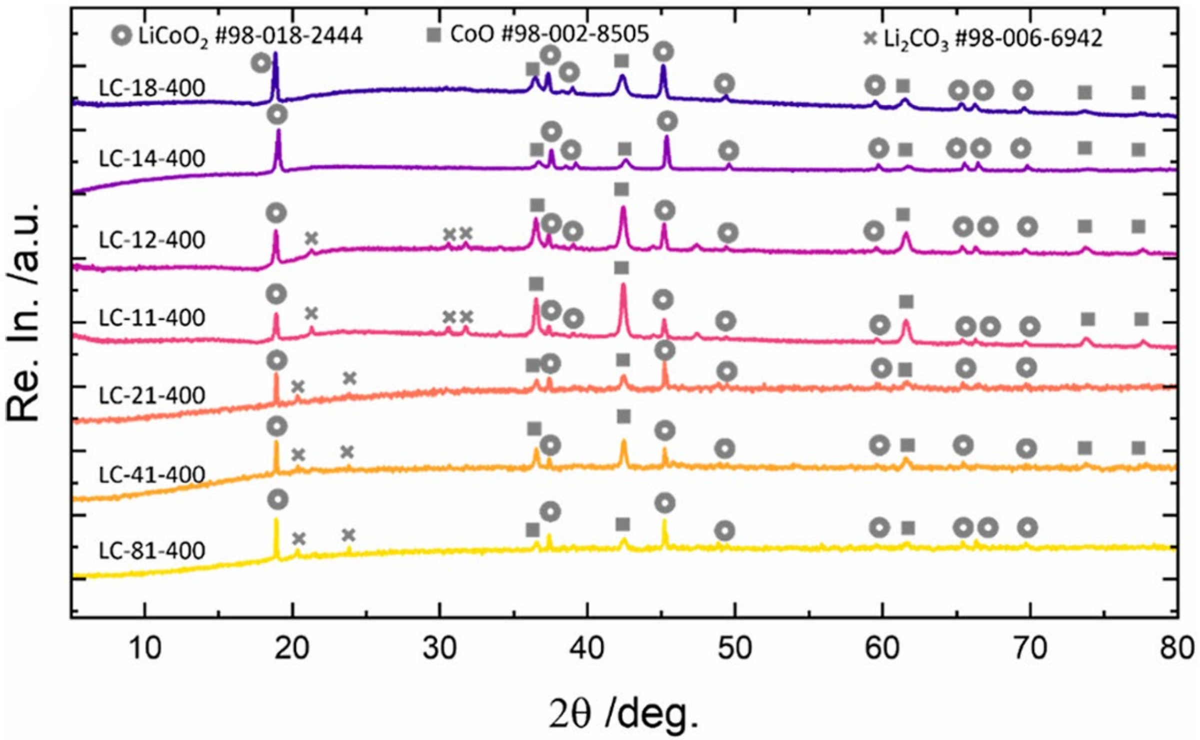
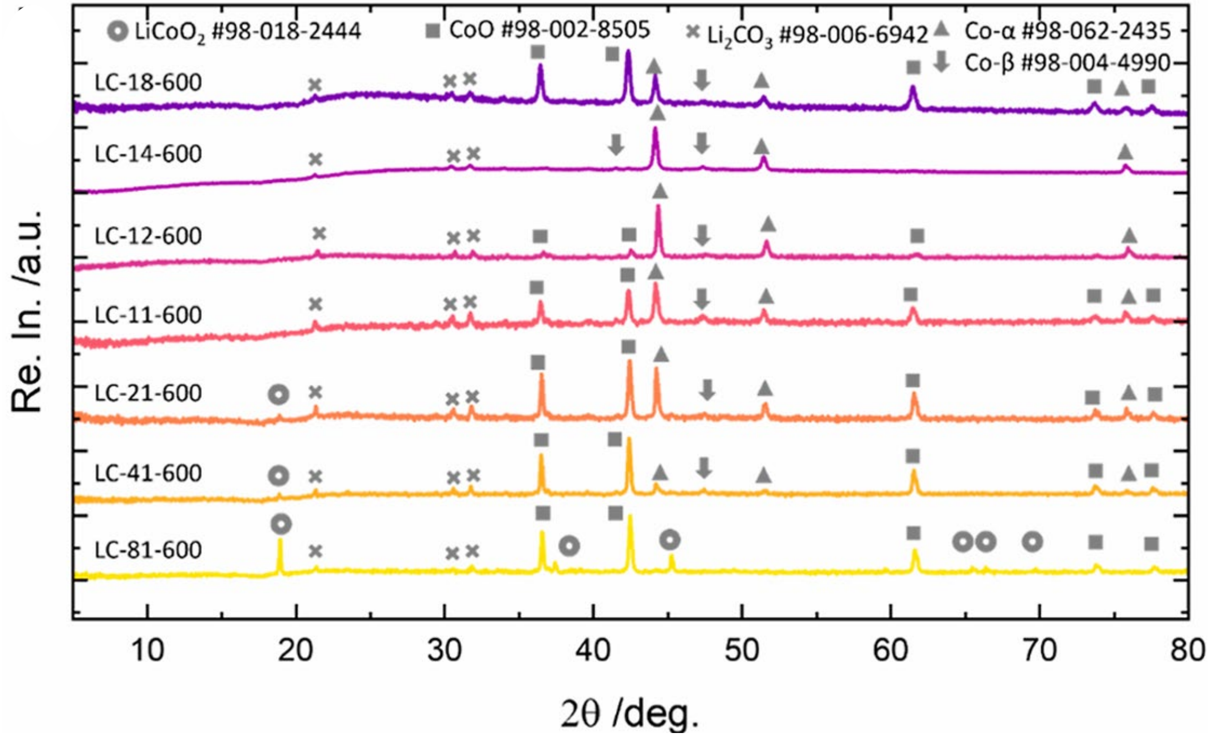
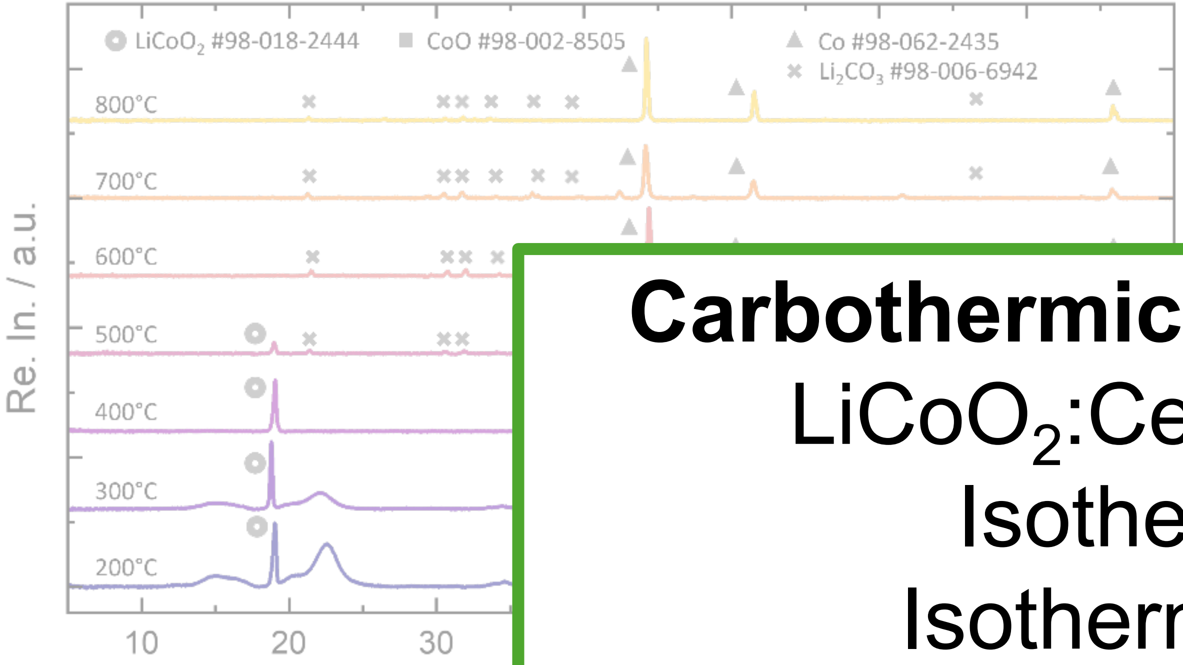


LiCoO$_2$:cellulose (XY), 1 hour holding time
- ✓ 400°C is not sufficient to completely reduce LCO



LiCoO$_2$:cellulose (XY), 1 hour holding time
- ✓ Variable CoO/Co ratio, tunable with starting XY composition → 1:4 only Co

Identification of the experimental parameters



LiCoO$_2$:cellulose (1:4), 1 hour holding time

- ✓ 600°C as the lowest T to have only one compound of Co

Carbothermic Reduction Protocol

LiCoO$_2$:Cellulose (1:4 w:w)

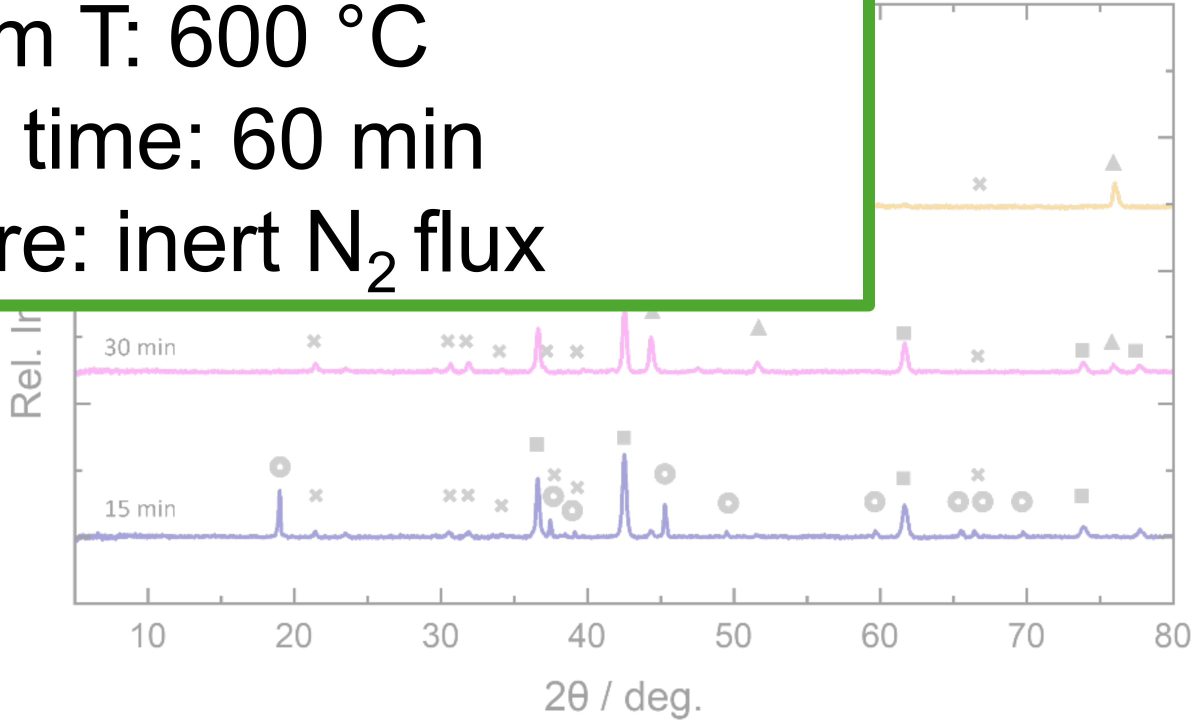
Isotherm T: 600 °C

Isotherm time: 60 min

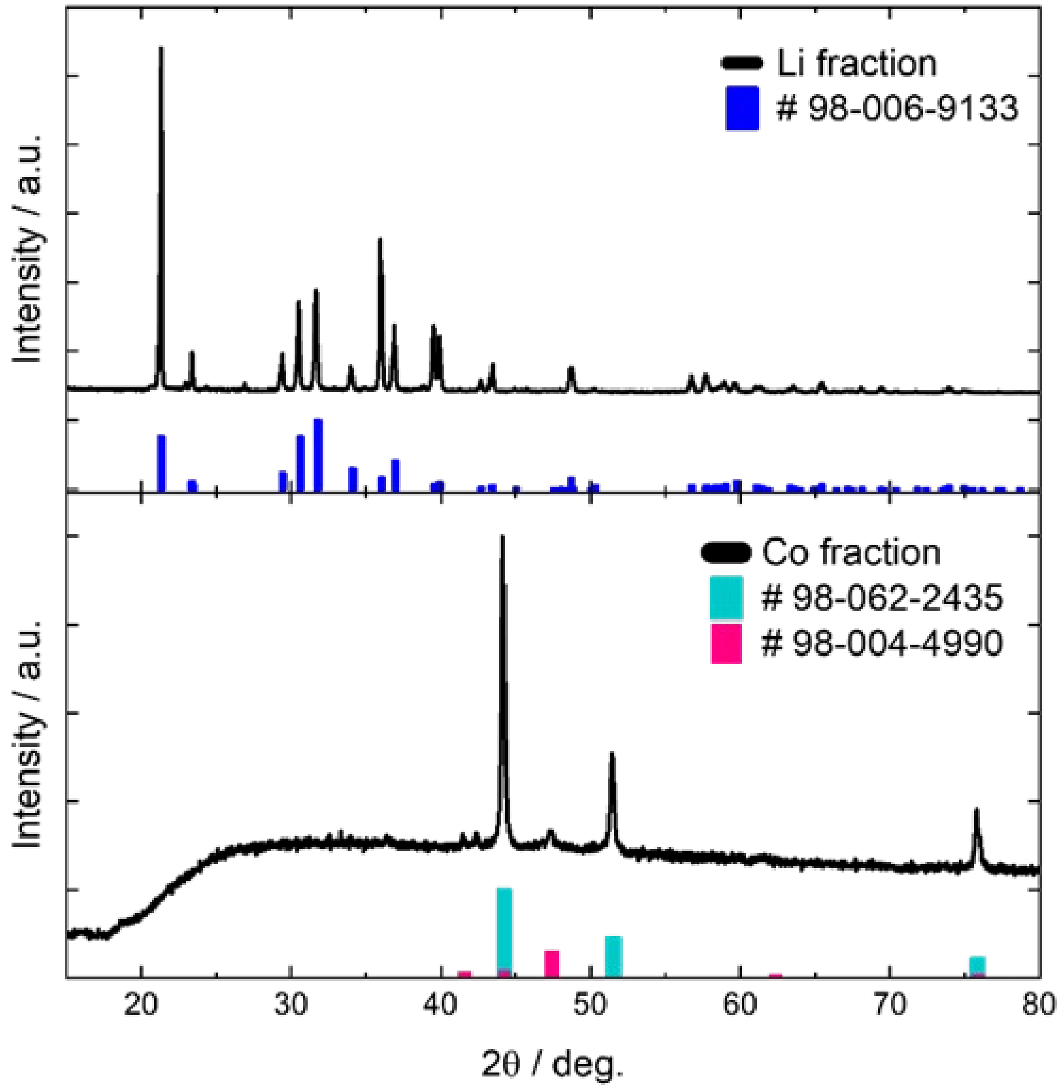
Atmosphere: inert N$_2$ flux

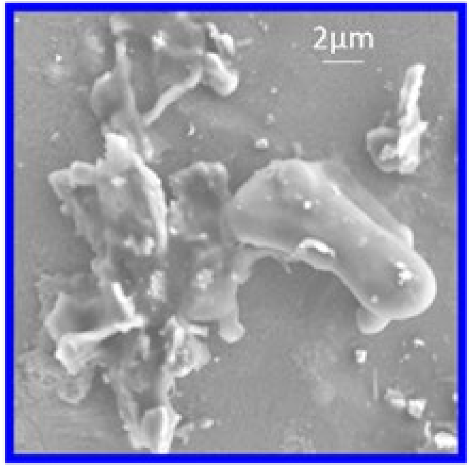
LiCoO$_2$:cellulose (1:4), 600°C

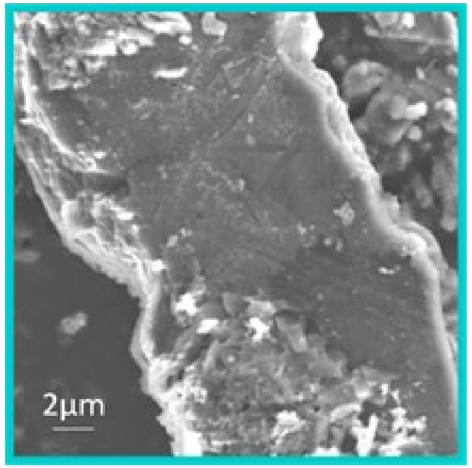
- ✓ 60 min as the lowest holding time to have only one compound of Co



Recovery of Co and Li



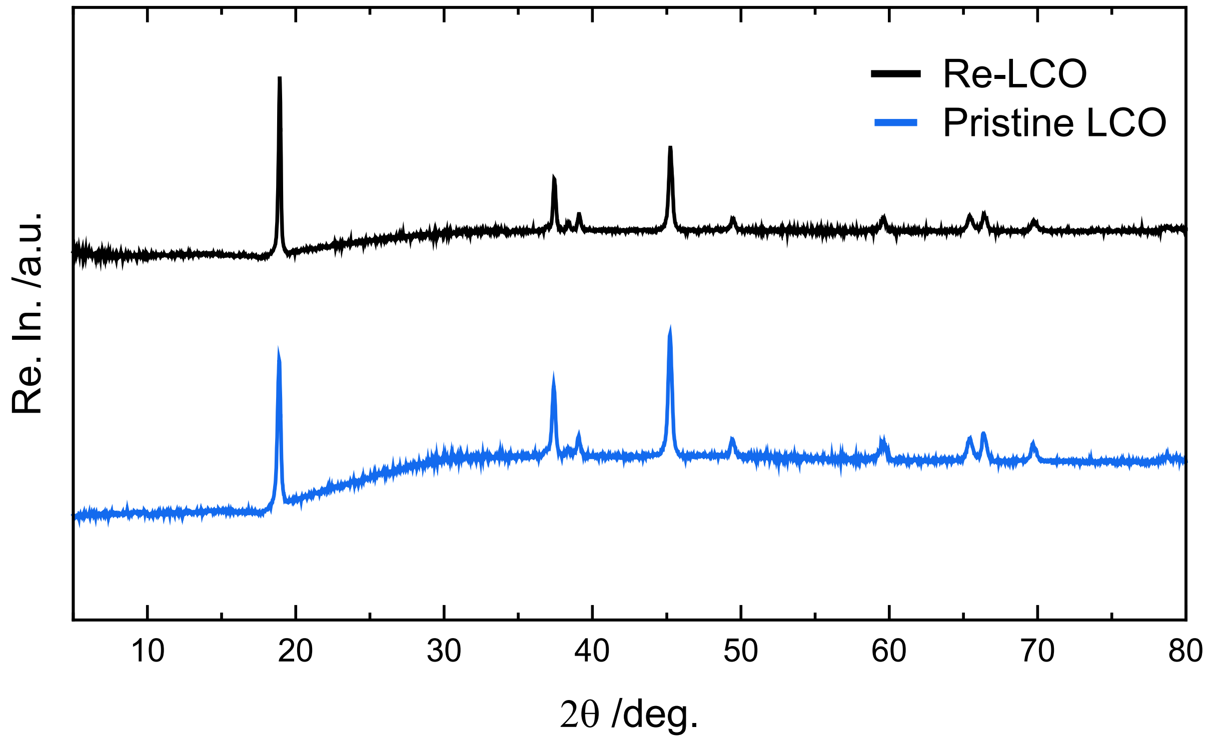


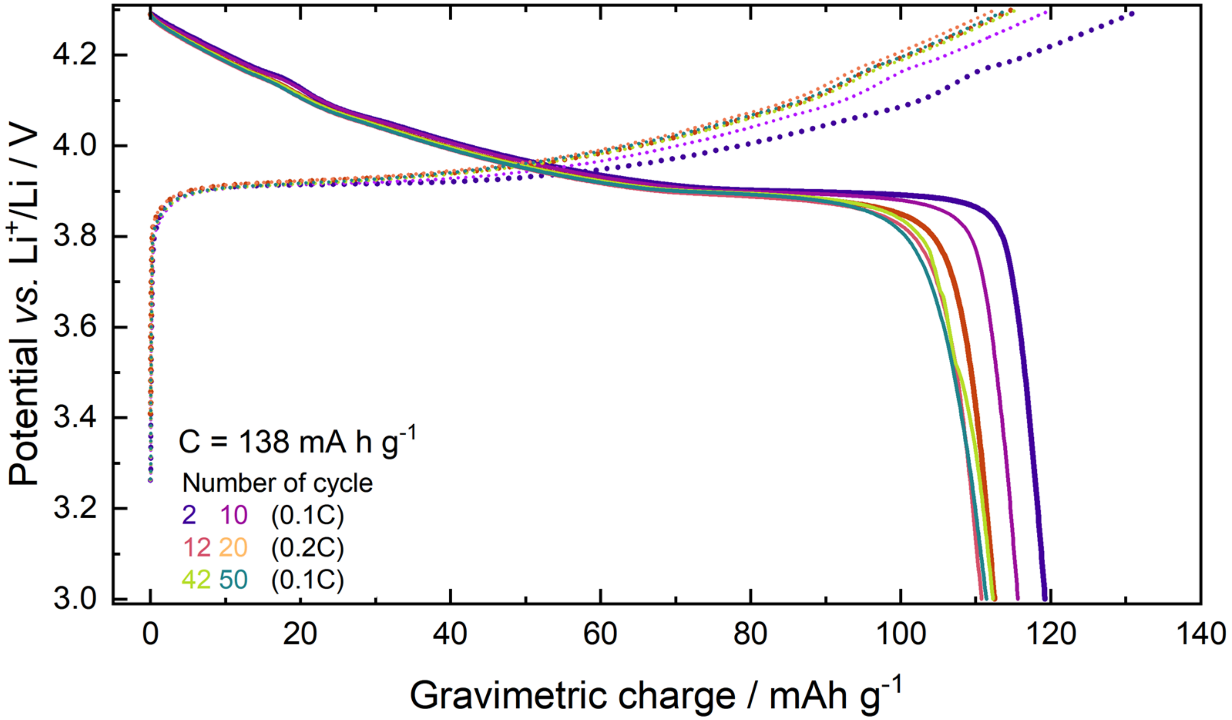


- ✓ Mixture of Co/CoO and Li_2CO_3 separable with water leaching
- ✓ Recovery of CoO and Li_2CO_3 (yields > 70%, purity >95%, cross-contamination <1%)

Proof of concept: LCO resynthesis

✓ Proof of concept of the closed-loop recycling scheme





Resynthesis conditions 800°C, 60 min
Reagents molar ratio Co:Li = 1:1.1

Next steps

1 Study a carbothermic reduction system with effective biowaste materials (potato peels, 40% cellulose), exploring different parameters: mass ratio, temperature, time of isotherm

2 Expansion of the study to other CRMs-rich cathodes e.g. NMC type

3 In-situ diffraction study in temperature control of the process in order to track the process (November 2024)

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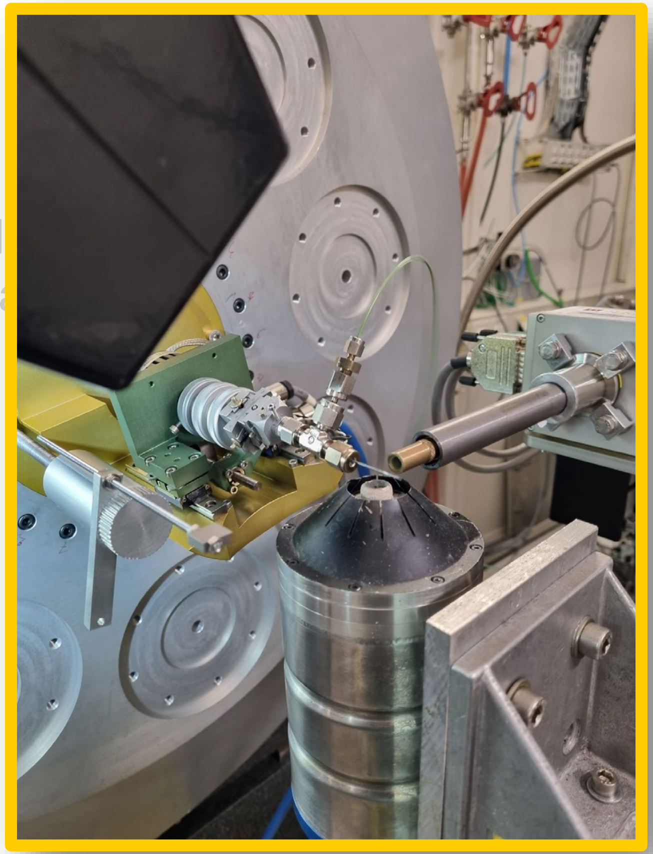

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Published as part of Energy & Fuels special issue "2024 Energy and Fuels Rising Stars".

Eleonora Carena, Dario Brambilla, Matteo Vergani, Riccardo Morina, Nicolò Pianta, and Chiara Ferrara*

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Thank you!

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