Funded by the Horizon 2020 Framework Programme of the European Union

Grant Agreement N°814389

SPIDER Deliverable D8.4

SPIDER workshop

WP	**8**	**Project and IP Management, Dissemination and Communication activities**
Task	8.4	Dissemination and Communication

Dissemination level[1]	PU
Nature[2]	R

Due delivery date	30/04/22
Actual delivery date	04/05/22

Lead beneficiary	CRF
Contributing beneficiaries	CRF, CEA

Document Version	Date	Author	Comments[3]
V0	20.04.22	Mattia Giuliano, CRF	Initial draft
V1	04.05.22	Mylène Pelloux-Prayer & Cédric Haon, CEA	Update & Final review

[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** =Other

[3] Creation, modification, final version for evaluation, revised version following evaluation, final

Deliverable abstract

SPIDER aims at the development and evaluation of a novel chemistry for next generation lithium-ion batteries; namely the use of LTS as cathode, a Si/C composite as anode and a chemically compatible and efficient electrolyte. The main advantage of such novel cells is the very high energy density that can be achieved (up to ~ 400 Wh/kg). The main application area is BEV (Battery Electric Vehicles) and SPIDER envisages further use of the same battery cells for stationary second life applications.

Within the objectives of WP8 there are the following ones:

- To ensure helpful leadership via strategic project coordination as well project management, follow-up, problem-solving and reporting.
- To set-up and implement procedures for data and IP management.
- To increase impacts via dissemination and communication.

The Task 8.4 "Dissemination and Communication" has been designed to help in reaching previous objectives, managing all the communication activities performed to share the results obtained during the project.

Deliverable Review

	Reviewer #1: WP Leader		
	Answer	Comments	Type*
1. Is the deliverable in accordance with			
(i) The Description of actions?	☒ Yes ☐ No		☐ M ☐ m ☐ a
2. Is the quality of the deliverable in a status			
(i) That allows it to be sent to European Commission?	☒ Yes ☐ No		☐ M ☐ m ☐ a
(ii) That needs improvement of the writing by the originator of the deliverable?	☐ Yes ☒ No		☐ M ☐ m ☐ a
(iii) That needs further work by the Partners responsible for the deliverable?	☐ Yes ☒ No		☐ M ☐ m ☐ a

* Type of comments: M = Major comment; m = minor comment; a = advice

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1. Introduction

SPIDER aims at the development and evaluation of a novel chemistry for next generation lithium-ion batteries; namely the use of LTS as cathode, a Si/C composite as anode and a chemically compatible and efficient electrolyte. The main advantage of such novel cells is the very high energy density that can be achieved (up to 400 Wh/kg). The main application area is BEV (Battery Electric Vehicles) and SPIDER envisages further use of the same battery cells for stationary second life applications.

The main purpose of this document is to summarize the contents of the workshop organized by CRF in April. In particular, this document:

- Summarize the topic and the content of the presentations performed during the workshop;
- Give a general overview of the general outcome of the conference.

2. Workshop Organization

The Spider workshop was held on-line on April 14th. The registration format was shared through the project website and it collect 46 answers (Table 1):

Name	Organization
Haon Cedric	CEA
Susan Sananes Israel	CIDETEC
Iratxe de Meatza	CIDETEC Energy Storage
Elie Paillard	Politecnico di Milano
Karun Kamaleshdatta Mishra	Resil Chemicals Pvt Ltd
Isaac	Ole! Lighting by FM Iluminación S.L.U.
Shijil Anamkunnath Nediyirakkal	LTU
TAPABRATA DAM	IIT Kharagpur
HASAN ALI	National Centre for Physics Islamabad Pakistan
Herlin Nathalie	CEA
Matteo Dotoli	CRF
Arianna Tiozzo	CRF
Giovanna NICOL	CRF
Saravanan Karuppiah	Uppsala University
Giovanna NICOL	CRF
Vasiliki Zacharopoulou	CERTH
Riccardo Taormina	Politecnico di Milano
Giovanna NICOL	CRF
Debashis Tripathy	Indian Institute of Science
Omokafe Seun Michael	Federal University of Technology Akure
Alice Bouchez	CEA
Jouve Juliette	CEA
Randrema	CEA
LIOTARD Cindy	CEA
Mayousse	CEA

GAUTHIER Esteban	CEA
Lavisse	CEA
JF BLACHOT	CEA
Dimitrios Zarvalis	CERTH
Linda Ager-Wick Ellingsen	Transportøkonomisk institutt
Víctor Román	CIDETEC
PATOUX Sébastien	CEA
Lorenzo Usai	NTNU
Iratxe de Meatza	CIDETEC Energy Storage
Balasubramaniyan Rajagopalan	FZJ
Emmanouil Daskalos	CERTH/CPERI
Neethi Rajagopalan	VITO
Odile Capron	VITO/EnergyVille
Zhangqi Wang	Accurec-Recycling GmbH
Isaac Sananes	FM Iluminación S.L.U.
Víctor Román	CIDETEC
Almut Schwenke	SGL Carbon
Peter Bleith	SGL
Benedikt Stumper	Technical University of Munich
JF BLACHOT	CEA
Benedikt Stumper	Technical University of Munich

Table 1: Workshop participant list

3. Presentations

The presentations performed cover a wide window of topics in the frame of the new prospective in the batteries field:

- **"Spider Project short presentation" –** *Cedric Haon (CEA):* General presentation of the Spider project features and excellences.
- **"Influence of the ambient storage on NMC811-based Li-ion cathode performance and overview of CIDETEC pilot line facilities" -** *Susana Sananes (CIDETEC*): after a brief introduction of the CIDETEC capability in terms of manufacturing and cells production, the presentation was focused on the evaluation of the storage effects on NMC 811 material. These phenomena were evaluated comparing the results obtained on an electrode prepared using a NMC powder stored for 1 year in ambient air with an electrode prepared with a fresh active material and aged in the same conditions. The results highlight worst performance in terms of electrochemical performance for the aged electrode compared with the performance showed by the electrode prepared with the aged powder. This behaviour could be link to the formation of carbonate layer on the NMC aged powder and to the formation of higher Ni^{2+} fractions due to cation mixing phenomena, which are decreased to the electrode manufacturing processes.
- **"How to limit cobalt in cathode materials"** – *David Peralta (CEA):* The presentation is focused on the increase of the performances of the cathodic active material. The achievement of this goal could be reached following many approaches, for example by improving the morphology features of the active material particles, in order to increase specific capacity and the cycle life. Another important point is the decrease the content of

critical raw elements, in particular Co. Different Co-free materials have been developed, as Li-rich layered oxides, which show good performance in terms of capacity and energy but are affected by voltage decay. Another material developed is the 5V spinel, which shows good performances and improved cycle life if coating layer is applied. One of the last application developed in this field is based on the synthesis of sulphur-selenium solid-solutions prepared with disordered rocksalt structure. This material shows a promising specific capacity, but a low cycle life and its development is under progress. The last approach tested to reduce the Co impact on the cathodic material is linked to the recycling of this critical element. In particular a recovery method based on the formation of Co-MOF (metallic organic framework) is applied in spent Li-ion battery leaching solution to extract this element, obtaining promising results.

- **"Current status and future prospects of the LCAs of Li-ion batteries"** - *Lorenzo Usai (NTNU)*: Overview on LCA application to Li-ion battery field. Different approaches are applied, based on data coming from different sources. This leads to a high uncertainty and variability in the results obtained within the same chemistry, due to a lack of primary data for manufacturing phase of battery cells and the quick evolution of LIBs technologies. To Overcome this issues, NTNU is working on a new cradle-to-gate model, based on explicit value chain and process based models. The variability of the raw material value chain represents an issue linked to the regional and technological features of the production processes. The use of parametrized models can help reducing uncertainties, but primary data would be needed for validation. CO_2 is only one issue, materials demand and production/recycling require planning.
- **"Fundamentals of physics-based modelling and its application to batteries" -** *Odile Capron (VITO)*: General overview on the application of the physics-based modelling on Li-ion batteries field. Mathematical tools translating electrochemical behaviour of batteries by means of set of partial differential equations and have the capability for integration as embedded models within Battery Management Systems. This models could enable the predictions of many phenomena as: the battery behaviour by means of cell design optimisation, its State of Charge, the temperature during the operation and the degradation mechanisms leading to ageing of battery cells. For the ageing modelling large experimental ageing dataset is a priori needed.
- **Stellantis plan for vehicle electrification –** *Daniele Pullini (CRF)*: The future steps announced by Stellantis management for the electrification of the automotive field. The strategic plan of the company targeting to have 100% of sales in Europe and 50% of sales in the United States to be BEVs by the end of this decade. Stellantis has also committed to becoming "the industry champion in the fight against climate change", reaching carbon net zero emissions by 2038. The main bottle necks for the wide diffusion of this technology are linked to the availability of materials (as Li, Co, graphite, other critical raw materials), production costs, the sustainability (e.g. removal of NMP based processes), current performances, the diffusion of the charging infrastructure, the carbon footprint of electric energy production and the customer acceptance. In this framework, main advantages of the Spider cell concept is linked to the potential increase of cell performances with respect to current Li-ion cells in terms of energy and power densities and in terms of cycle life, avoid the use of critical raw material (Co) in cathode material manufacturing for SSB applications and the sustainability of the process (water based, NMP-free). About the possible models for future production of Spider cells the first option could be that Stellatins/ACC could take care of the industrialization of the process obtaining a license by the Spider partners holding the IPR. The second possible option, Stellatins/CRF could support Spider partners in a follow-up project, in order to increase the TRL of the technologies developed, closing the gap with the possible industrialization of the processes.

4. Conclusion

The workshop was organized and held involving many people and entities, coming from Spider consortium and outside from this. The presentations performed cover a wide range of topics, related to the activities performed inside the project and to the future prospective for the battery application, not only in terms of materials, but also for LCA and modelling applications. A link with current vision on the next challenges from the automotive industry point of view was presented, giving an insight of the needs of one of the main driving force in this field.

5. Appendix : Workshop presentations

SPIDER Workshop

Safe and Prelithiated hIgh energy DEnsity batteries based on sulphur Rocksalt and silicon chemistries (SPIDER)

Online Workshop, 14/04/2022

This project has received funding from the European Union's Horizon 2020 research and innovation programm under grant agreement No 814389

Project Overview

<u>SPIDER:</u> **S**afe and **P**relithiated h**I**gh energy **DE**nsity batteries based on sulphur **R**ocksalt and silicon chemistries

LC-NMBP-30-2018 - Materials for future highly performant electrified vehicle batteries (RIA)

START DATE	01/01/2019	**END DATE**	31/08/2022
TOTAL BUDGET (M€)	7,975	**EU FINANCIAL CONTRIBUTION (M€)**	7,975
PROJECT COORDINATOR	**Commissariat à l'Energie Atomique et aux Energies Alternatives -** cedric.haon@cea.fr		
WEBSITE	www.project-spider.eu		

Project Overview: Objectives

SPIDER specific objectives:

- SO1 – Increase cell energy density by 65% vs. State of the Art with non-critical, sustainable materials
- SO2 – Reach power density at 800W/kg
- SO3 – Reach 50% cost reduction for batteries by 2022
- SO4 – Cycle life increase to 2000 cycles by 2022
- SO5 – Increase cell safety by increasing thermal runaway temperature above 200°C and limiting the thermal energy dissipation to 4 kW/kg
- SO6 – Develop a circular value chain for sustainable, recyclable (60wt%) batteries in Europe

Project Overview: Concept

A multidisciplinary approach to develop safe and long lifetime, high energy density cells:

HIGH CAPACITY MATERIALS: LTS Cathode

- Optimization of the synthesis parameters to obtain a material with a capacity higher than 400 mAh/g
- Tuning the material composition to increase the average potential of the material
- Active materials will be optimized and processed at kg batch scale

HIGH CAPACITY MATERIALS: Silicon - Carbon composites anode

- Development and preparation Si-C composite-based anode materials with a target capacity of 1000 - 1500 mAh/g
- Preparative work and development partly on large lab scale in order to investigate processing aspects as well, i.e. in the range of up to 3-5 kg

PRELITHIATION:

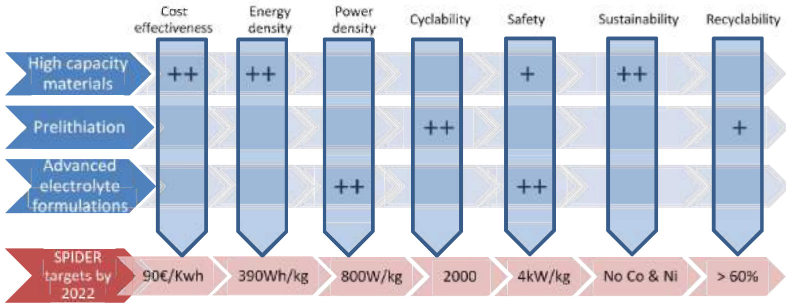
- Implementation of selected prelithiation process at cell level compatible with industrial requirements

ADVANCED ELECTROLYTE FORMULATIONS:

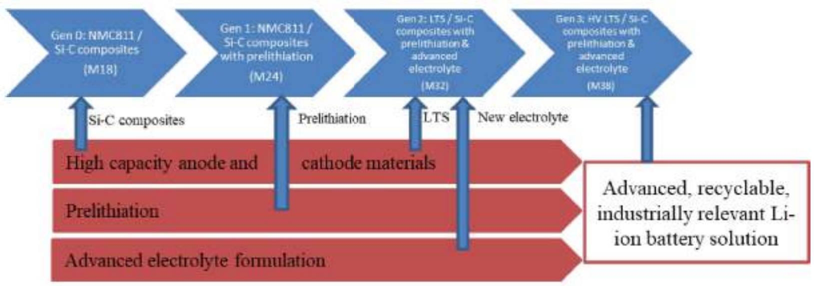
- Development and optimization of safe electrolyte for HV LTS / Si – C composite chemistry

Project Overview: Concept

A multidisciplinary approach to develop safe and long lifetime, high energy density cells:



4 cell generations to implement successively the developments:

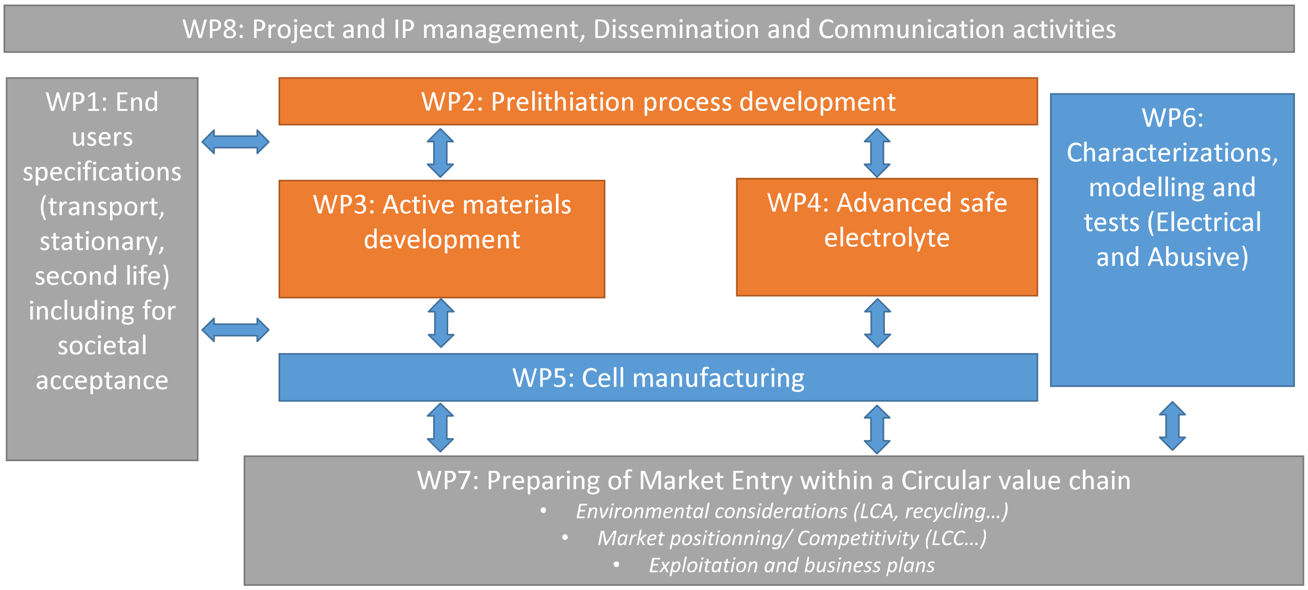


Project Overview: Targeted performances

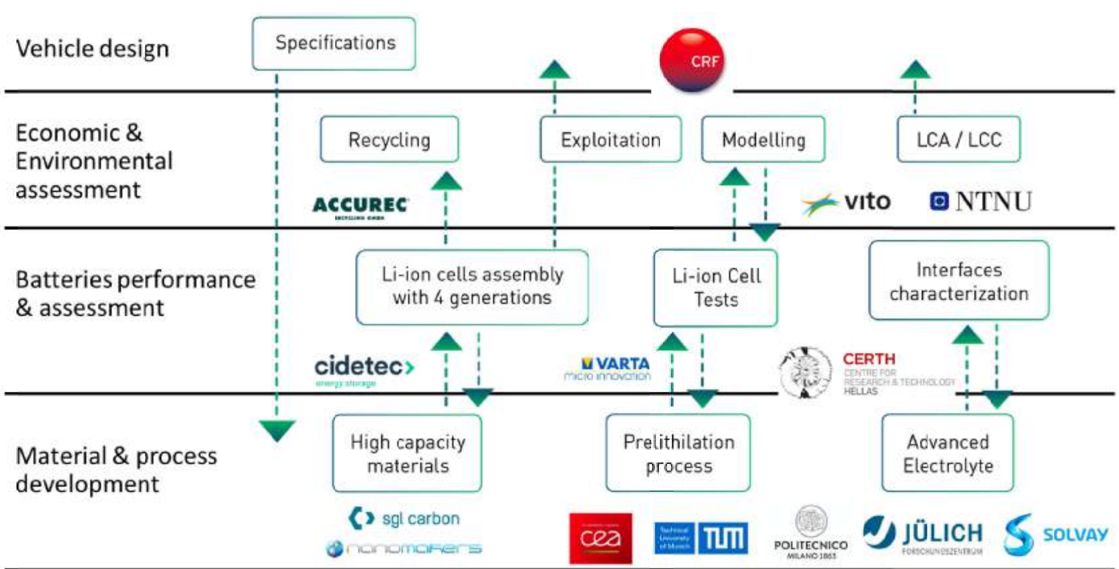
Key Performance Indicator at cell level	Baseline (NMC622/Graphite)	SPIDER technology	
		2022	2030
Energy density (Wh/kg)	240	390	450
Power density (W/kg)	700	800	800
Durability (number of cycles)	500 – 1000	Up to 2000	Up to 5000
Cost (€/KWh)	180	90	75
Safety (Thermal energy dissipation (kW/kg)	20	4	4
Recyclability (recycling efficiency in %)	55	60	60
Sustainability (dependence on Critical Raw Materials)	Cobalt, Nickel	Absence of Cobalt and Nickel	Absence of Cobalt and Nickel

Project Overview: Organization

The project is organized in 8 work packages:



Project Overview: Consortium – 14 partners



cidetec energy storage

VARTA
VARTA Innovation GmbH

CERTH
CENTRE FOR RESEARCH & TECHNOLOGY HELLAS

vito

This project has received funding from the European Union's Horizon 2020 research and innovation programm under grant agreement No 814389

SPIDER

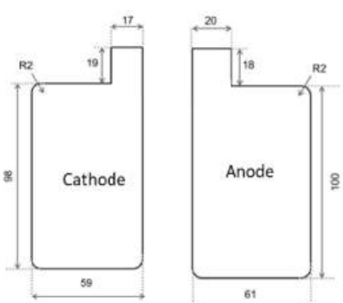
Cell Manufacturing and Electrical tests

Performances evaluation: Gen0 cells preparation

SPIDER

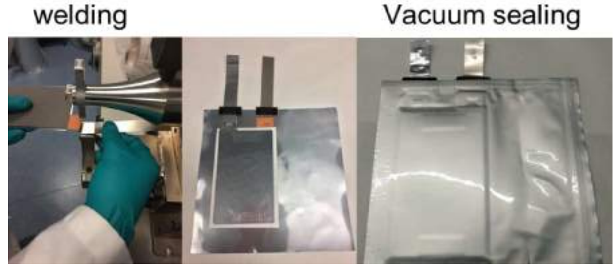
Cathode: NMC811/CB/PVDF (95/2/3) LL=4.0mAh/cm^2
Anode: Si – carbon /CB/Binder(CMC+SBR) (94/1/5) LL=4.2mAh/cm^2
Electrolyte: 1M $LiPF_6$ in carbonate mix + additives

Electrode dimensions



Pouch cell assembly

Ultrasonic welding | Stacking | Electrolyte filling Vacuum sealing

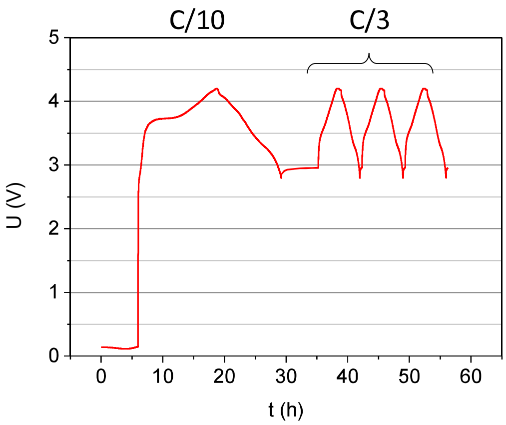


Gen0 cells delivery (07.2020)

- 68 single layer pouch cells for electrochemical characterization & modelling activities [200 mAh]
- 10 stacked pouch cells for abuse test [>500mAh]

Performances: Electrochemical characterization

Single layer pouch cells
Cathode: NMC811/CB/PVDF (95/2/3) LL=4.0mAh/cm^2
Anode: Si – carbon /CB/Binder(CMC+SBR) (94/1/5) LL=4.2mAh/cm^2
Electrolyte: 1M $LiPF_6$ in carbonate mix + additives



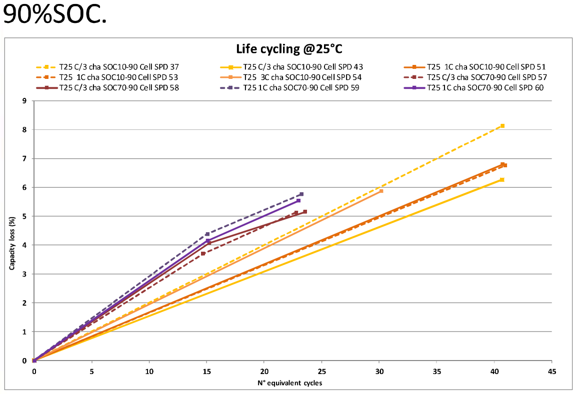
Gen0 cells	
Pouch cell geometry	
Dimensions LxWxT	145 mm x 95 mm x 1.2 mm
Weight	~14 g
Electrical data	
Nominal capacity	**0.2 ± 0.005 Ah (C/10, 25ºC)**
Nominal energy	**0.7 Wh**
Nominal voltage	**3.5 V**
Electrochemical performances (25ºC)	
Cycle life	**80 cycles (>80%SOH, C/3)** **120 cycles (>70%SOH, C/3)**
Energy density	**440-480 Wh/kg$_{electrode}$** **71 Wh/kg$_{total\ cell}$**
Voltage range	**2.8-4.2 V**
Charge	**CCCV, max current 0.6A (3C)**
Discharge	**CC, max current 0.2A (1C)**
Storage and transport	
Storage Temperature	**25 ºC**
Resistance @30%SOC	**103±9 mΩ @ 1kHz**

Energy density improved by 20% for Gen0 (NMC811/Si-Gr) vs SoA (NMC662/Gr)

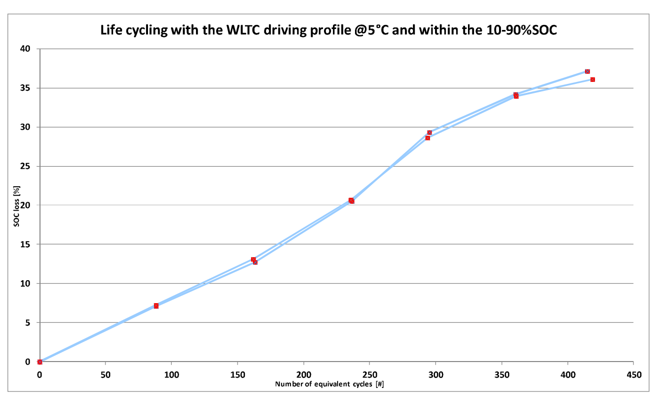
Performances: Electrochemical characterization

Assessment of the Gen 0 cell lifetime performances at different uses and environmental conditions

The cells were aged at three different temperatures (5; 25 and 45°C) and within two different voltage windows corresponding to 10-90%SOC and 70-90%SOC.



Cells were also aged using a real driving profile within the same cycling window and at two different temperatures.



250 equivalent cycles until the cells reached 80%SOH @5°C

Technical University of Munich

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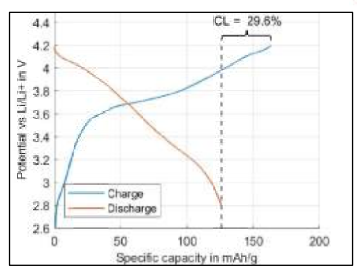
Prelithiation

Prelithiation: overview and necessity

Challenges in battery cycling

- SEI formation at the anode accounts for an initial capacity loss (ICL) of up to 30%*.
- During cell operation, the lithium in the cell is irreversibly consumed and the reversible capacity is reduced.
- As a consequence, cycle life is reduced and the battery needs premature replacement, which results in an elevated consumption of resources



First formation cycle of a NMC811 vs Si-C CR2032 coin cell[1]

Solution approach: Prelithiation

- ➢ Introduction of additional lithium to compensate for lithium loss during formation and cycling
- ➢ Various prelithiation methods possible: direct contact prelithiation (mechanical), addition of sacrificial salt, use of Li metal power

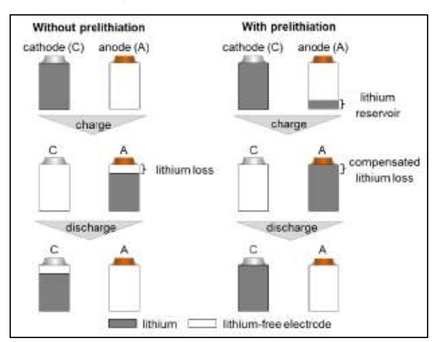


Illustration of the first charge and discharge cycle
a) Without prelithiation; b) With prelithiation [2]

[1] Based on results gathered by the Technical University of Munich within SPIDER Project
[2] Stumper et al. 2020

*depending on the material

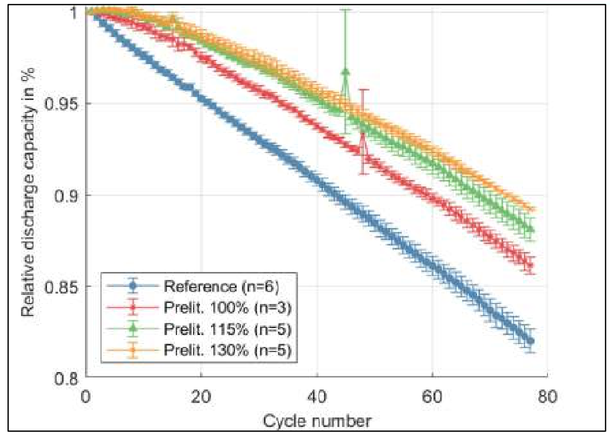
Extending the cycle life of lithium-ion batteries through prelithiation

Direct contact (mechanical) prelithiation:

- Lithium was successfully introduced to the cell
- A complete absorption of lithium within the electrolyte and electrodes was shown
- The ICL in full cells could be reduced by 15%
- The capacity retention after 80 cycles was increased by 5-7% (depending on lithium fraction)
- A gradation of the different quantities was observed

Conclusion:

➢ Prelithiation has the possibility to *reduce* the *ICL* and *increase the cycle life*.
Hence, the *battery life* can be *increased* and *resources* can be *saved*.



Capacity retention of prelithiated cells in relation to reference cells (NMC811 vs. Si-C)[1]
(n= number of cells used for mean value)

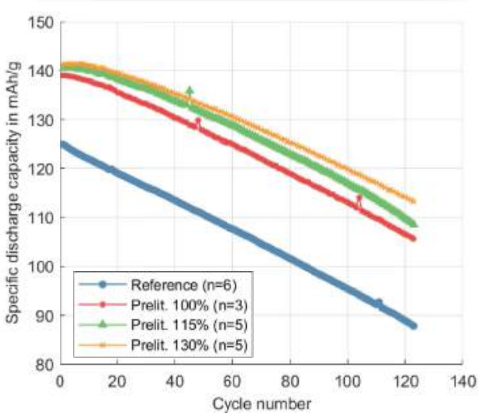
[1] *Based on results gathered by the Technical University of Munich within SPIDER Project*

	Reference	Prelit. 100%	Prelit. 115%	Prelit. 130%
Lithium fraction [%]	0	0,83	0,95	1,24
Mean ICL [%]	29,8	16,1	15,6	14,6
Std ICL [%]	0,82	0,16	0,06	0,14

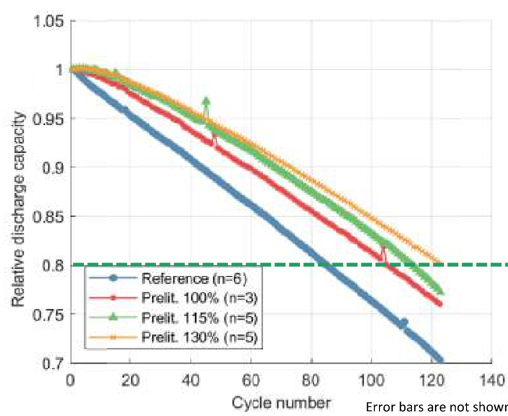
*ICL = Inital capacity loss

Increasing capacity and cycle life of lithium-ion batteries through prelithiation

Specific discharge capacity



Relative discharge capacity



Summary	Cycle life
Reference	83±4
Prelit. 100%	103±3
Prelit. 115%	112±6
Prelit. 130%	123±3

Error bars are not shown due to small error <5%.

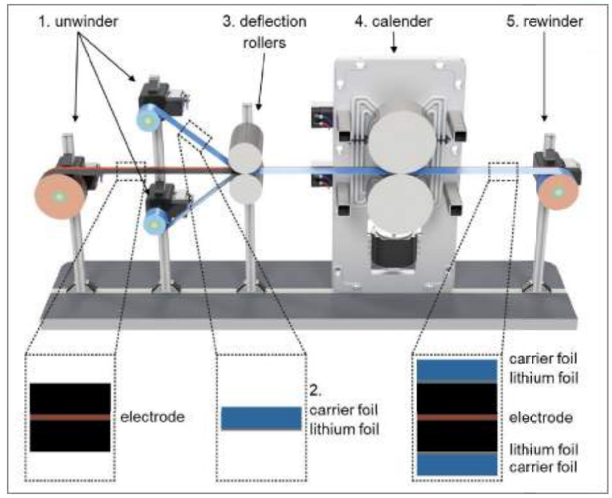
Specific discharge capacity (left) and relative discharge capacity (right) of prelithiated NMC811 vs. SiC coin cells[1]
(n= number of cells used for mean value)

Capacity retention is prolonged for prelithiated cells (higher lithium reservoir)

Conceptual process for direct contact prelithiation[2]

Possible implementation of direct contact prelithiation into lithium-ion battery production through a scalable roll-to-roll process[2]:

1. Simultaneous unwinding of the electrode and the lithium foil
2. Carrier foil for stabilization and better handling
3. Applying the lithium foil on the electrode via adjustable deflection rollers
4. Inline calendering of the lithium foil on the electrode ensuring adhesion
5. Rewinding of the electrode with applied lithium foil and carrier foil on the outside



Concept process for the roll-to-roll application of lithium foil on electrodes with selected sectional views [2]

[2] Stumper et al. 2020

Conclusion

This project has received funding from the European Union's Horizon 2020 research and innovation programm under grant agreement No 814389

Next steps

Assessment of performances improvement:

Cells	Gen1	Gen2	Gen3
Anode	Si/C 700 mAh/g	Si/C 1000 mAh/g	Si/C 700 mAh/g
Cathode	NMC 811 Organic formulation	NMC 83%Ni Organic formulation	NMC 83%Ni Organic formulation
Electrolyte	Carbonates mix + additives		
Prelithiation	Mechanical		

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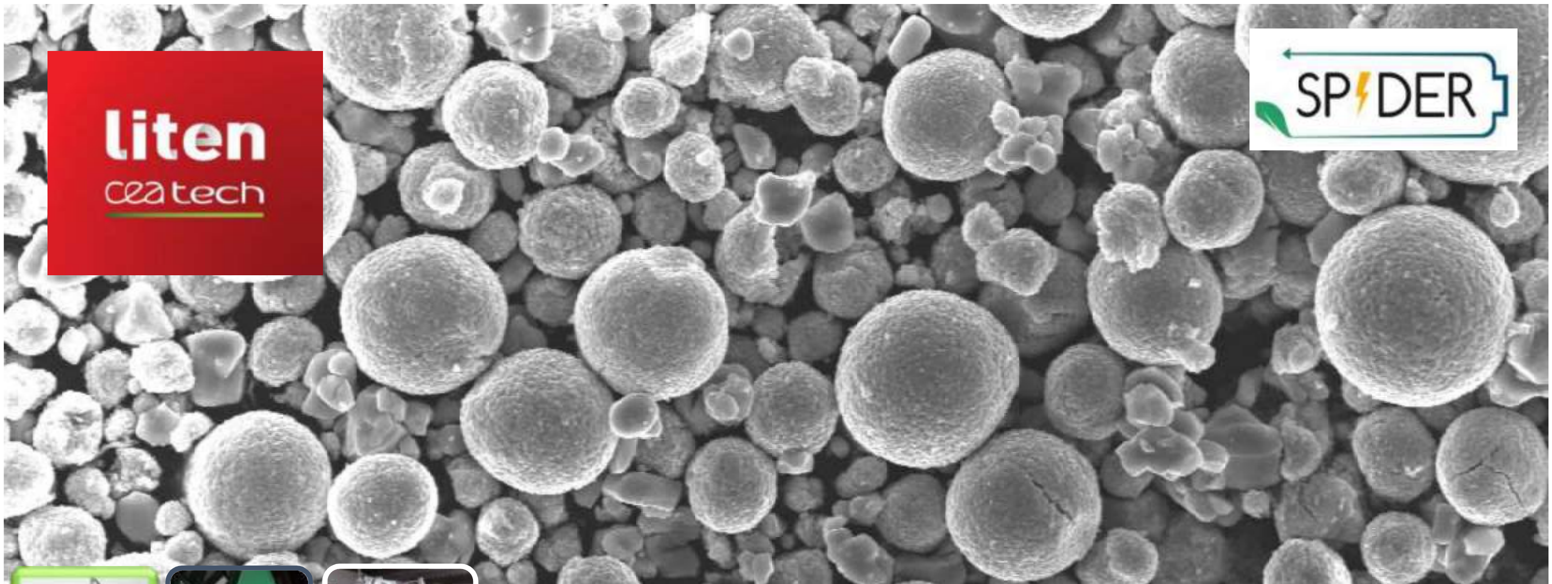


CEA strategy for reducing cobalt in cathode material

liten

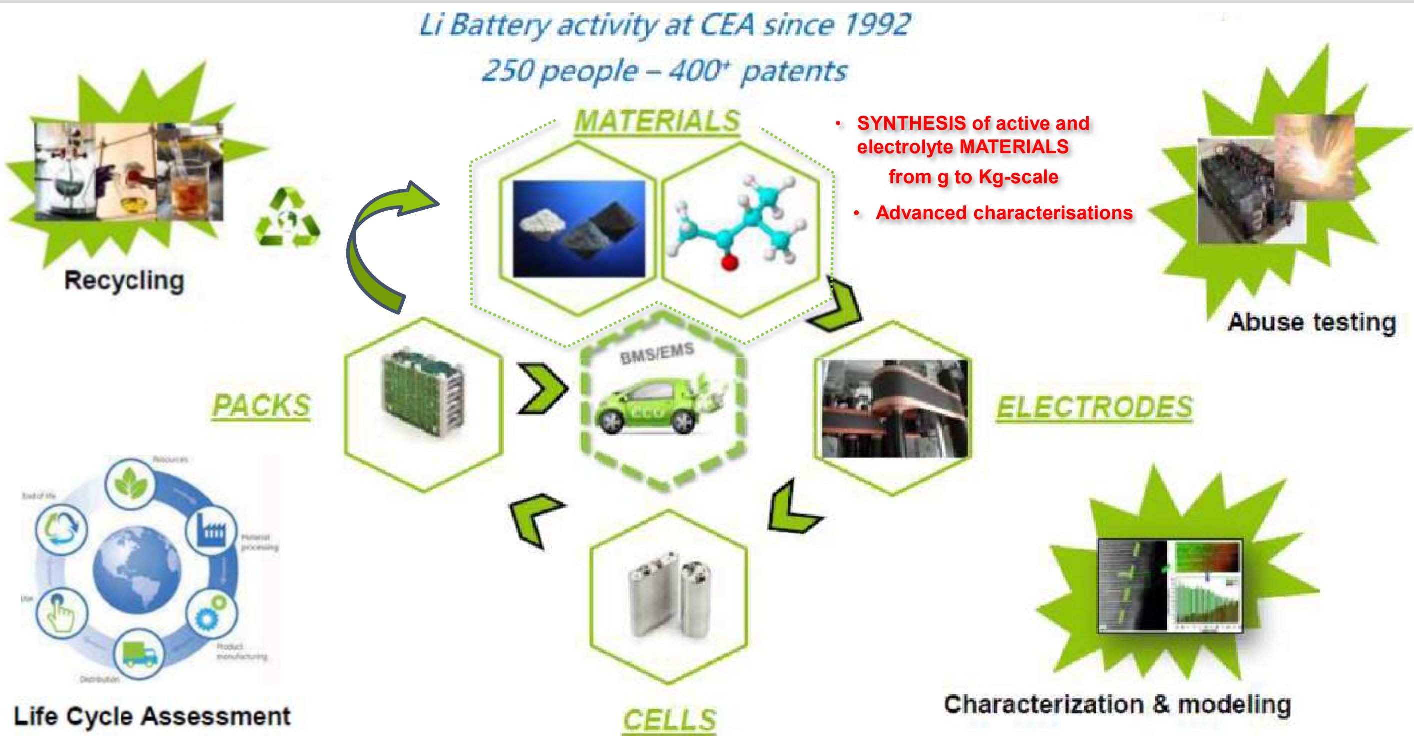
CEA - www.cea.fr

CONFIDENTIEL

Spider Workshop
14th of april 2022

cea

BATTERY DEPARTMENT



BATTERY MATERIALS LAB

50 people

23 permanent pos. (5HDR)
8 non permanent pos. (3 PDs)
15 PhDs
8 interns

Plateform

1 000 m² of chemistry lab
+ 200 m² dedicated to scale up
10 glove boxes

€ **30 projects**
5,5 M€/year

(2/3 industrial
1/3 institutional)

Objectives of the lab

Synthesis and characterization of new materials for electrodes and electrolytes of Li-ion and post Li-ion technologies

Performance improvement (energy density, cycling, safety…)

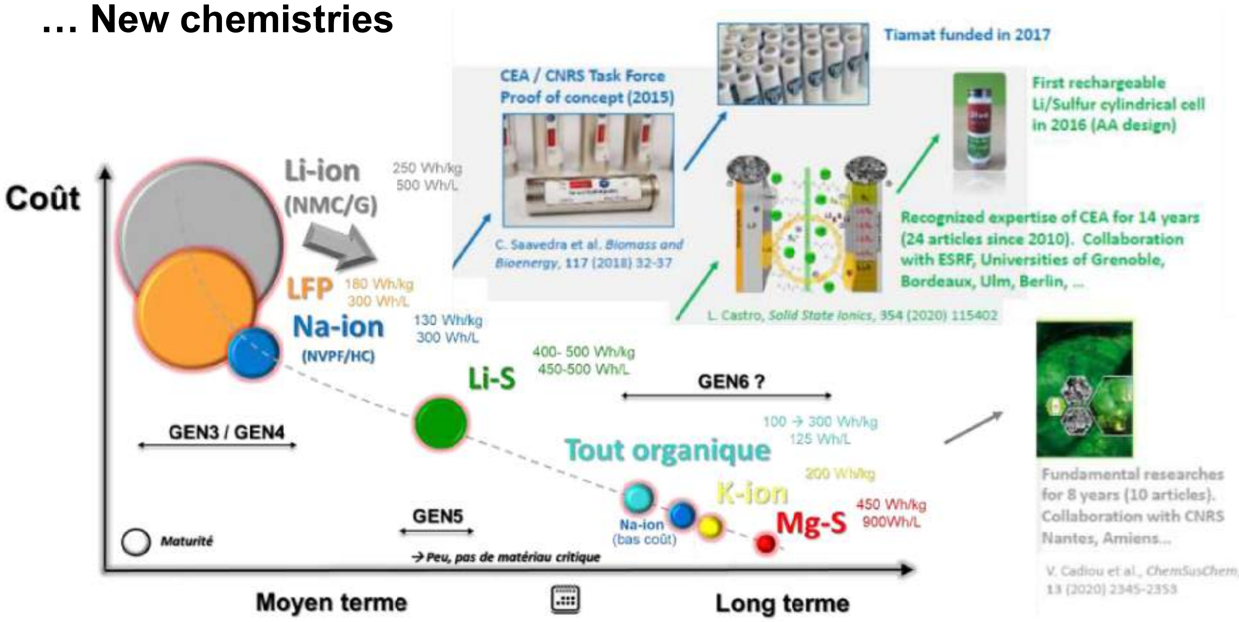
Enhancement of recycled materials (blackmass, metallic precursors…)

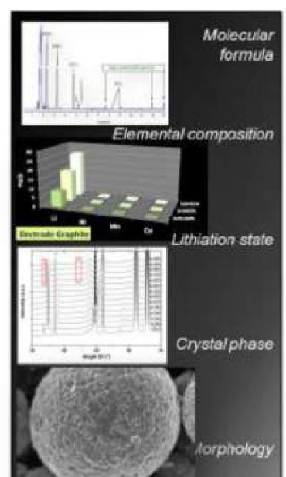
New low cost and low environmental impact chemistries

All solid state Na-ion, Li-S, organic batteries, K-ion

MATERIALS LAB

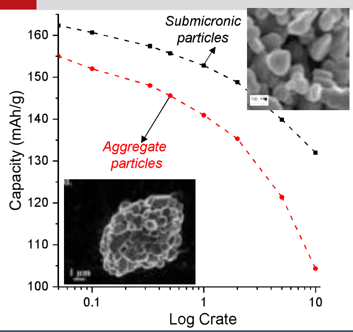
… New chemistries



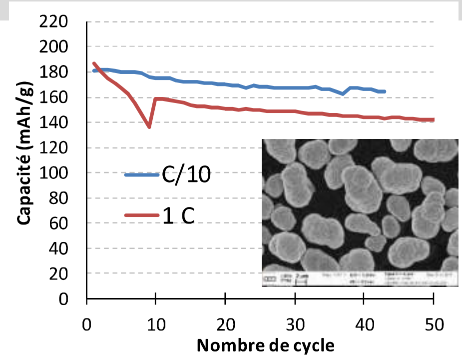


Advanced characterizations

HOW TO REDUCE THE COBALT IMPACT: THE CEA APPROACH



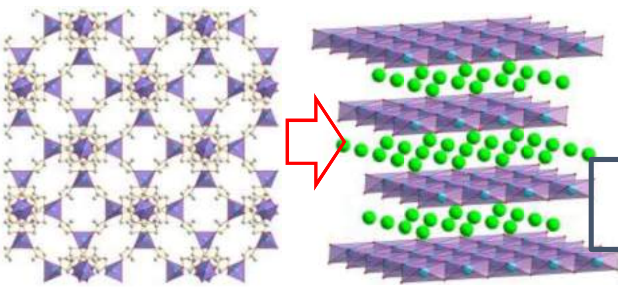
Reducing cobalt in commercial cathode materials

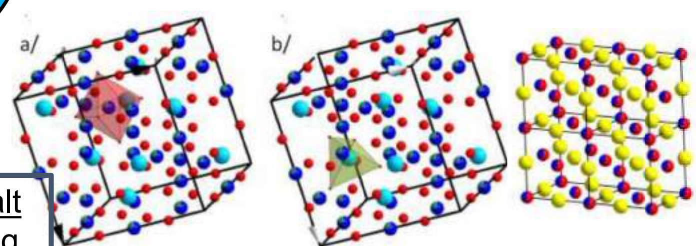


How to reduce cobalt in Li-ion Batteries

Increasing materials energy density for lowering the cells number per battery pack

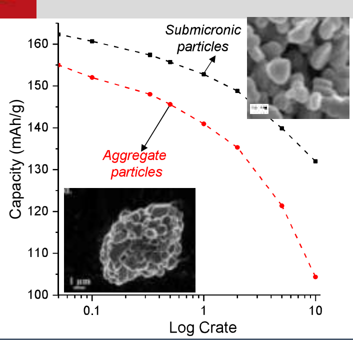
New cobalt free cathode materials





Improving cobalt recycling/mining

HOW TO REDUCE THE COBALT IMPACT: THE CEA APPROACH

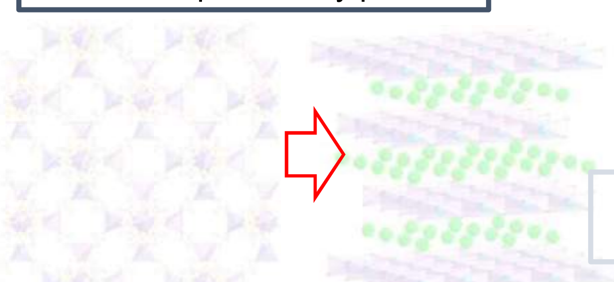


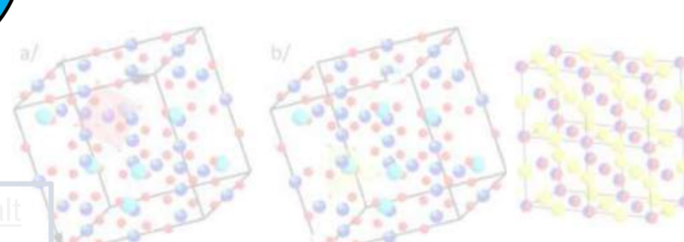
Reducing cobalt in commercial cathode materials

How to reduce cobalt in Li-ion Batteries

Increasing materials energy density for lowering the cells number per battery pack

New cobalt free cathode materials

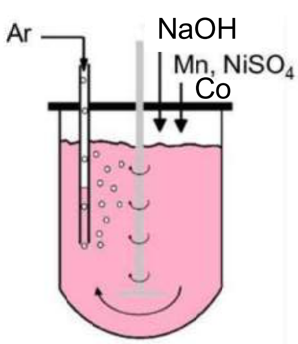




Improving cobalt recycling/mining

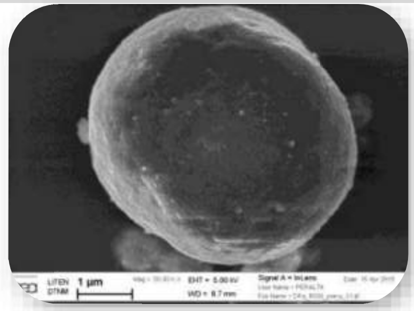
Improving the efficiency of classic cathode materials: role of the morphology

1[st] step: liquid synthesis



Several parameters have to be controlled:

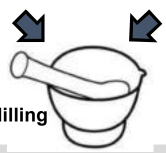
- pH
- feeding flow
- Mode of injection
- Temperature
- Concentration
- Blades geometry
- Stirring speed



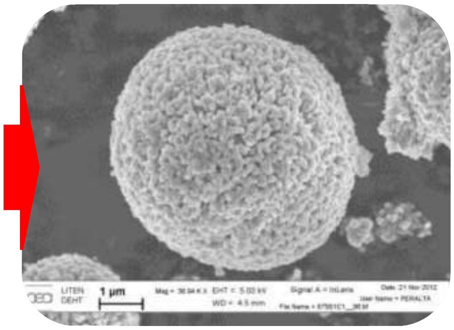
$Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ With controlled morphology

2[nd] step: dry synthesis

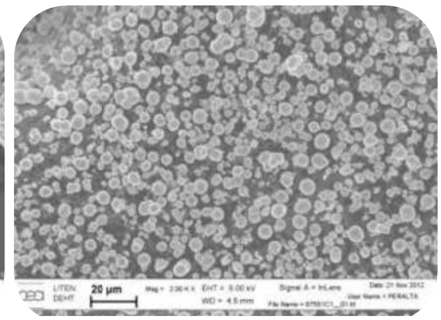
$Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ LiOH



Calcination



$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

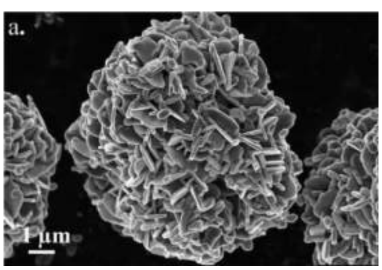


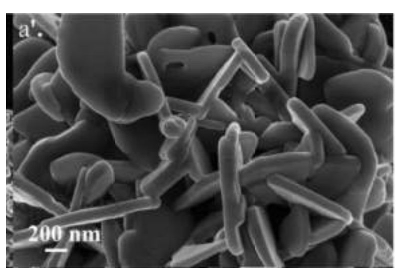
Calcination does not change the morphology

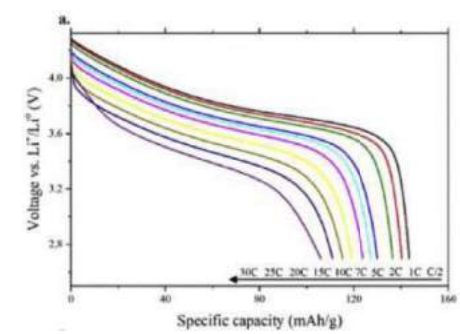
Improving the efficiency of classic cathode materials: role of the morphology

Comparison of the materials morphology :

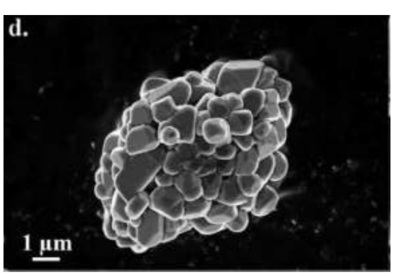
Spherical but porous particles

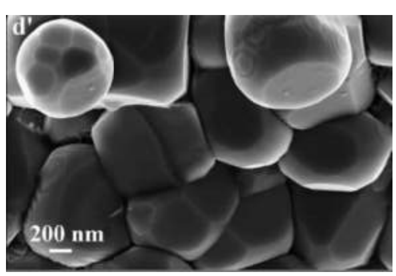


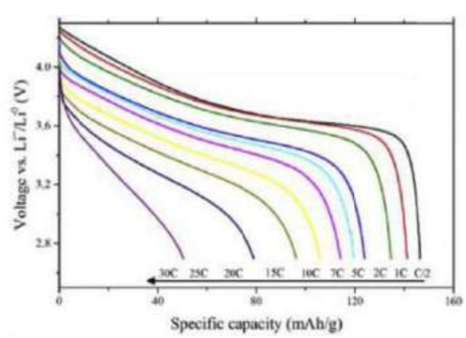




Spherical but very dense particles



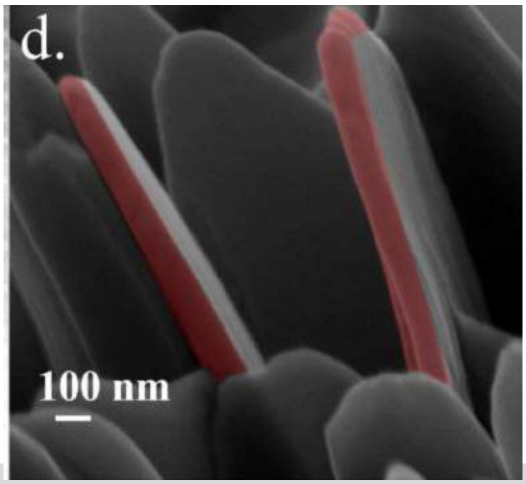


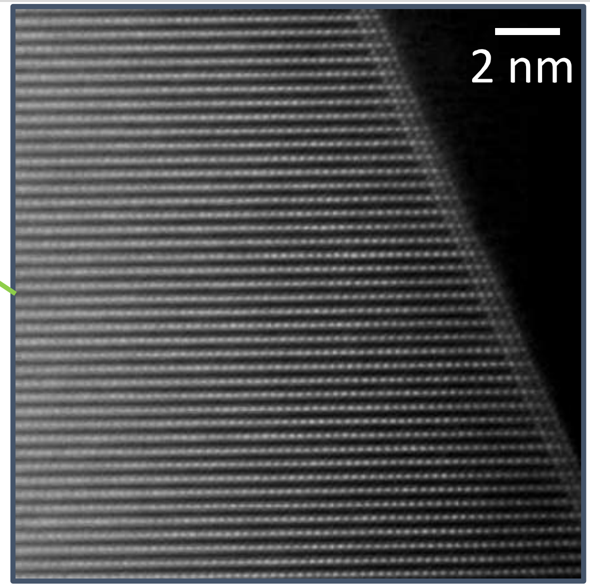


Cabelguen et al., j. power sources, 346 (2017) 13
Cabelguen et al., advance sustainable system, 2017, 1700078

Improving the efficiency of classic cathode materials: role of the morphology

Comparison of the materials morphology :





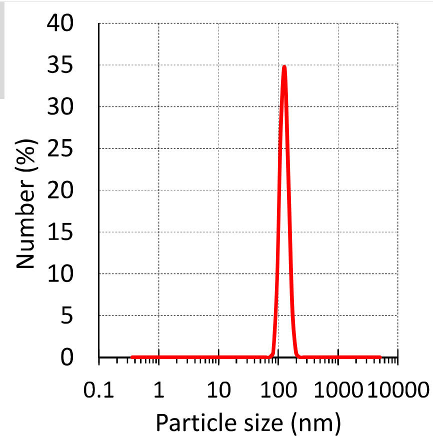
Because the layered structure,
the electrochemical active surface is improved when the grain boundaries decreases

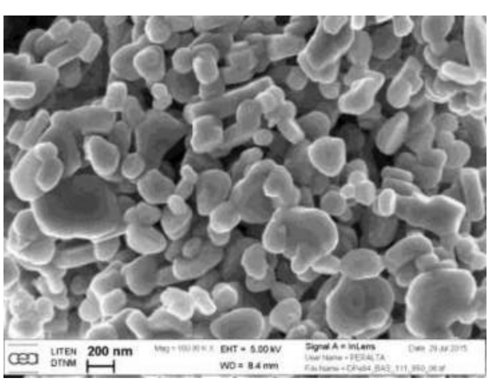
Cabelguen et al., j. power sources, 346 (2017) 13
Cabelguen et al., advance sustainable system, 2017, 1700078

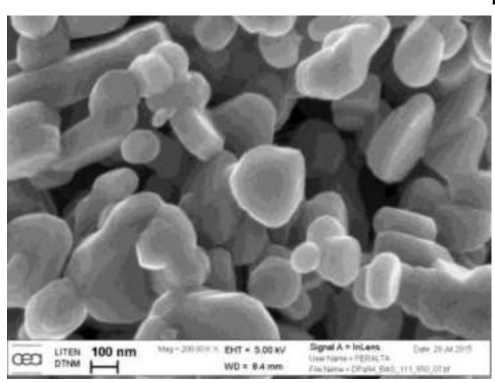
Improving the efficiency of classic cathode materials: role of the morphology

Increasing the pH and decreasing the amount of ammonium hydroxide seems to make the nucleation step faster and to limit the growing step.

It is possible to produce submicronic and single crystals NMC particles with large electroactive specific surface area
by using processes with well-known industrially scaled analogs

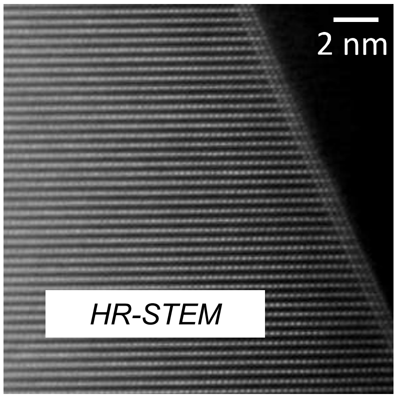


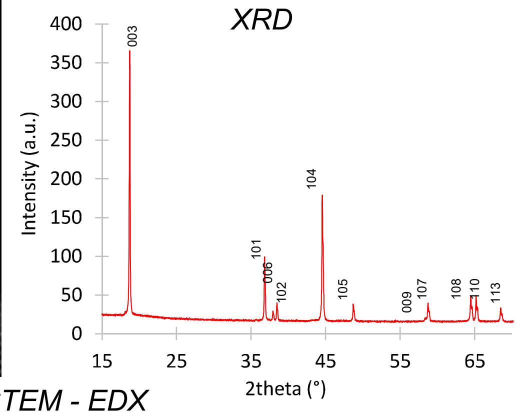




Peralta et al., Journal of Power Sources 396 (2018) 527–532
Peralta et al. WO2018134536

Improving the efficiency of classic cathode materials: role of the morphology



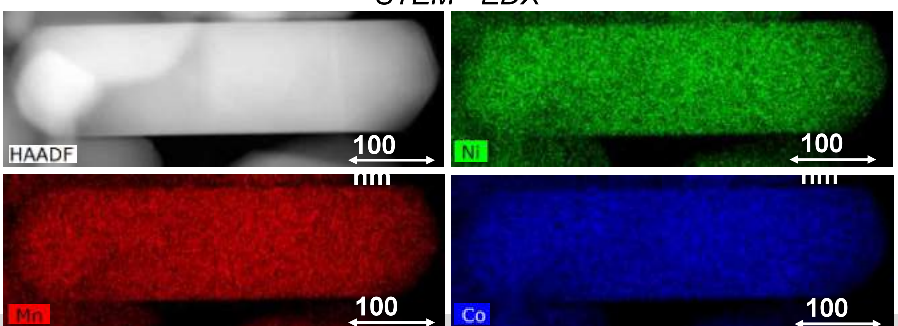


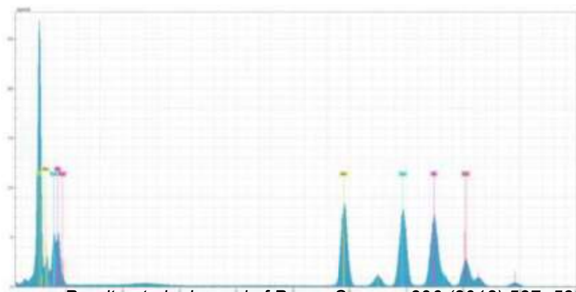
- Peaks ratio in XRD reveal low cation mixing

- Confirm with HR-STEM pictures

- STEM EDX on one primary particle and ICP-AES confirm the formula: NMC 111

STEM - EDX



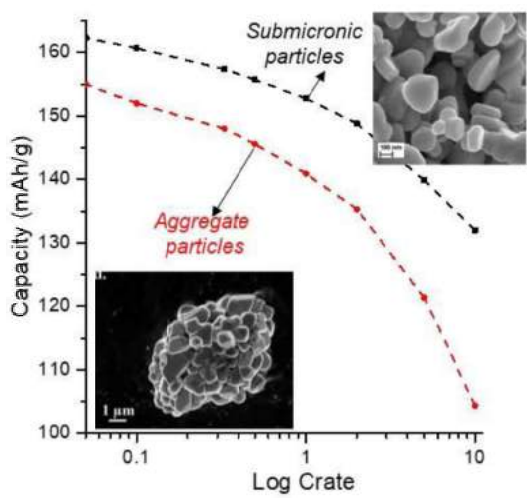


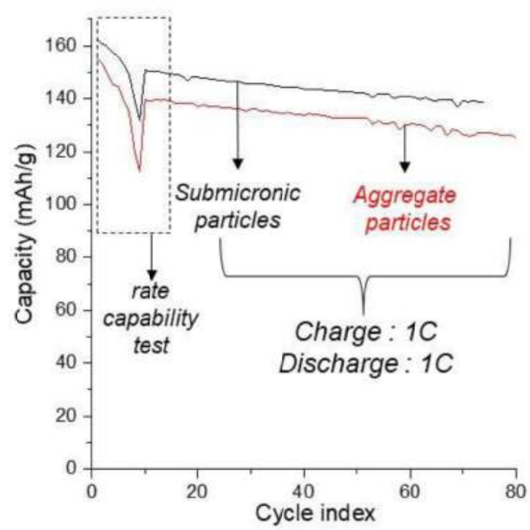
Peralta et al., Journal of Power Sources 396 (2018) 527–532
Peralta et al. WO2018134536

Improving the efficiency of classic cathode materials: role of the morphology

Comparison of the materials morphologie :

- Aggregate particles were obtained by coprecipitation : *Cabelguen et al, J. Power Sources, 2017*)
- Half-cells: Li metal, organic formulation, loading cathodes: 2.9 mg/cm²

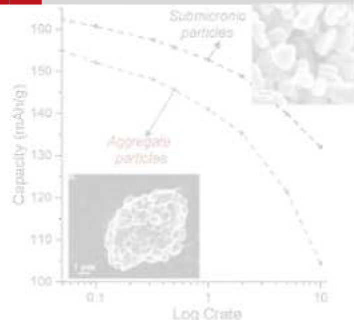




- Cycle lives are comparable
- An higher capacity is reached at all Crates with the submicronic particles
- Good performances at high Crate: 132 mAh/g at 10C

Peralta et al., Journal of Power Sources 396 (2018) 527–532
Peralta et al. WO2018134536

HOW TO REDUCE THE COBALT IMPACT: THE CEA APPROACH



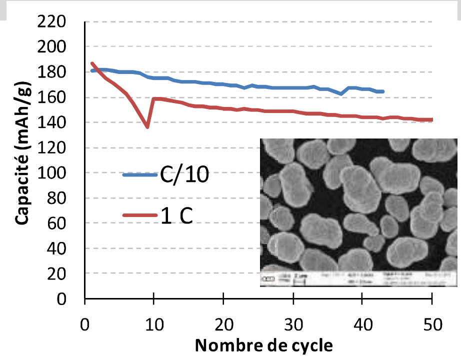
Reducing cobalt in commercial cathode materials

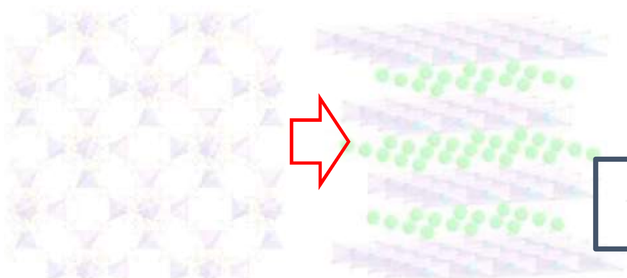
How to reduce cobalt in Li-ion Batteries

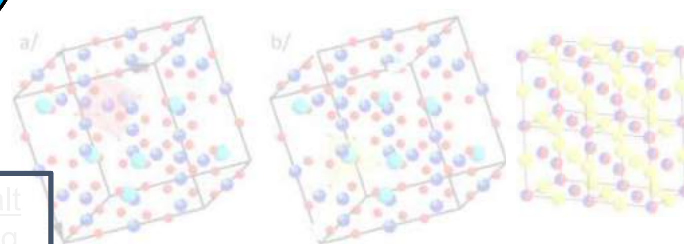
Increasing materials energy density for lowering the cells number per battery pack

New cobalt free cathode materials

Improving cobalt recycling/mining

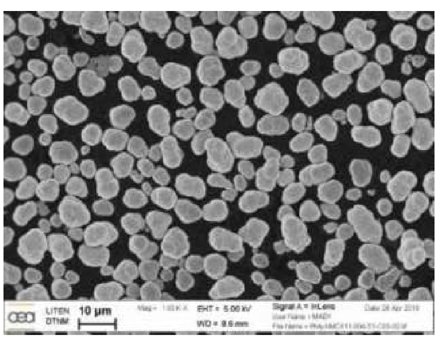


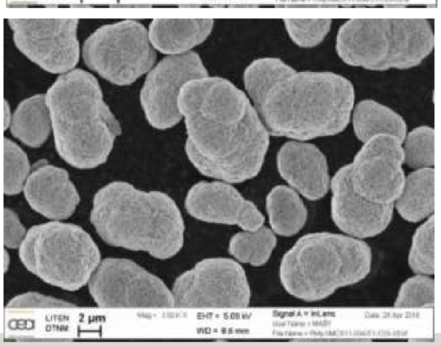


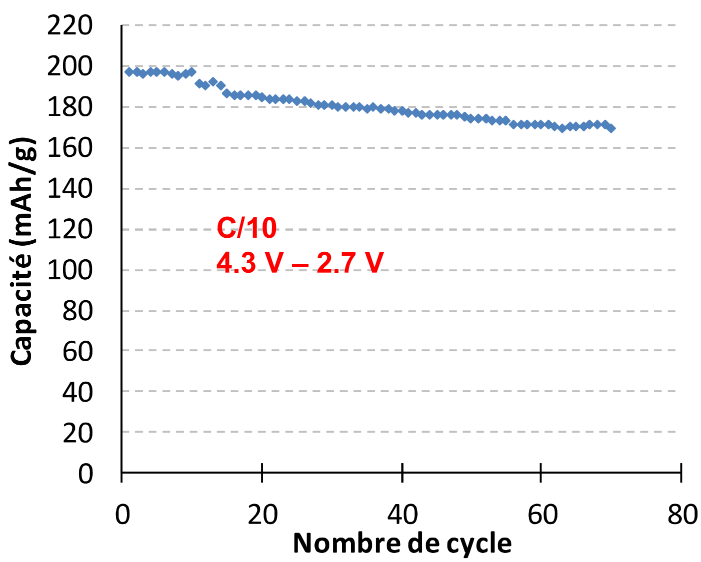


Reducing cobalt in commercial cathode materials

NMC 811 synthesised via coprecipitation : no dopant no coating



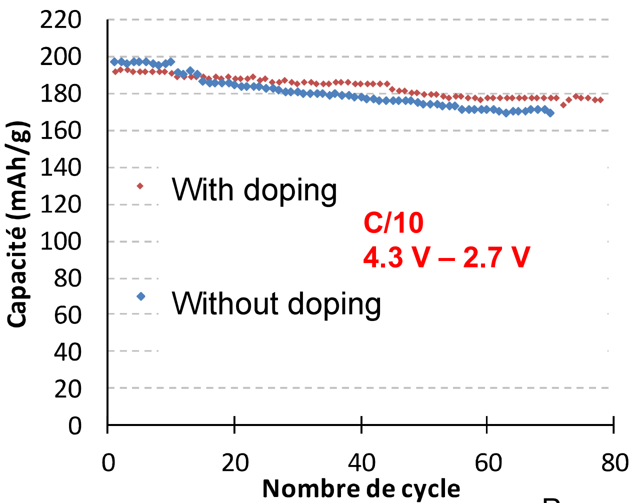


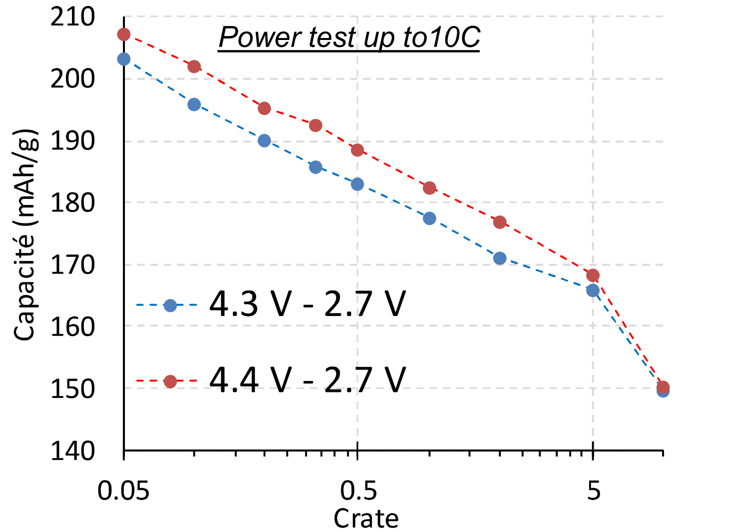


- Optimisation still ongoing

Reducing cobalt in commercial cathode materials

Development of a new CEA formula by using new dopant (insert in coprecipitation) $LiNi_{0.8}Mn_{0.1}Co_{0.1}M_xO_2$





Perspectives:

➔ Optimisation of the synthesis (morphology and performances)
➔ Optimisation of the formulation
➔ Coating

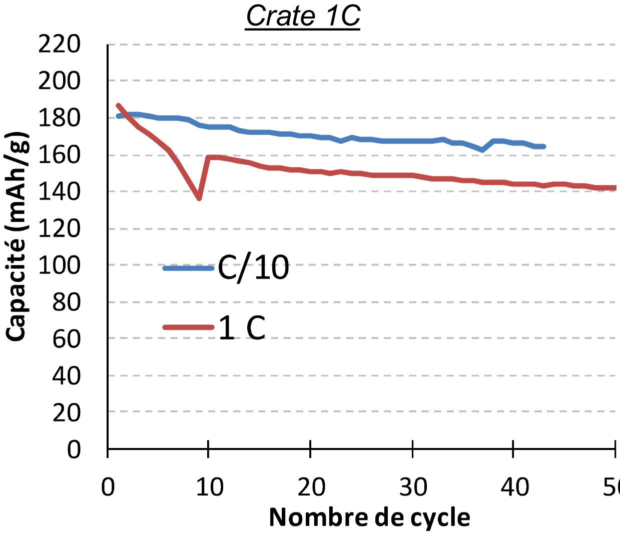
Towards very high Ni content

Reducing cobalt in commercial cathode materials

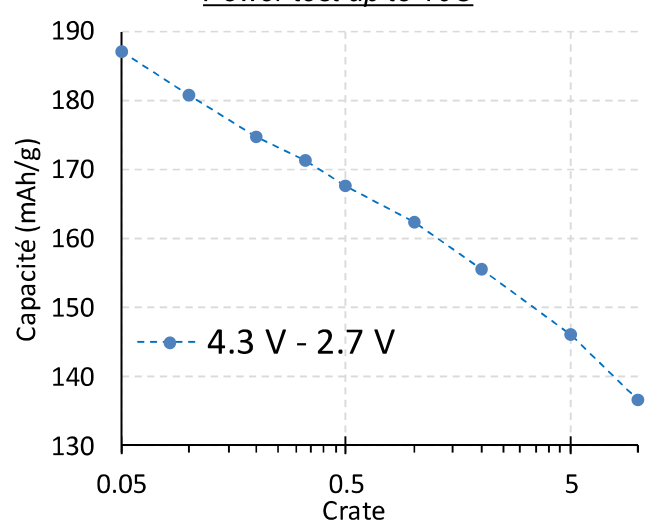
Increasing **Ni to >0.9 F**irst trial

$LiNi_{0.9}Co_{0.05}M_{0.05}O_2$

Crate 1C

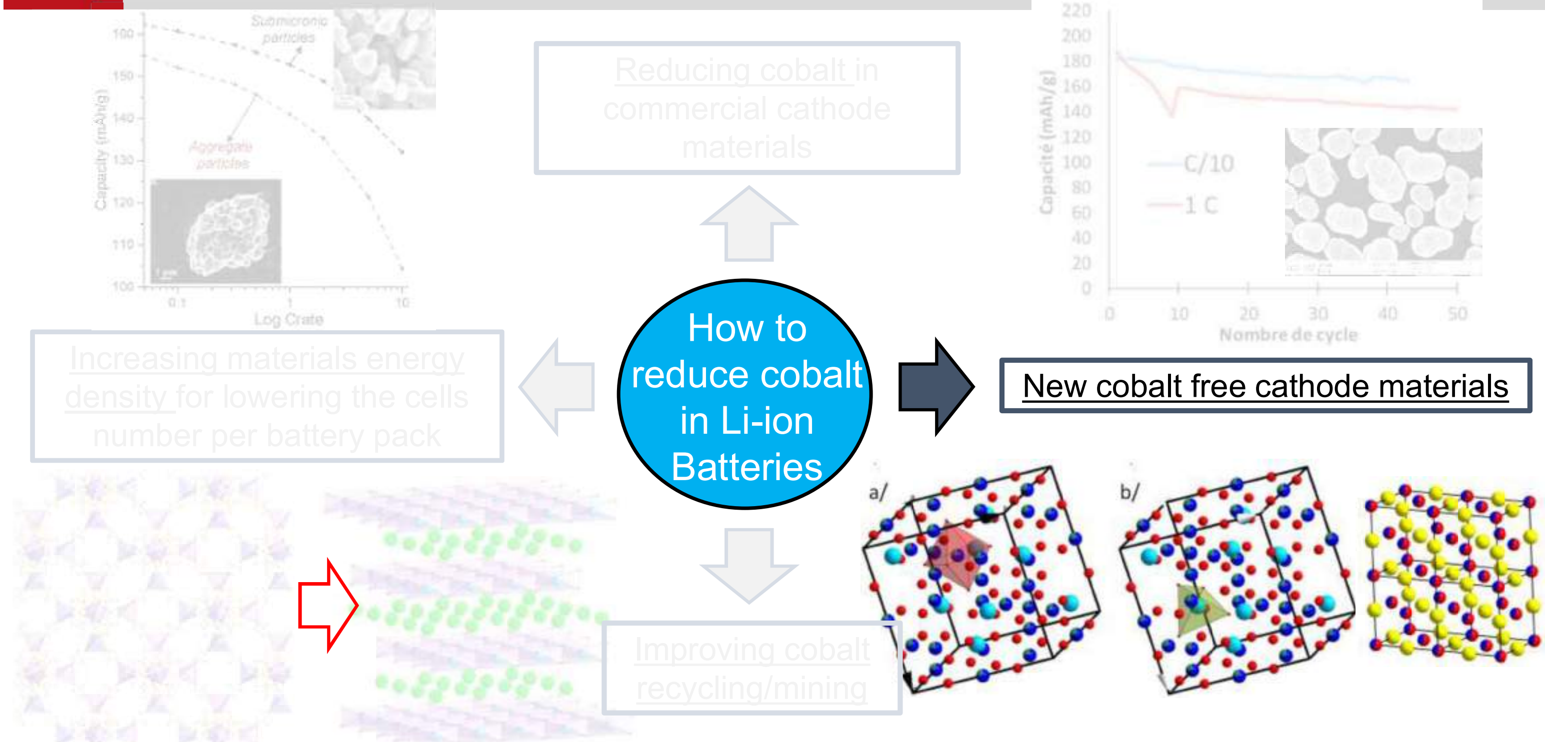


Power test up to 10C

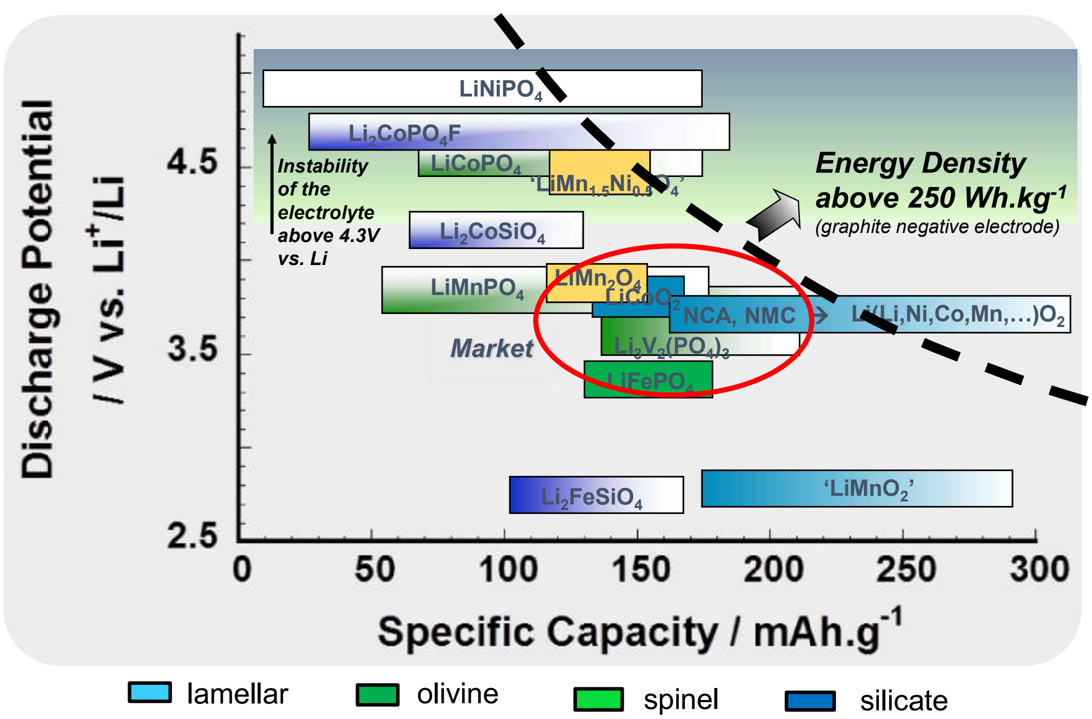


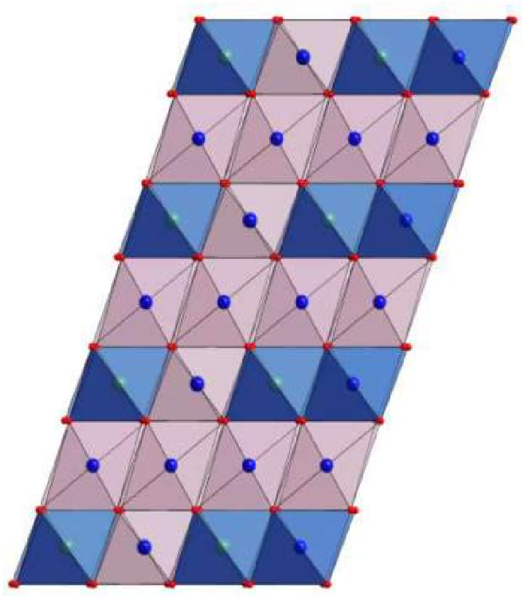
The next step will be to completely supress the cobalt from the formula.

HOW TO REDUCE THE COBALT IMPACT: THE CEA APPROACH



Materials for positive electrode



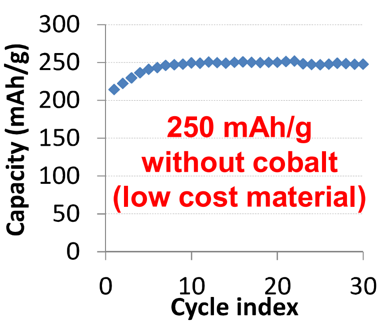


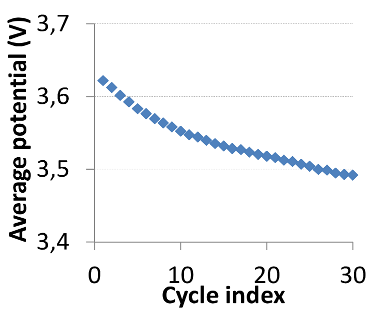
Lithium rich layered oxides

Cobalt free cathode materials: Li-Rich

CEA Patent: WO2015014807A1

Electrochemical performances at the state of the art:

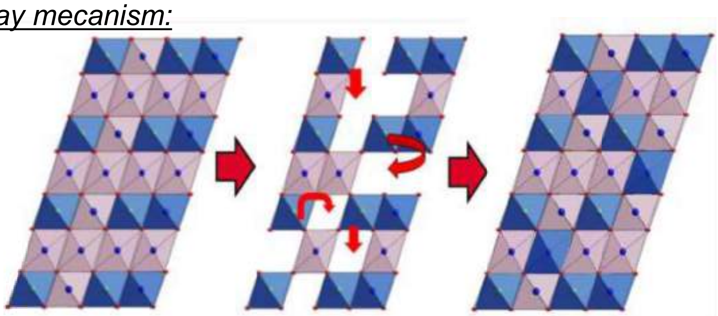




☺ High capacity
☺ High energy
☹ Voltage decay

The voltage decay is the reason why this material is not yet commercialized
All research groups have the same issue

Voltage decay mecanism:



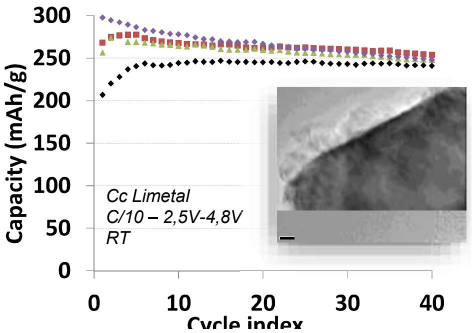
CEA scientific contribution:

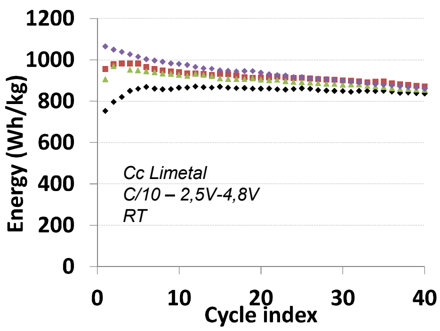
1- Boulineau et al.; Chem. Mater. 2012, 24, 3558–3566
2- Simonin et al.; J. Mater. Chem. 2012, 22, - 11316-11322
3- Boulineau et al.; Nano Lett., 2013, 13 (8), pp 3857–3863
4- Peralta et al.; J. Power sources, 2015, 280, 687-694
5- Peralta et al.; Electrochimica Acta 400 (2021) 139419

Cationic migration and Li_2MnO_3 layers activations are responsive of the voltage fading.

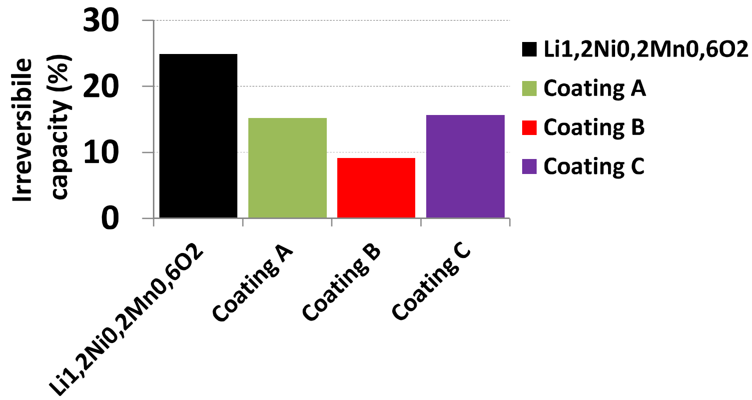
Cobalt free cathode materials: Li-Rich

1st Solution: increase the specific capacity at the maximum and then, reduce the upper limit voltage





Coatings applications:



❖ Irreversible capacity decrease : **from 25% to 9 %**

❖ Specific capacity increase : **up to 290 mAh/g** *(1st discharge)*

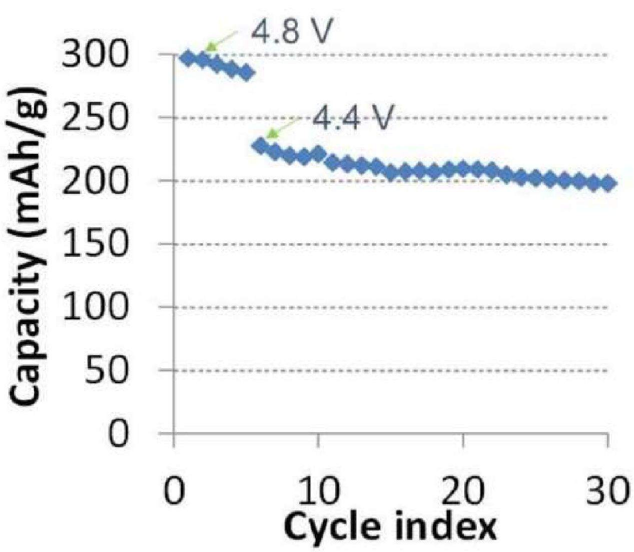
❖ Massic energy density increase : **up to 1100 Wh/kg**

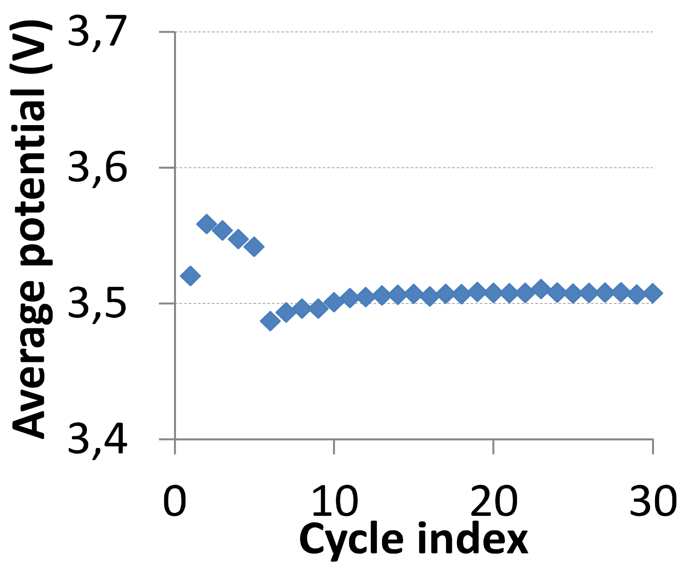
cea

Cobalt free cathode materials: Li-Rich

CEA Patent: FR3023070

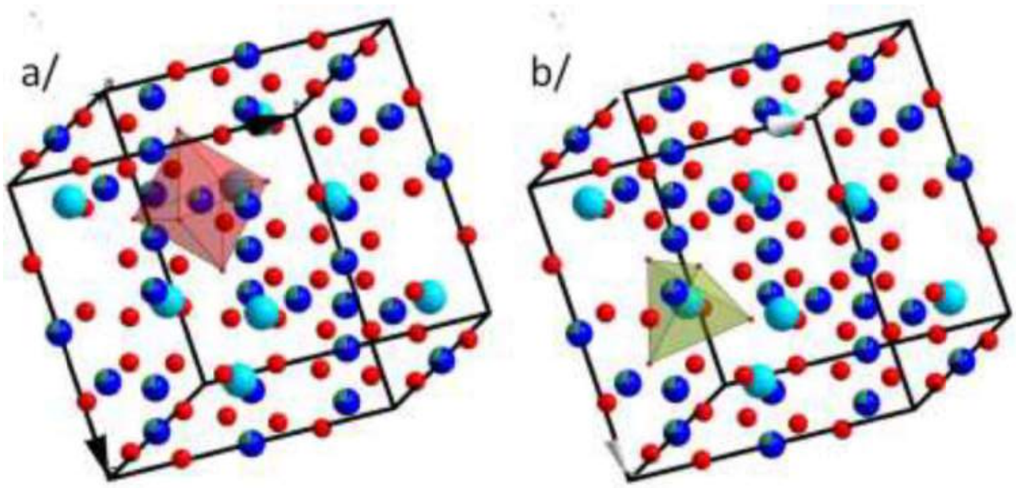
1st Solution: increase the specific capacity at the maximum and then, reduce the upper limit voltage





☺ The fading of the potential could be stopped

☹ The capacity and the final energy decreases but performances are similar to NMC.



5V spinel

Cobalt free cathode materials: 5V Spinel

Good results were obtained with solid state synthesis but it is difficult :

- to obtain an homogeneous mix of 3 elements by solid state synthesis.
- to control the morphology and the porosity of the material.

CEA coprecipitation facilities:

- Laboratory scale : 4 reactors (3L, 5L and 10 L)
- Pilot scale : 2 reactors 35 L and 65 L
- Use of Hydroxide or carbonate routes of synthesis

Pilot-scale

COPRECIPITATION

5 Liters lab reactors

Scale up the synthesis

35 Liters reactor

65 Liters reactor

Laboratory scale:
~ 50 g/Batch

Pilote scale:
> 1Kg /Batch

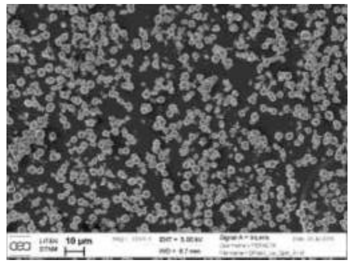
Specificity of the CEA coprecipitation process

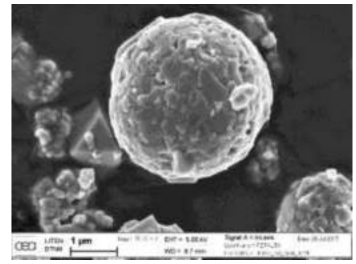
Synthesis of a « multi-layers » core-shell in only one synthesis step

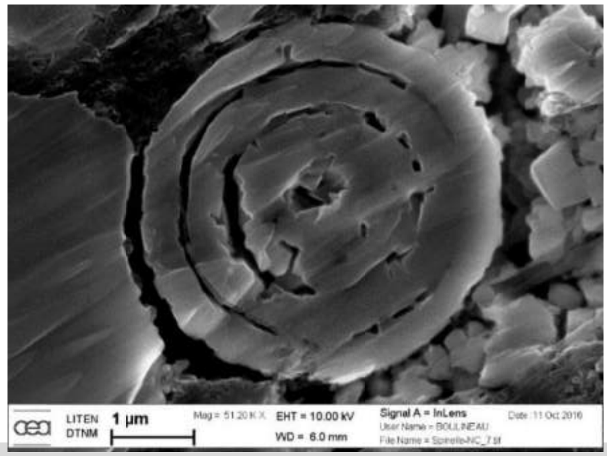
Proof of concept already done for :

✦Lirich Layered oxide

✦ 5V Spinel

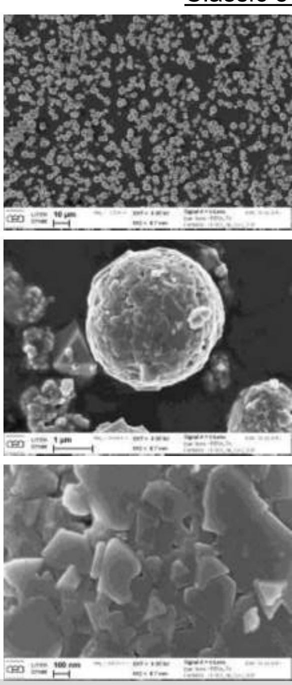


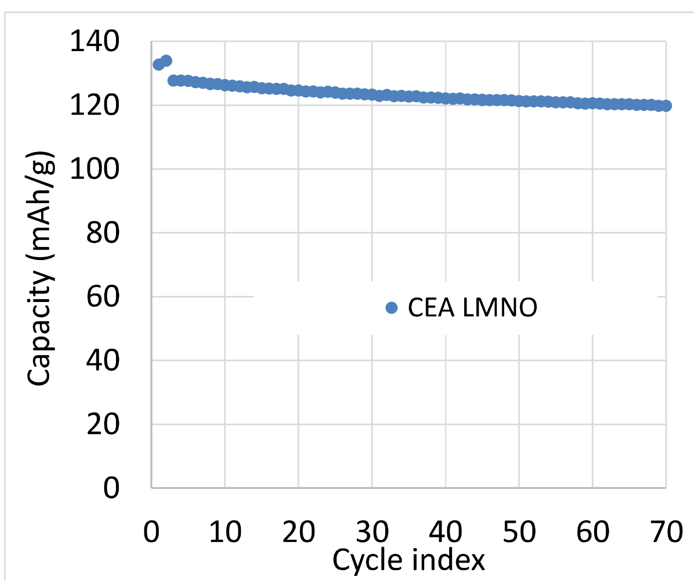


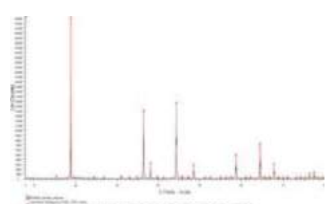


Cobalt free cathode materials: 5V Spinel

- Classic 5V LNMO obtained by coprecipitation at pilot scale: $LiNi_{0.5}Mn_{1.5}O_4$







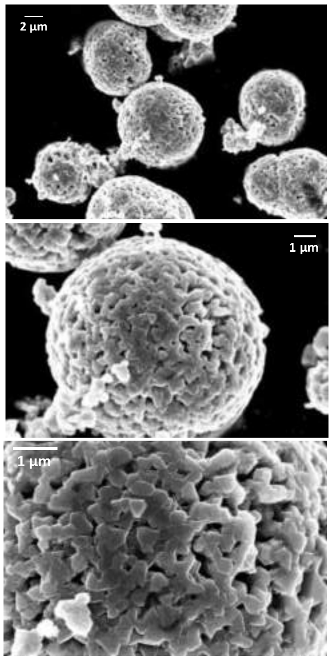
Capacity : 133 mAh/g
Potential: 4.75 V
Spherical morphology

Performances at the state of the art

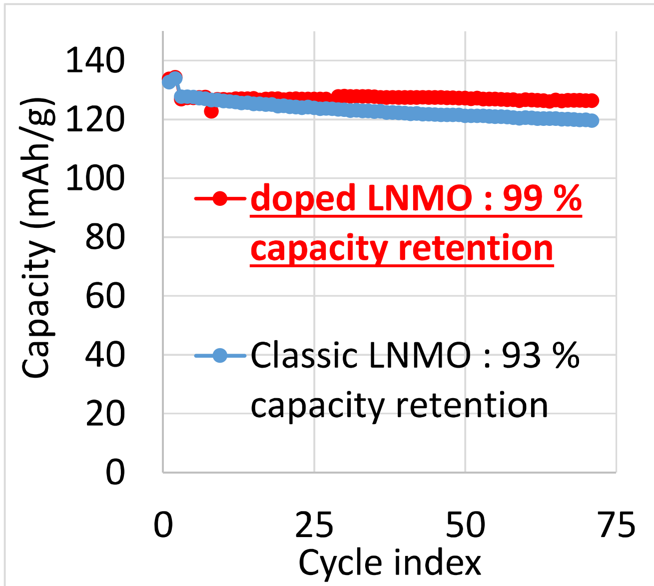
Cycle life could be improved

Cobalt free cathode materials: 5V Spinel

5V LNMO obtained by coprecipitation at pilot scale: Doped and coated sample

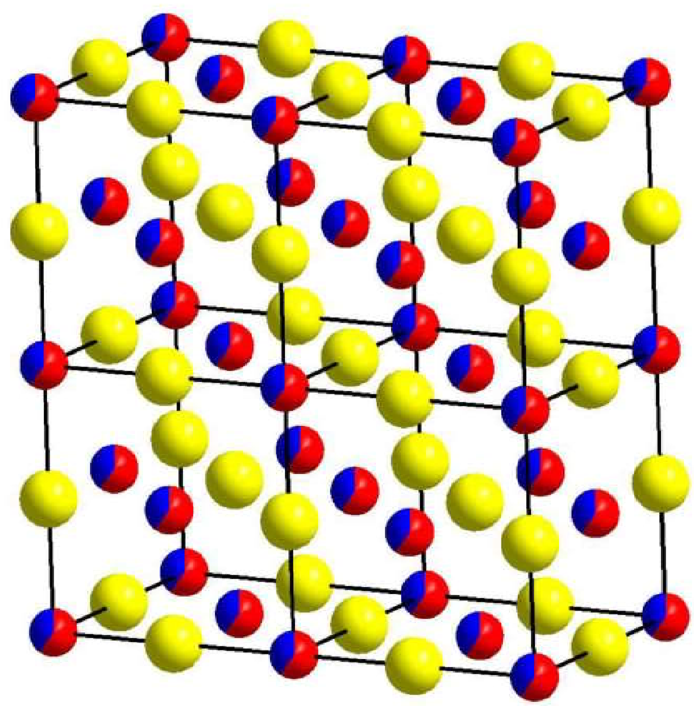


Doped 5V Spinel has a better cycle life



Possible surface treatment
$Li_2O.2B_2O_3$
AlF_3
MgO
Al_2O_3
MgF_2
MnO_x

Disordered Rocksalt family



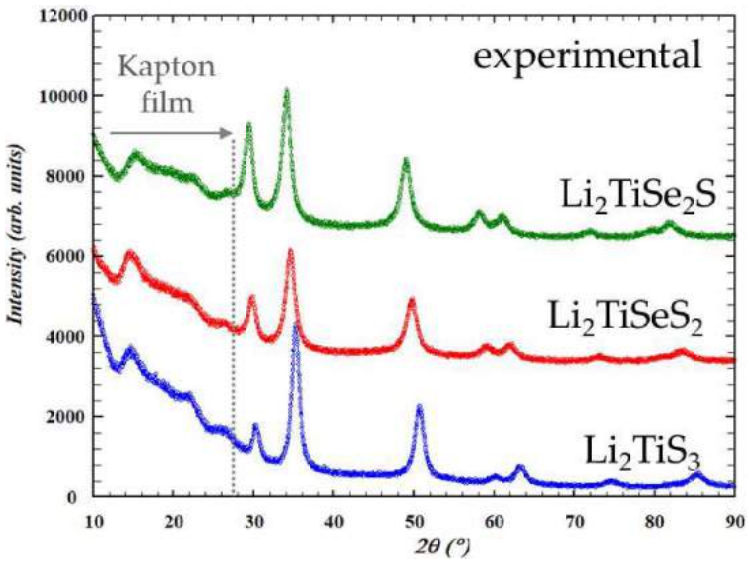
Cobalt free cathode materials: Rocksalt

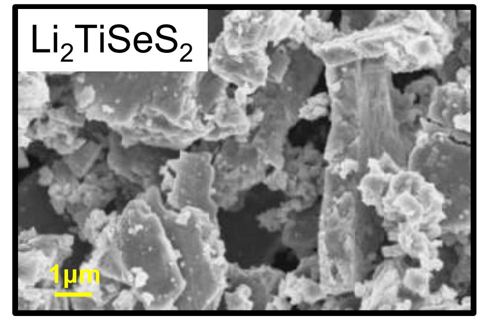
2 CEA Patents:
FR3085950
FR3085949

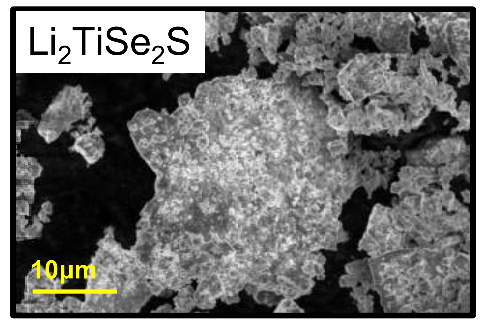
$Li_2TiSe_xS_{3-x}$

Synthesis of sulfur-selenium solid-solutions

$Li_2TiSe_xS_{3-x}$ compositions are prepared in disordered rocksalt phase with patented synthesis method





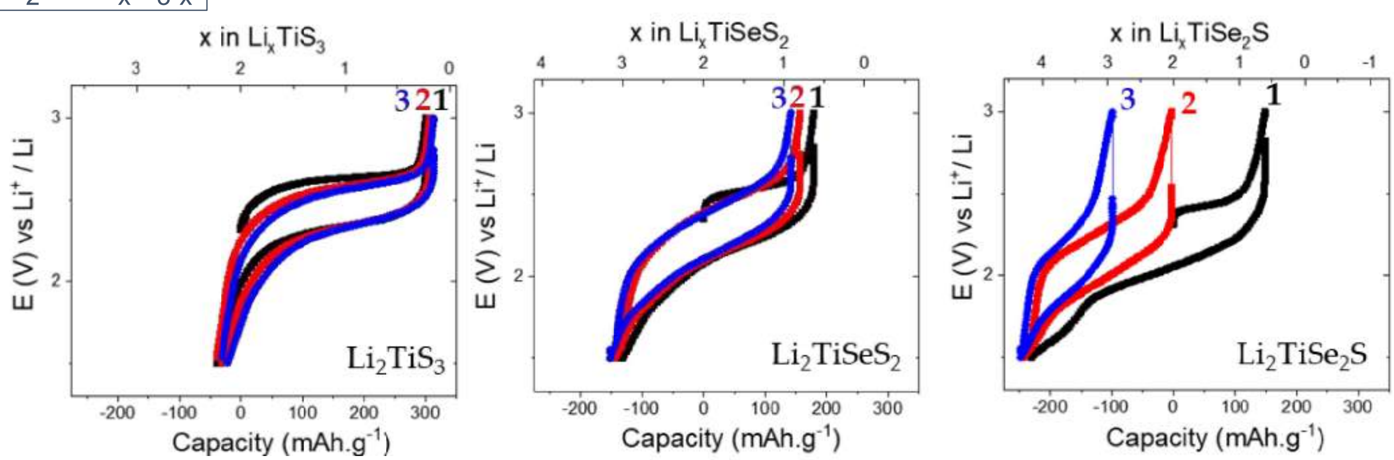


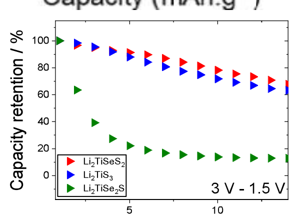
 Celasun et al. Materials 2022,15, 3037.

Cobalt free cathode materials: Rocksalt

$Li_2TiSe_xS_{3-x}$

Electrochemical performances of sulfur based rocksalt





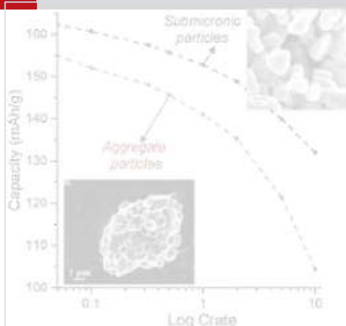
☺ Very high capacities > 400 mAh/g

☹ Poor cycle life

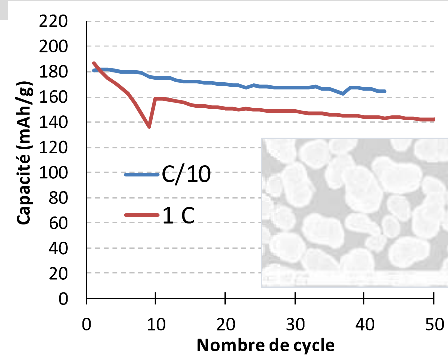
➔ Still in progress

 Celasun et al. Materials 2022,15, 3037.

HOW TO REDUCE THE COBALT IMPACT: THE CEA APPROACH



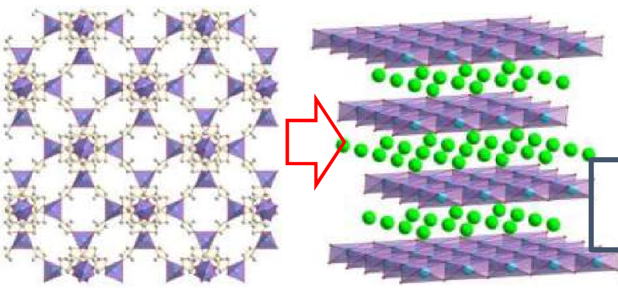
Reducing cobalt in commercial cathode materials



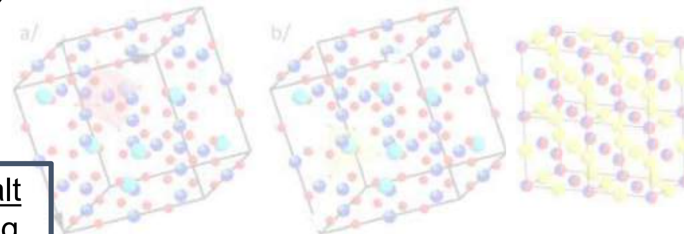
Increasing materials energy density for lowering the cells number per battery pack

How to reduce cobalt in Li-ion Batteries

New cobalt free cathode materials



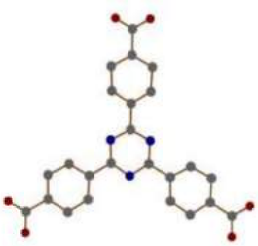
Improving cobalt recycling/mining



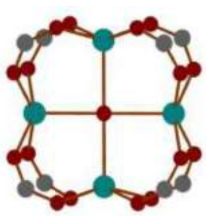
WHAT'S A METAL-ORGANIC FRAMEWORKS ?

- **Metal-Organic Frameworks (MOFs)**

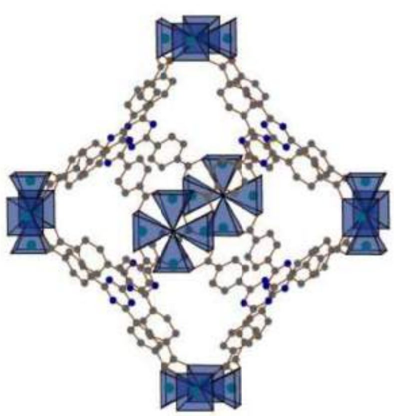
Organic unit:



Inorganic unit:



Metal-Organic Frameworks:



MOF : PCN-9

A MOF is composed of a mix of Organic and inorganic units.

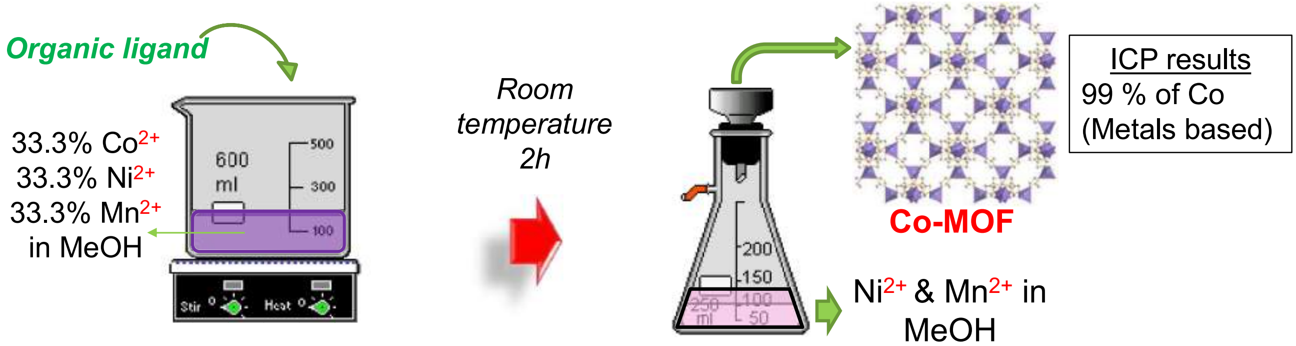
This assembly results in microporous materials.

In literature, MOFs have been studied for many applications and especially:
- Catalysis
- Adsorption

 Ma et al., JACS., 2006, 128, 11734

WHAT'S A METAL-ORGANIC FRAMEWORKS ?

By well selecting the organic ligand, it is possible to selectively remove the cobalt from a solution composed of nickel/manganese/cobalt



The organic ligand can be directly inserted in its solid form (salt)
➔ Limiting the amount of liquid waste

Room synthesis conditions
➔ Limiting the energy consumption

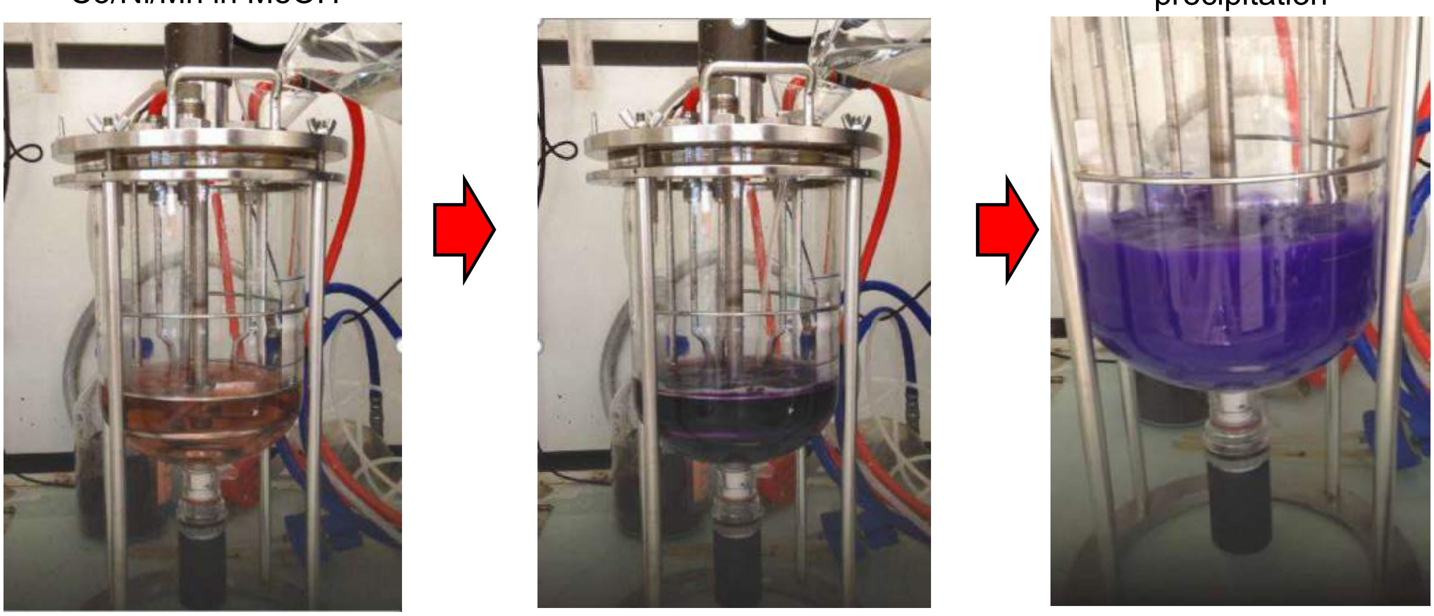
Porous material with very high cobalt content
➔ Recovery of cobalt in only one step
➔ High value product (catalyst, adsorbent…)

WHAT WE FOUND?

Equimolar solution of Co/Ni/Mn in MeOH

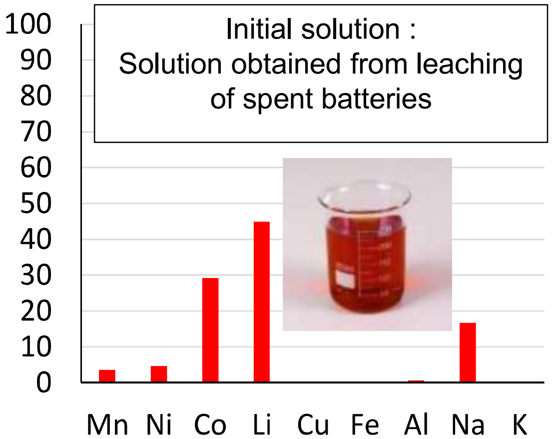
After just a few seconds

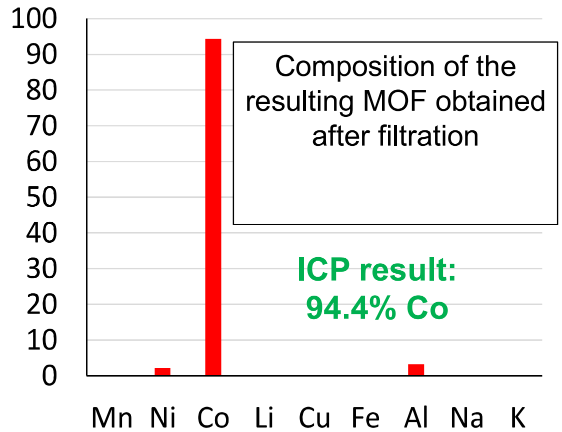
After 1 hour of precipitation



IS THE SOLUTION USABLE IN REAL CONDITIONS ?

A spent Li ion batteries solution was obtained by leaching a NMC (lithium layered oxide materials) cathode-based black mass with a solution of sulfuric acid (1M) and hydrogen peroxide





Very promising results:
our process is suitable in real conditions

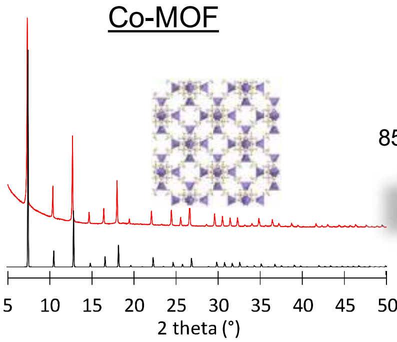
HOW TO PROMOTE THE RESULTING CO-MOF ?

1/ Directly use MOF as catalyst or adsorbent

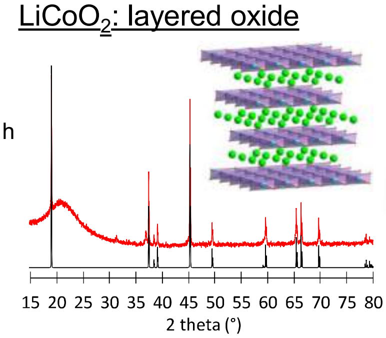
2/ Use MOF as Synthesis Precursor to create new coumpounds

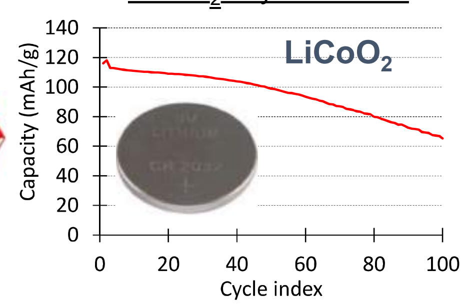
MOF are mainly composed of carbon and hydrogen.
As an exemple, ICP reveals that our MOF contains 21% of metal and we can considere that the 79% remaining part is composed of hydrogen carbon

Synthesis of $LiCoO_2$ cathode material by using Co-MOF as precursor



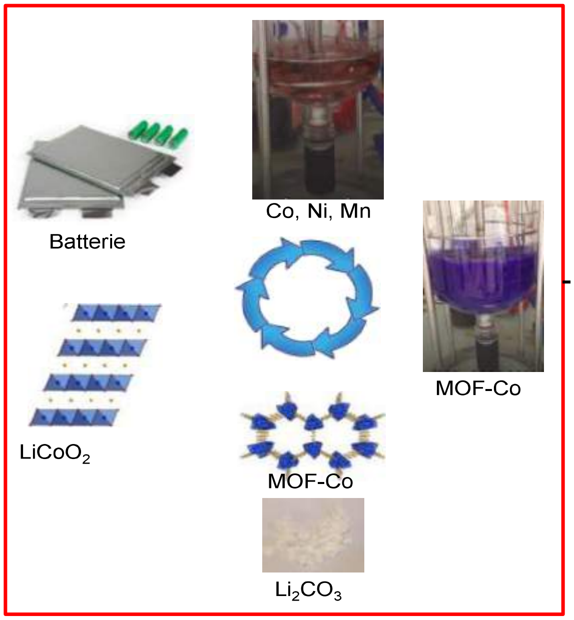
Li_2CO_3
850°C/12 h





We validated a first proof of concept of a new closed loop process

New closed loop process for recycling Cobalt



<u>*2 CEA Patents:*</u>
WO2019243728
WO2019243729

We found that some organic ligands can selectively react with cobalt ions.

Resulting MOF could be used in:

- An opened loop process: MOFs are used as catalist or adsorbent
- A closed loop process: Co-MOFs are directly reused as precursor for the synthesis of Li-Ion cathode materials

<u>Related publication</u>

Original pathway to selectively precipitate cobalt from an old battery solution thanks to imidazole linker
<u>D. Peralta</u>, A-C. Lavergne-Bril, E. Billy, J-F. Colin, D. Bloch, S. Patoux ; **Separation and Purification Technology,** 2022, 281, 119890.

MERCI POUR VOTRE ATTENTION

THANKS FOR YOUR ATTENTION

Current status and future prospects of the LCAs of Li-ion batteries

SPIDER Workshop
14th April 2022

Lorenzo Usai
Industrial Ecology Programme

lorenzo.usai@ntnu.no

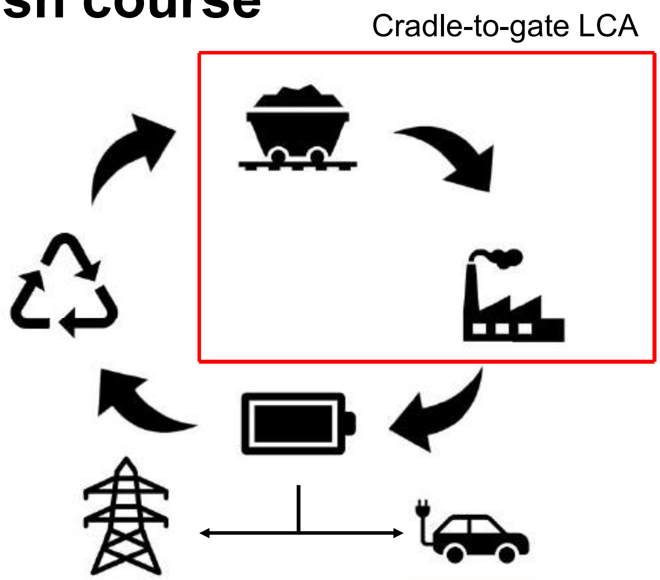
NTNU

Outline

- LCAs of Li-ion batteries
- NTNU's ambition within SPIDER
- Beyond LCA and CO_2

2 NTNU

LCA crash course



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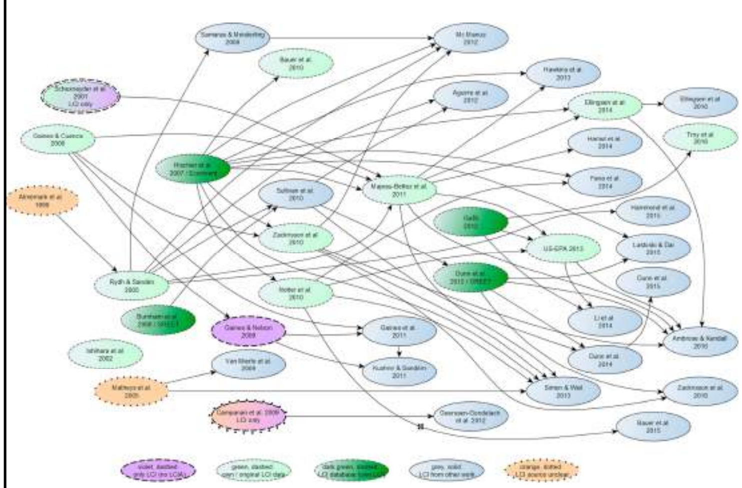
LCA studies on LIBs



- Since ~2009:
  - Many research groups worked on impacts stemming from LIBs' life cycle
  - Few original inventories; Many re-analyses of the same datapoints

4

Peters et al., 2017 - The environmental impact of Li-Ion batteries and the role of key parameters – A review - https://doi.org/10.1016/j.rser.2016.08.039

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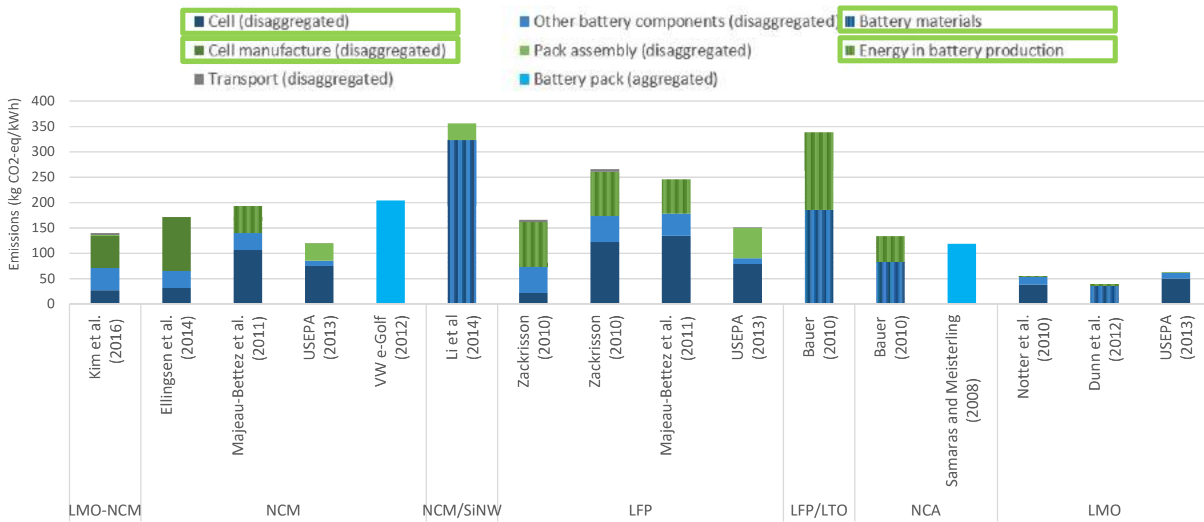
GHG footprint of Li-ion batteries – Key drivers



5 Ellingsen et al. 2017 - Identifying key assumptions and differences in life cycle assessment studies of lithium-ion traction batteries with focus on greenhouse gas emissions https://doi.org/10.1016/j.trd.2017.06.028

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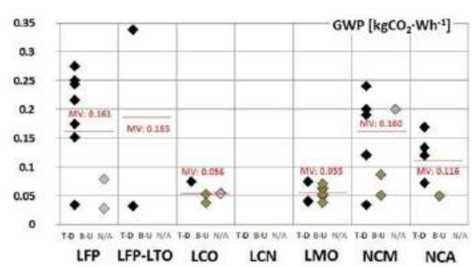
Uncertainty in results

- Uncertainty and variability of results within the same chemistry due to:
  - Use of standardized datasets for the extraction and refining impacts of raw materials
  - Lack of primary data for manufacturing phase of battery cells
  - Evolution of LIBs is happening quickly
    - Knowledge gap between academia and industry



6 Peters et al., 2017 - The environmental impact of Li-Ion batteries and the role of key parameters – A review - https://doi.org/10.1016/j.rser.2016.08.039

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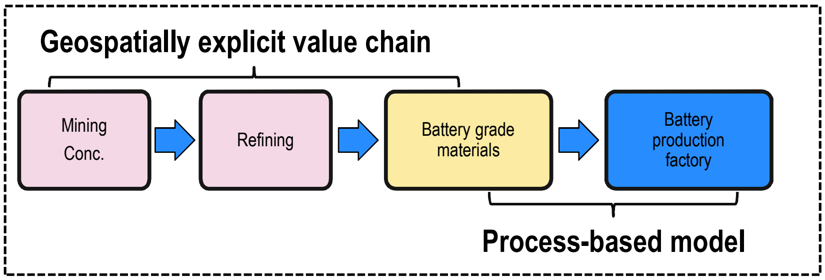
How to increase robustness of LCAs

To overcome the confidentiality of LIB industry and disentangle complexity of value chains, we are currently developing the following cradle-to-gate model:



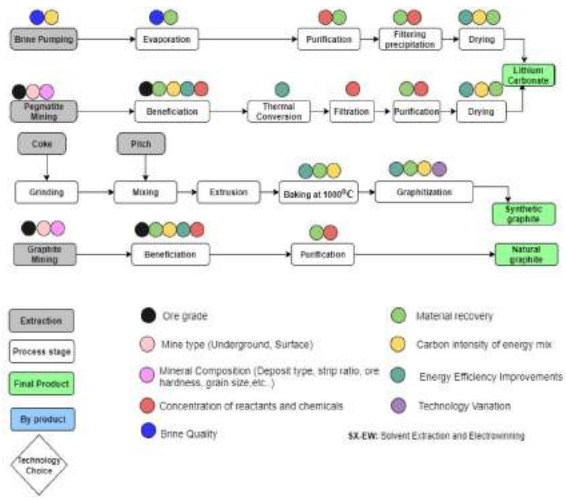
Variability in materials’ value chains

- Aggregated raw material inventories from databases dilute the precision of LCA and do not capture variations in process parameters
- What factors are responsible for variabilities in the impacts of LIB raw materials?
- What is the degree of influence that these factors have on the overall footprint of the materials?
  - Spatial variability (Electricity mix, resource quality etc..)
  - Tecnological variability (Smelting technology etc..)

Raw materials production

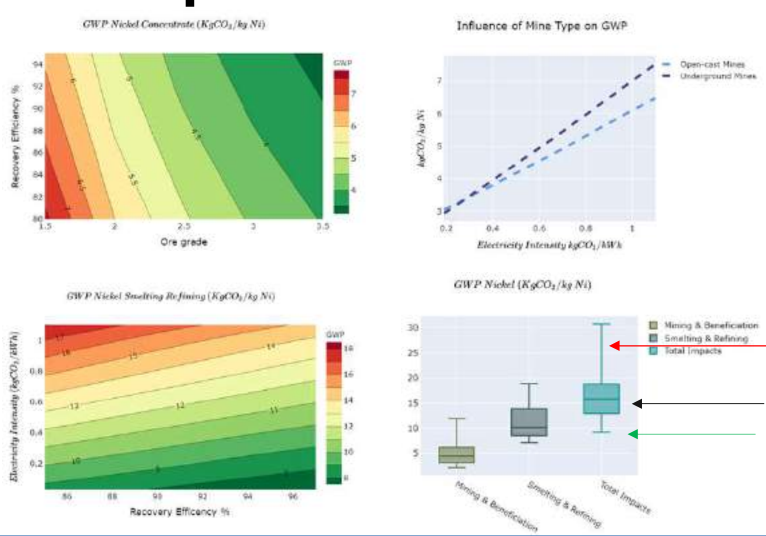
Key features:

- Variability of parameters:
  - Regional
  - Technological
- Track:
  - Energy flows in each step
  - Material flows and waste streams
  - Direct emissions
  - Overal footprint (not only CO_2)
- Covers a wide range of key LIB raw materials
  - Li carbonate and hydroxide; Co sulfate; Al; Cu; Mn; Synthetic and natural C; Ni



 Source: Manjong, Usai, Burheim, Strømman., 2021 https://doi.org/10.3390/batteries7030057

Example: Nickel

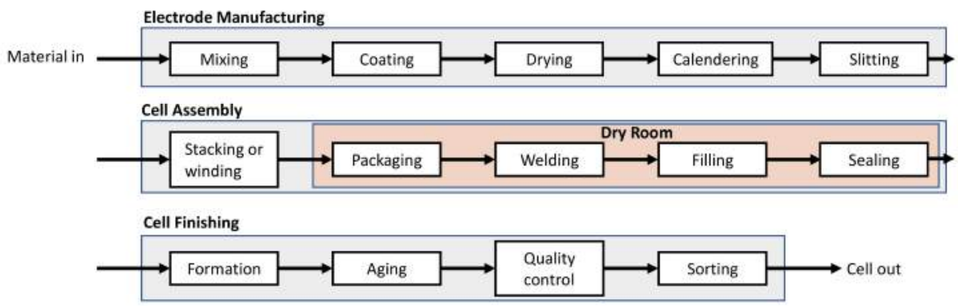


Asian Average=**26** kgCO2e/kg Ni

Global Average=**14** kgCO2e/kg Ni

Nordic Average=**9.8** kgCO2e/kg Ni

LIB production model



The model can be used within the LCA framework to spot where the highest emissions are being generated across the production line.

11 Source: Jinasena, Burheim, Strømman., 2021 https://doi.org/10.3390/batteries7010014

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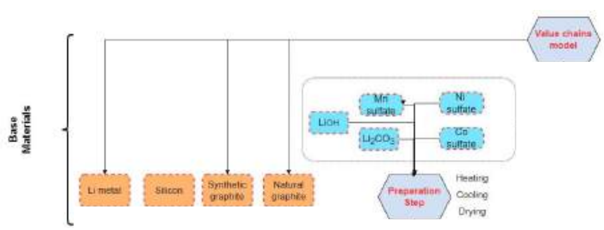
Combined mining and production



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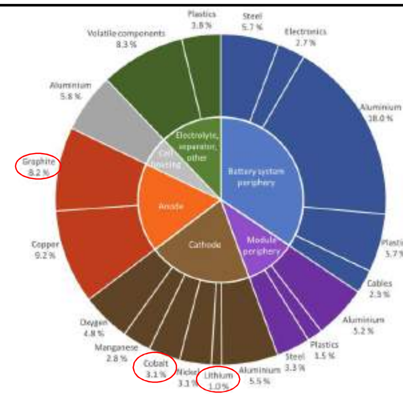
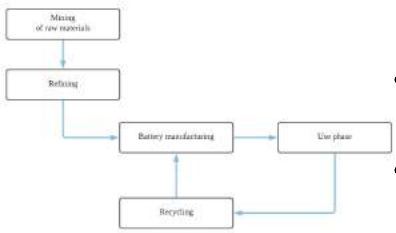
Besides CO_2



- Key metals used in batteries are in the list of the EU Critical Raw Materials
- We therefore need to estimate the future material flows, both during production and at the end-of-life

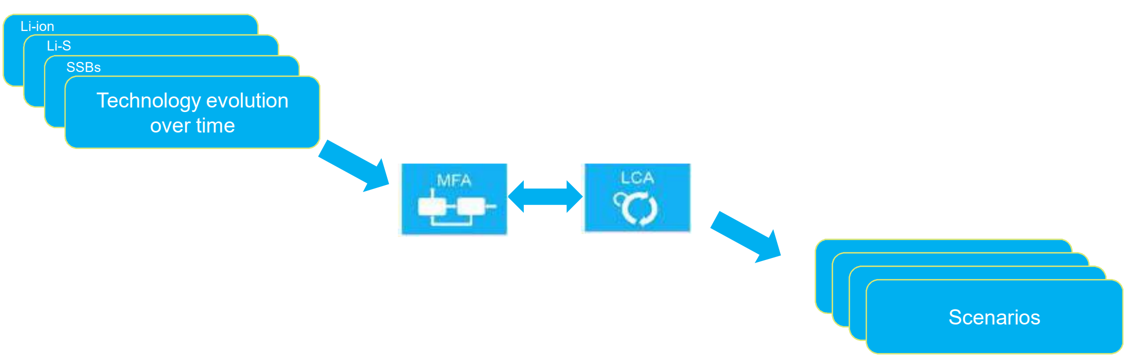


- Devise strategies on total production capacity needed
- Recycling potential and opportunities for reuse of recovered materials

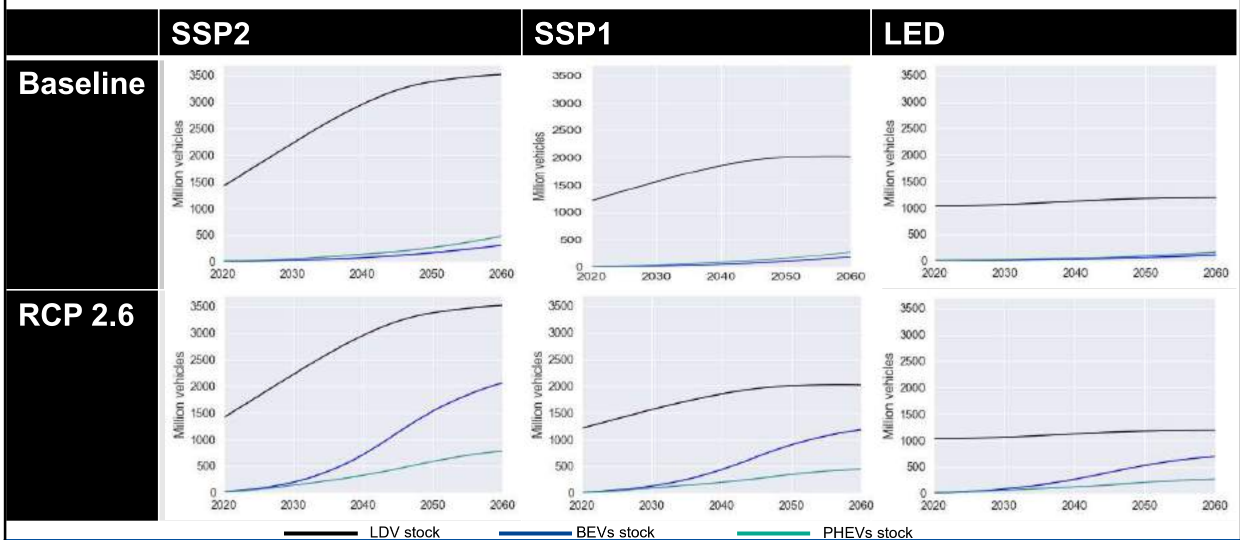
Diekmann et.al 2017, Ellingsen et.al 2018

Beyond LCA – IndEcol toolbox

To fully understand the trade-offs of the EV transition and of the deployment of novel chemistries, we need to look at the system-wise implications.



EVs deployment and LIBs demand



Source: Usai et al., 2022 **https://doi.org/10.1088/2634-4505/ac49a0**

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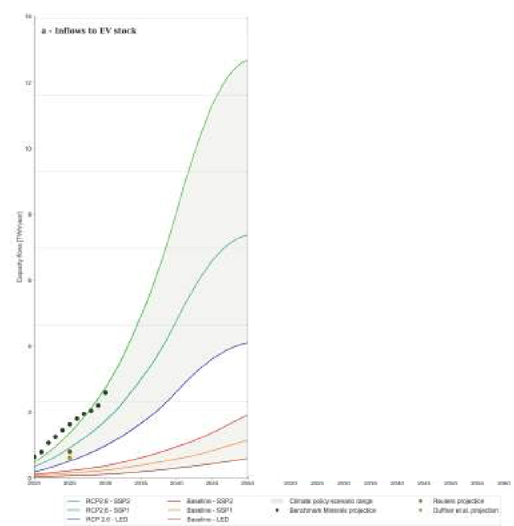
Production and recycling needs



- Recycling industry will have to be in place to process Mt of materials
- As of now, in EU only 50% must be recovered. New regulation was proposed in 12/2020

Recycling industries do not recover everything due to low/non profit margins.
How can that be solved?

 Source: Usai et al., 2022 **https://doi.org/10.1088/2634-4505/ac49a0**

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Key messages

- To increase resolution and precision of LCA studies, there is the need of many data points:
  - Value chains of materials → Geography, tecnology, yields
  - Production of cells → Geography, scale, energy/heat, yields, scrap rates
- The use of parameterized models can help reducing uncertainties, but primary data would be needed for validation
- CO_2 is only one issue, materials demand and production/recycling require planning

SPIDER

Questions?

Influence of the ambient storage on NMC811-based cathodes and presentation of Cidetec facilities

SPIDER Workshop Online meeting
14th april 2022

Susan Sananes Israel

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 814389

Agenda

- Presentation of Cidetec facilities
- Study of ageing of NMC811

Introduction to Cidetec facilities

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 814389

CIDETEC

CIDETEC Energy Storage Value Chain

> from Powder to Power <

FROM MATERIALS TO CELL

Testing and Characterization

FROM CELL TO PACK

Materials
Formulations
Mixing
Scaling
Coating
Prototyping
MP modelling

Functional tests
Cycling
Durability
Impedance spectroscopy
Thermal analysis
Abuse Testing
Post-mortem tests

Modelling
SOC, SOH Algorithms
Electronic Control
Thermal design
Mechanical design
Prototyping
Product development

Electrode Formulations & Slurry Preparation

- Lab-scale electrode slurry batches: 20-50 g of solids
  - Solid content to solvent ratio >40 wt%, preferably >50% for lower drying (solvent evaporation) requirements
  - Mechanical mixing: Critical to adapt teflon-lined Blades to slurry volume and container (beaker)
- Pilot-scale electrode slurry: 1-5 kg of solids
  - Planetary mixer
  - Coating in R2R line

Pilot-scale

Planetary mixer (5L)

R2R coating line

Lab-scale

Dispermat (dissolver)

Doctor-blade table-top (DIN A4)

CIDETEC Energy Storage Battery Cell Manufacturing Pilot Plant Facility – breakdown of manufacturing steps

Pouch cell assembly and characterisation

- Tunable cell formats

6x5 cm^2 active area

6x10 cm^2 active area

14x23 cm^2 active area

- Tunable chemistries for advanced Li ion

Cathode materials

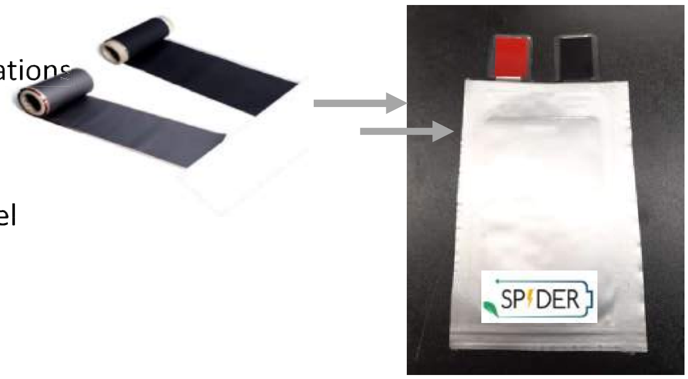
- LFP, LTO
- NMC, NCA
- Aqueous-based processing

Anode materials

- Graphite
- Si, SiOx
- TNO

CIDETEC activities in SPIDER Project:

- <u>WP5: cell manufacturing</u>
  - Production of cathode electrodes with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) layered oxide material
  - Assembly of prototype pouch cells of the different materials developed in the project
  - Delivery for cell testing
- <u>WP6: cell testing</u>
  - Electrochemical testing of different cell generations
  - Modelling of Gen0 and Gen2 cell chemistries
- <u>WP4: advanced safe electrolytes</u>
  - Validation of the electrolytes at pouch cell level



SPIDER PROJECT: How to store NMC811 powder and electrodes?

Influence of the ambient storage of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ powder and electrodes on the electrochemical performance in Li-ion technology

Iratxe de Meatza, Imanol Landa-Medrano, Susana Sananes-Israel, Aitor Eguia-Barrio, Oleksandr Bondarchuk, Silvia Lijó-Pando, Iker Boyano, Verónica Palomares, Teófilo Rojo, Idoia Urdampilleta

<u>Submitted to</u> : Journal of Energy Storage

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 814389

$LiNi_xMn_yCo_zO_2$ materials

Layered structure cathode materials $LiNi_xMn_yCo_zO_2$ (x + y + z = 1, NMC)

- Li insertion during lithiation of NMC material
- Lower Co content than LCO → less expensive
- Various NMC grades available

Goal: understand the sensibility of NMC811 material to ambient air

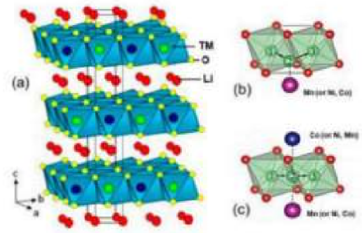


Figure 2. (a) Layered structure of NCM compound. Colors of atoms are green (Li), red (O), and silver/purple/blue are Ni, Mn, Co transition-metal cations, respectively. (b) Tetrahedral site pathway. (c) Oxygen dumbbell pathway for Li^+ ions.

→ Specific capacity, Lower Cost

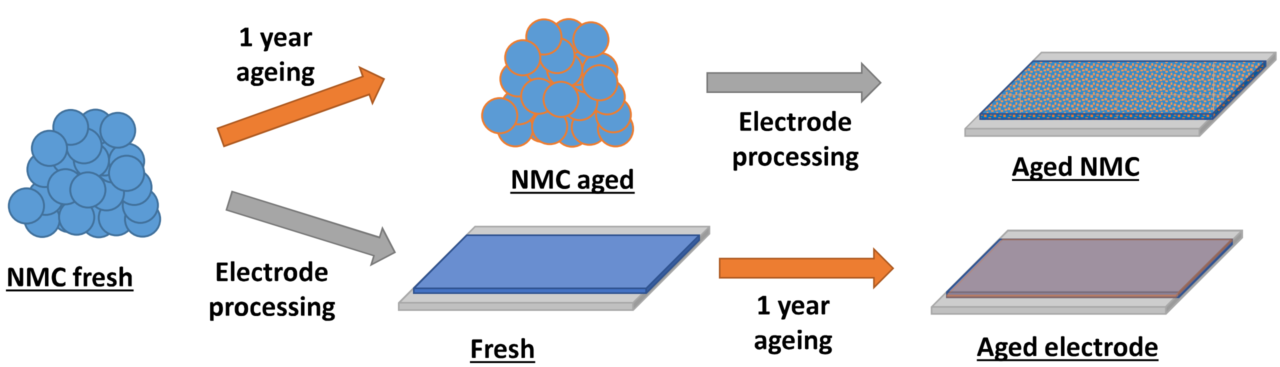
NMC111	NMC532	NMC622	NMC811
Specific capacity 140 mAh/g	Specific capacity 160 mAh/g	Specific capacity 170 mAh/g	Specific capacity 200 mAh/g

← Cycle life stability, Safety

Energies 2020, 13, 6363; doi:10.3390/en13236363
https://researchinterfaces.com/know-next-generation-nmc-811-cathode/

Ageing of NMC811 powders and electrodes

NMC811 processing : AM/C65/PVDF: 95/2/3; LL=4,0 mAh/cm²; 21 mg/cm²



Electrochemical characterisation in Full coin cell
- Cycle life ageing with DVA, EIS and 1C pulse test every 25 cycles
- Power test at 50%SOC

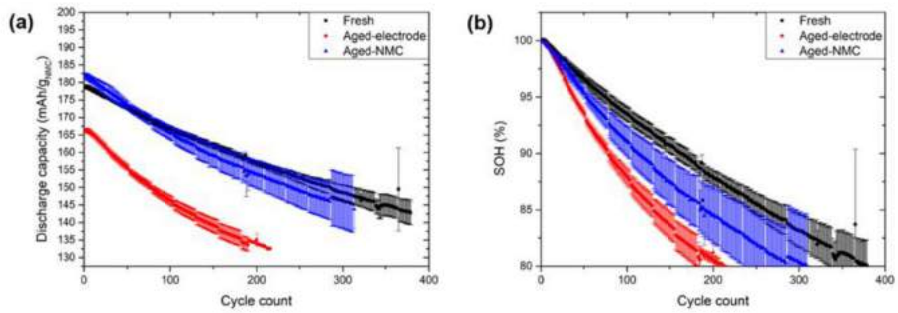
Physicochemical characterisation
- XRD of NMC811 powders &electrodes
- XPS of NMC811 powders &electrodes
- FE-SEM & EDX

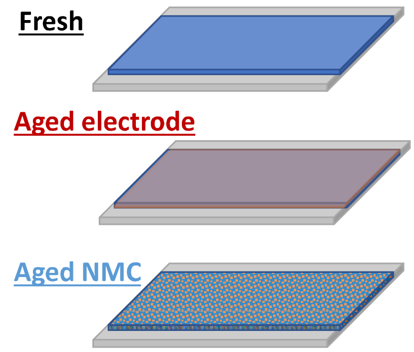
Electrochemical characterisation: cycle life

Galvanostatic cycling experiments at C/3 [2,8-4,2V]

Graphite anode, N/P = 1,15

Electrolyte: 1M $LiPF_6$ in EC:DMC 1:1 + 2%VC



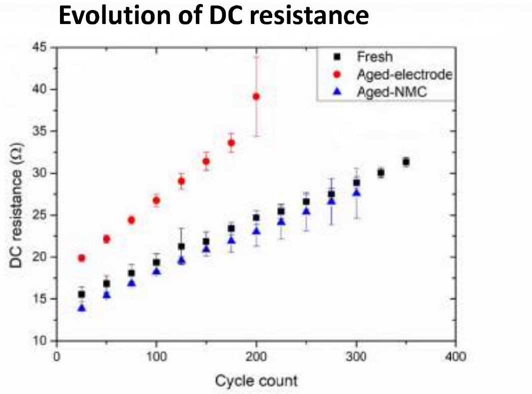


- Lower discharge capacity obtained for aged electrodes & lower cycle life
- Electrodes processed with aged NMC showed a higher initial discharge capacity at BoL but lower cycle life than fresh electrodes

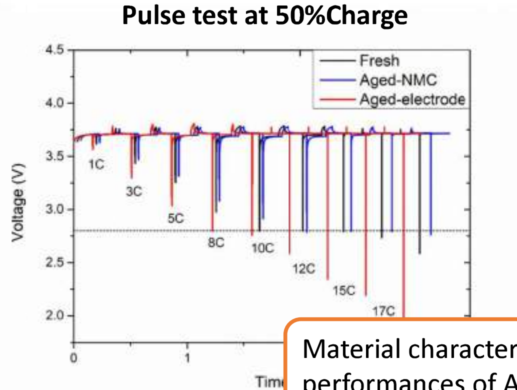
Electrochemical characterisation: DC resistance & pulse test

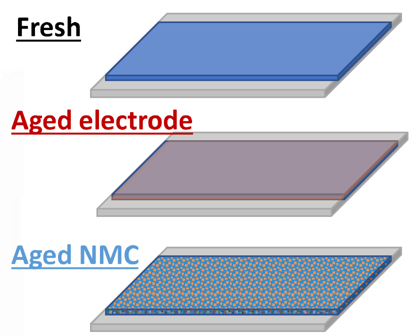
DC resistance measurement over cycle life: 1C discharge pulse of 30 s every 25 cycles

Evolution of DC resistance



Pulse test at 50%Charge

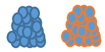




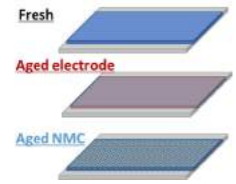
Material characterisation needed to understand EC performances of Aged-NMC

- Aged electrode: higher double layer resistance (Rdl) at both BOL and EOL → formation of a resistive layer (EIS)
- DC resistance is higher for cells with Aged electrode → in agreement with previous results (unable to widthstand 8C discharge pulse without reaching 2,8V cut-off.
- Aged NMC and fresh cells presented a similar resistance increase upon cycling → in agreement with cycle life measurements

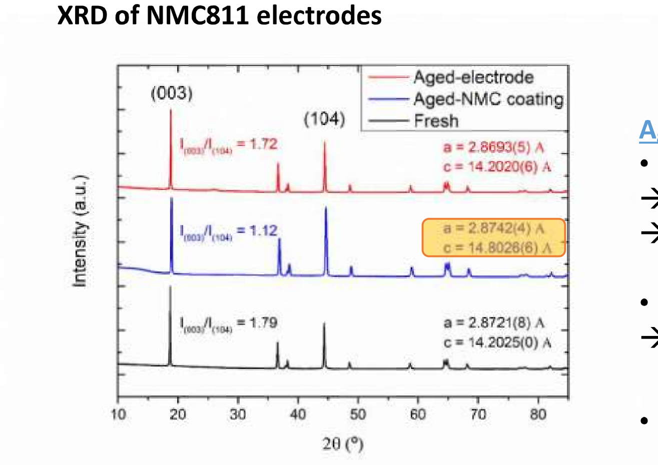
Materials characterisation: X-Ray Diffraction (XRD)

XRD of NMC811 powders 

- No observable differences in the bulk structure



XRD of NMC811 electrodes



Fitted with:
NMC: R −3m hexagonal space group (JCPDS No. 00-85-1968, $Li_{0.89}Ni_{1.01}O_2$)
Aluminium: (Fm −3m, cubic, JCPDS No. 03-65-2869)
Graphite: (R −3m, hexagonal, JCPDS No. 01-73-5918)

<u>Aged NMC electrode:</u>

- High *c* value: Enlarged interlayer distance in the crystal structure

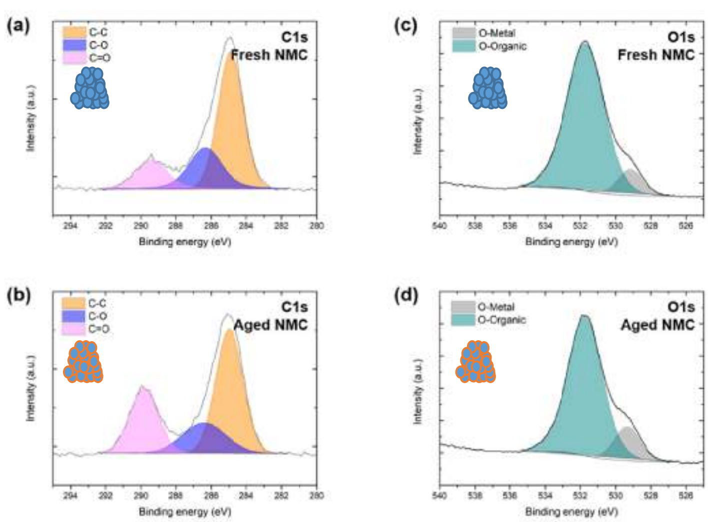
→ Increase of Li^+ mobility
→ in agreement with EIS and DC resistance measurements

- $I_{003}/I_{104} < 1.2$: cation mixing (interchange between Li^+ and Ni^{2+} ions)

→ Lower cycle life performances

- Same structural differences observed after cycle life.

Materials characterisation: XPS of NMC powders



<u>Deconvolution of the C 1s region:</u>

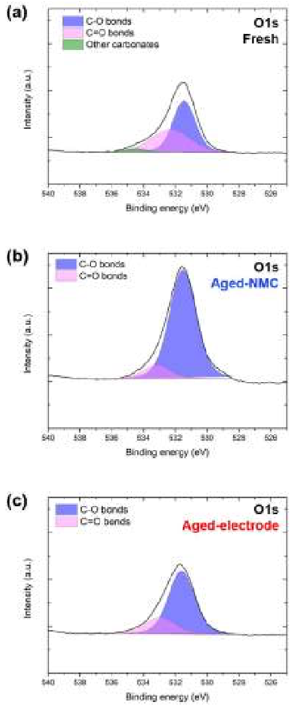
C-C 284.9 eV → conductive layer
C–OR 286.4 eV
C=O 289.6 eV
} carbonate-like species

<u>Deconvolution of the O 1s region:</u>

O-Metal 529.2 eV
O-Organic 531.7 eV

Fresh NMC: presence of native carbonates layer in fresh particles
Aged NMC: Air exposure of NMC811 → formation of carbonate-like species (↑C=O) in the surface of NMC811 particles

Materials characterisation: XPS of NMC electrodes



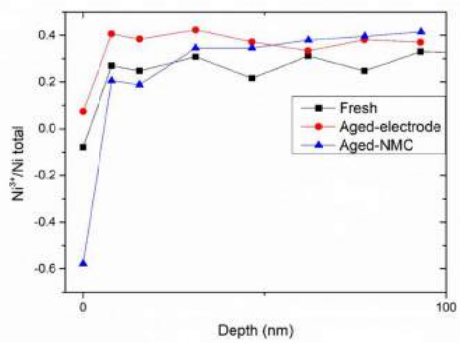
<u>O1s Similar signal for Fresh and Aged NMC electrode</u>

Area of carbonate signal is:

Fresh ≈ aged-NMC < aged-electrode

→ Carbonate layer is washed during electrode processing with NMP

<u>Ni^{3+}/Ni total fraction with the depth of the sample</u>



Ni^{3+}/Ni fraction calculated by the satellite method[1]

Presence of a nickel valence gradient from the particle surface (Ni^{2+} rich) to the core (Ni^{2+} poor) enhances the thermal and cycling stability of NMC811[2]

→ Gradient of Ni obtained by cation mixing can explain unexpected performances of Aged NMC cells

[2]R. Lin, et al, Hierarchical nickel valence gradient stabilizes high-nickel content layered cathode materials, Nat. Commun. 12 (2021)

[1]O. Bondarchuk, A. P. LaGrow, A. Kvasha, T. Thieu, E. Ayerbe, I. Urdampilleta, Appl. Surf. Sci. 2021, 535, 147699.

Conclusions of the study

<u>Context:</u>

- NMC811 powder and electrodes were exposed for 1 year to ambient air
- Materials were processed and the resulting electrodes were tested *vs.* graphite anode (cycle life and pulse test)

<u>Conclusions:</u>

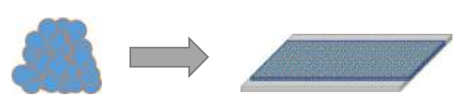
<u>Fresh</u>

- Highest cycle life

<u>Aged electrode</u>

- Lowest electrochemical performances
- Presence of a resistive carbonate layer (EIS, pulse test and XPS)

<u>Aged NMC</u>



- Electrochemical performances beyond expectations
- Low internal resistance measured

  <u>Explained by:</u>
  - *The formation of a carbonate layer in the NMC powder surface, redistributed during material processing*
  - *Formation of a buffer region with higher Ni^{2+} fraction in these electrodes in agreement with cation mixing observed by XRD*

➢ **Storage of NMC811 electrodes is critical → store under dry conditions after electrode coating**

➢ **Storage of NMC811 powder is less critical (similar EC performances) → removal of contaminants can be recommended to improve cycle life**

Acknowledgements

> EU Projects funding

> CIDETEC **Li-ion + Pilot Plant teams**

Jasmina Agote, Iñigo Arzac, Enara Bueses, Iker Boyano, Adrián Calzón, Iker Castrillo, Andoni Contreras, Aitor Eguia, Larraitz Gamborena, Pedro Lamas, Galyna Kvasha, Shaila Lanchas, Imanol Landa, Amane Lago, Silvia Lijó, Ane Muguruza, Carmen Palacios, Iratxe de Meatza, Idoia Urdampilleta

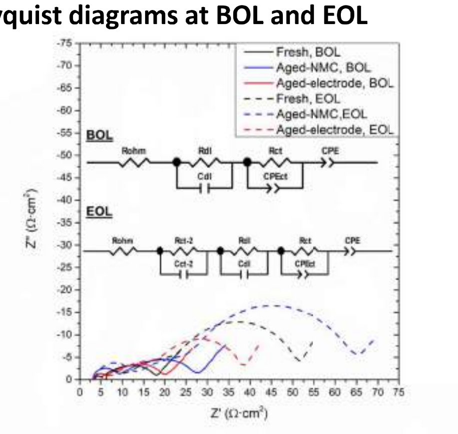
> NMC811 ageing study
Oleksandr Bondarchuk, Verónica Palomares, Teófilo Rojo

Thanks for your attention!!

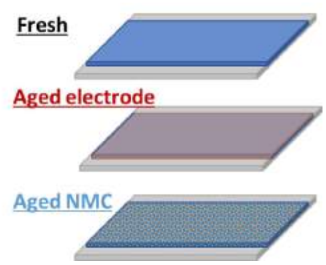
Electrochemical characterisation: EIS measurements

Resistance measurements: Electrochemical Impedance Spectrometry

Nyquist diagrams at BOL and EOL



BoL	R ohm / W	R DL / W	R CT / W
Aged electrode	1.47 ± 0.05	2.45 ± 0.14	0.11 ± 0.01
Fresh	1.47 ± 0.20	2.03 ± 0.20	0.22 ± 0.08
Aged NMC	1.14 ± 0.44	0.45 ± 0.39	0.04 ± 0.04



EoL	R ohm / W	R DL / W	R CT / W	Rct-2 / W·cm2
Aged electrode	3.95 ± 0.29	6.82 ± 0.38	30.57 ± 8.28	25.16 ± 3.32
Fresh	4.68 ± 1.50	3.04 ± 0.28	25.96 ± 5.26	18.77 ± 2.21
Aged NMC	4.75 ± 1.00	1.73 ± 0.28	17.25 ± 2.25	21.00 ± 7.83

- Aged electrode: higher double layer resistance (Rdl) at both BOL and EOL → formation of a resistive layer
- Aged NMC : lower double layer resistance (Rdl)
- Charge transfer resistance (Rct): Similar for aged electrodes and **fresh** → Particle core unaffected

Stellantis plan for vehicle electrification

XXX

14/04/2022

Syllabus

1. Company introduction and position in the supply chain
2. State-of-the-art
3. The (green) future
4. Challenges, bottlenecks, known limitations
5. The future beyond solid state cell technology with Li-metal
6. CRF's view on mass production of the SPIDER technology
7. CRF' view on cost, sustainability, impact on climate of your activities (within and beyond the project)

Company Introduction and position in the supply chain

STELLANTIS

CRF

1978 – 2022
More than 40 years
of automotive R&D

- To develop and transfer innovative powertrains, vehicle systems & features, materials, processes and methodologies together with innovation expertise in order to improve the competitiveness of Stellantis products
- To represent Stellantis in European and National collaborative research programs, joining pre-competitive projects and promoting networking actions
- To support Stellantis in the protection and enhancement of intellectual property

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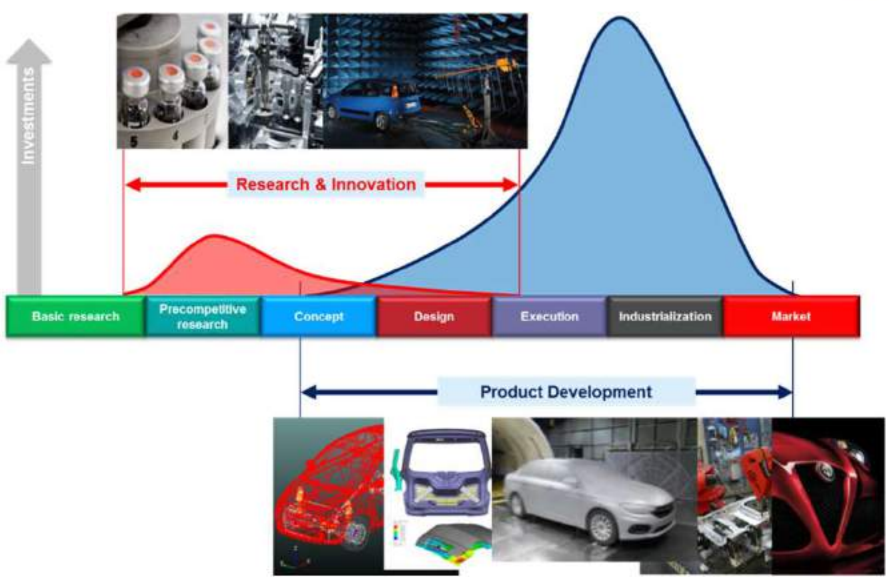
Company Introduction and position in the supply chain

STELLANTIS



CRF

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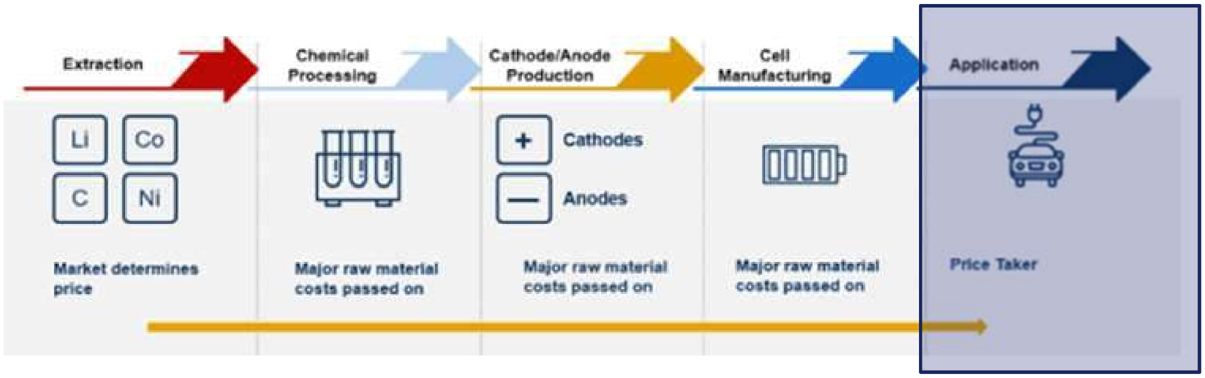
What is Stellantis?

Stellantis is a multinational automotive manufacturing corporation formed in 2021 on the basis of a 50-50 cross-border merger between the Italian-American Fiat Chrysler Automobiles and the French PSA Group.

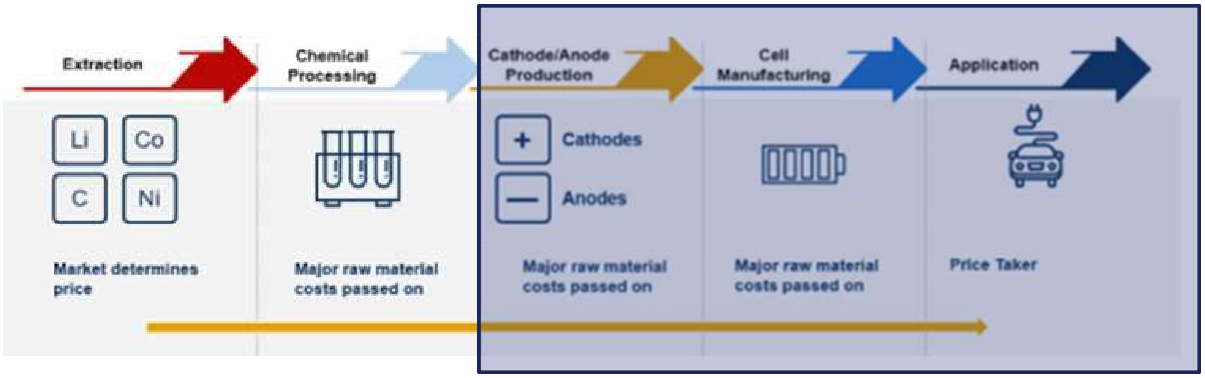
- Activity → design and manufacture of automobiles
- 6th largest automaker worldwide
- **6 Millions vehicles/year**
- Employees: 300,000
- Manufacturing facilities in 30 countries



Classical end user role...
(untill 2020)

Company Introduction and position in the supply chain

STELLANTIS



..but things are rapidly changing...

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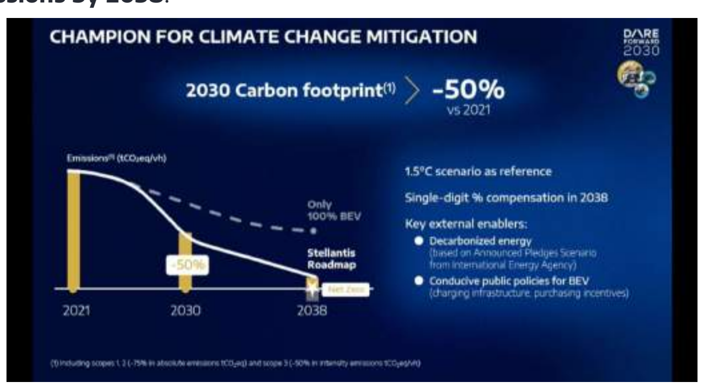
Stellantis plan for sustainability

STELLANTIS

- CEO Carlos Tavares recently presented the **strategic plan** of the company targeting to have **100%** of sales in **Europe** and **50%** of sales in the **United States** to be **BEVs** by the **end of this decade**.
- The plan is to have global annual **BEV** sales of **five million vehicles** by 2030.
- Stellantis has also committed to becoming “the industry champion in the fight against climate change”, reaching **carbon net zero emissions by 2038**.



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Stellantis plan for sustainability

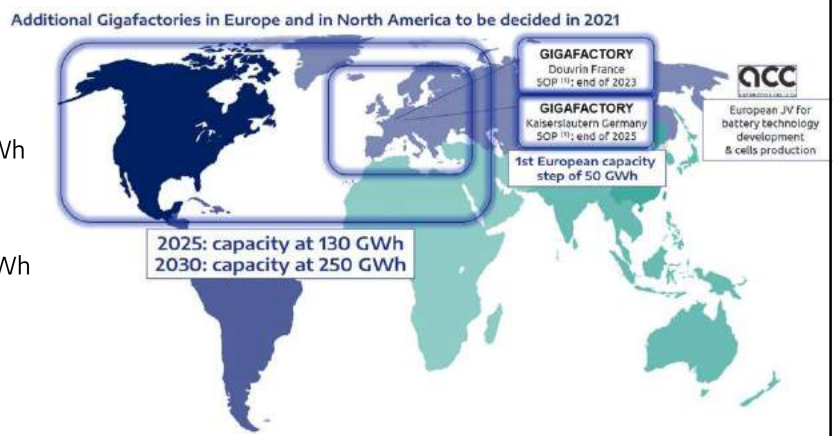
Stellantis announced at its EV Day 2021 on July 8 its global strategy to source over **260 GWh** of electric vehicle battery capacity **by 2030**, which will be supported by **5 gigafactories** in Europe and North America.

In **Europe**, Stellantis currently has **two gigafactory** projects, one in **France** and one in **Germany**, under its **joint venture with Total-SAFT**, called **Automotive Cells Company** (**ACC**).

Announced joint-ventures in USA:

- **Samsung SDI**
New plant with a capacity of 23 GWh by 2025

- **LG Chem**
New plant with a capacity of 40 GWh by 2040



ACC values

LOW CARBON FOOTPRINT

RECYCLABILITY

ETHICAL SUPPLY CHAIN

GREEN FACTORIES

Li-ion technologies

STELLANTIS

- **High energy-density** option
- **Nickel cobalt-free** alternative by 2024
- **Solid-state** battery technology planned in 2026

Stellantis is aiming to reduce battery costs using its technical expertise and manufacturing synergies, with it targeting to reduce EV battery pack costs by over 40% from 2020 to 2024 and by more than an additional 20% by 2030.

EV costs equivalent to ICE vehicles by 2026

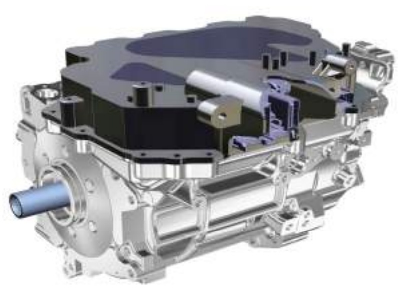
Electric powertrains « Emotors »

STELLANTIS

Nidec PSA emotors SAS → joint venture created on May 2018

The two 50/50 shareholders
- Japanese motor manufacturer, Nidec Corporation
- French OEM, PSA Groupe (now Stellantis)

Products: state of the art high-performance and competitive electric traction motor range for electrified vehicles from 48 V Mild Hybrid up to 400 V Full Electric vehicles.



Solid state batteries

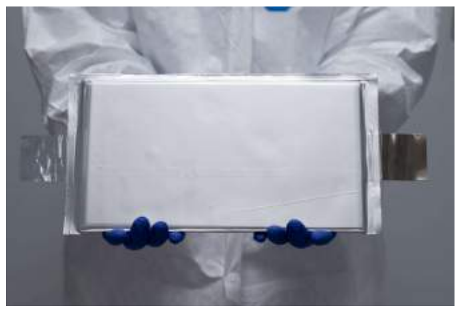
STELLANTIS

Joint development agreement between Stellantis and **Factorial Energy** in November 2021

From Factorial web site:

Factorial's advances are based on FEST™ (**Factorial Electrolyte System Technology**)→ proprietary solid electrolyte material that enables safe and reliable cell performance with high-voltage and high-capacity electrodes and has been scaled in 40Ah cells that perform at room temperature.

FEST™ is safer than conventional lithium-ion technology, extends driving range, and is drop-in compatible for easy integration into existing lithium-ion battery manufacturing infrastructure.



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Current bottlenecks

STELLANTIS

- Availability of materials: Li, Co, graphite → **Critical raw materials** → **Circular economy** approach
- **Production costs** (e.g. energy involved in the processes) → Cost of **energy**
- **Sustainability** (e.g. removal of NMP based processes) → New solutions for material processing
- Current **performances** (energy density and specific energy, fast charge) → need to improve
- **Charging infrastructure** → essentially missing in many countries
- **Carbon footprint** of electric **energy production** → need to increase the use renewable sources
- **Customer acceptance** →e.g. range anxiety (even if the EV is perceived as new and cool)

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Post Li metal technologies

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Hydrogen and fuel cells
→ Really zero emissions
→ Availability/cost of PGM and fuorinated polymeric membranes
→ H_2 production
→ Missing H_2 distribution infrastructure
→ Not feasible before 2035/2040

Bio/syntetic fuels
→ Obtained converting waste biomasses or directly CO_2
→ Can be carbon neutral
→ Noxiuos emissions are present (NOx, CO, HC)
→ Available in the short/medium term (2030)
→ Existing distribution infrastructure

Na/Mg batteries
→ No use of critical raw materials
→ Energy and power densities lower than Li-based systems
→ Difficult application in automotive field

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Mass production of Spider technology

STELLANTIS

Main advantages of the Spider cell concept for CRF

→ Potential **increase of cell performances** with respect to current Li-ion cells in terms of energy and power densities and in terms of cycle life.

→ **Avoid the use of critical raw material** (Co) in cathode material manufacturing for SSB applications.

→ **Sustainability** of the process (water based, NMP-free).

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Mass production of Spider technology

STELLANTIS

Possible models for future production of Spider cells

First option
Stellatins/ACC could take care of the industrialization of the process obtaining a license by the Spider partners holding the IPR

Second option
Stellatins/CRF could support Spider partners in a follow-up project, in order to increase the TRL of the technologies developed, closing the gap with the possible industrialization of the processes.

STELLANTIS

Thanks for your attention!