Recycling direct des batteries :

focus sur les technologies sous- et supercritiques

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N. Hayagan, I. Gaalich, L. Croguennec, M. Morcrette, P. Loubet, G. Sonnemann,
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Site ICMCB – Light^TECH
Université de Bordeaux / IUT

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Bordeaux INP / Ensmac

MATERIALS AND SUPERCRITICAL FLUIDS AT ICMCB

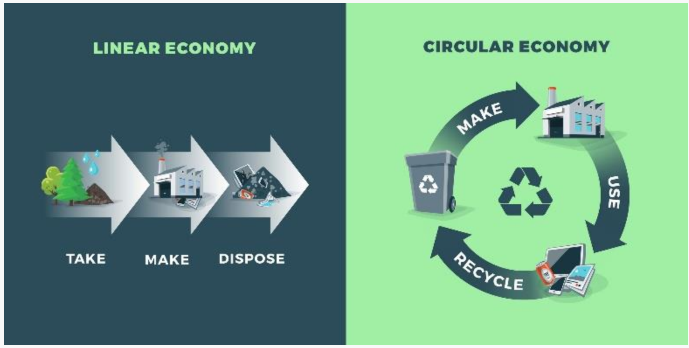
Advanced Materials by Design

Geominerals
Nitrides
Oxydes
Metals
Sulphides
Phosphides

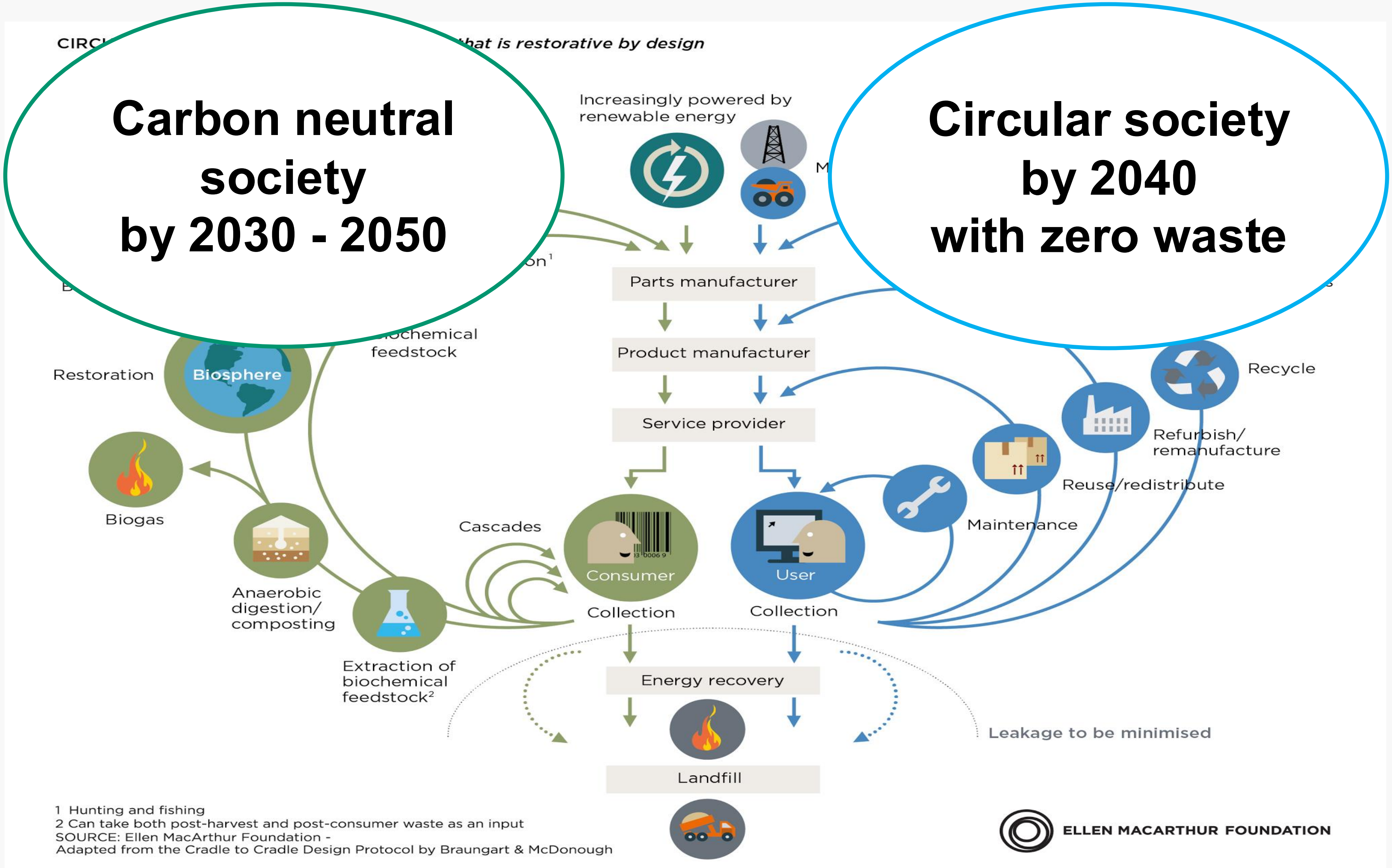
Recycling of Materials

Carbon fibers
Catalysts
Solar cells
Food packagings
Permanent magnets
Batteries
Medical devices

FROM SUSTAINABLE DEVELOPMENT
TO
CIRCULAR ECONOMY



CIRCULAR ECONOMY BUTTERFLY DIAGRAM



MATERIAL RECYCLING – WHY ?

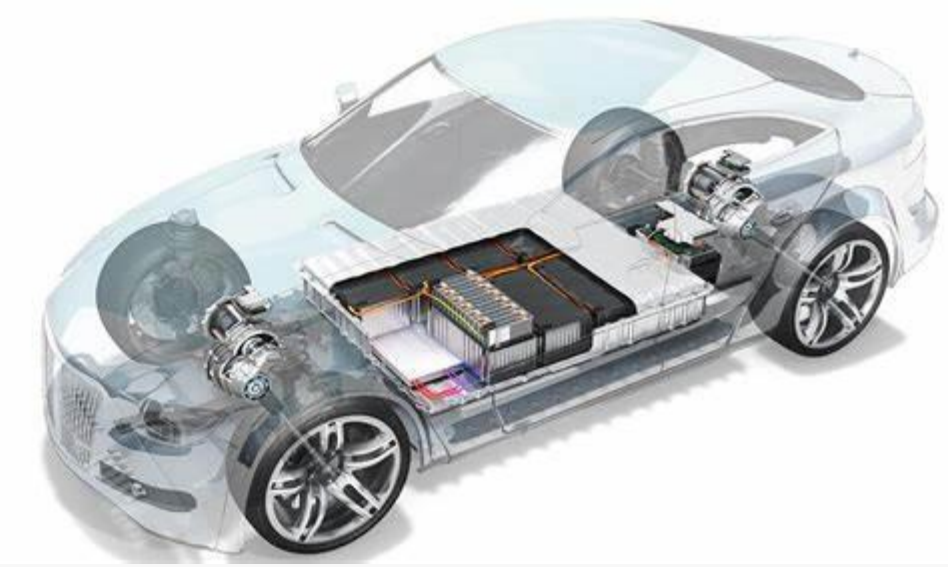
Il faut purifier huit tonnes et demi de roche pour produire un kilo de vanadium, seize tonnes pour un kilo de cérium, cinquante tonnes pour l'équivalent en gallium, et le chiffre ahurissant de mille deux cents tonnes pour un malheureux kilo d'un métal encore plus rare, le lutécium. (…) La seule fabrication d'une puce de deux grammes implique le rejet de deux kilogrammes de matériaux environ, soit un ratio de 1 à 1000 entre la matière produite et les déchets générés.

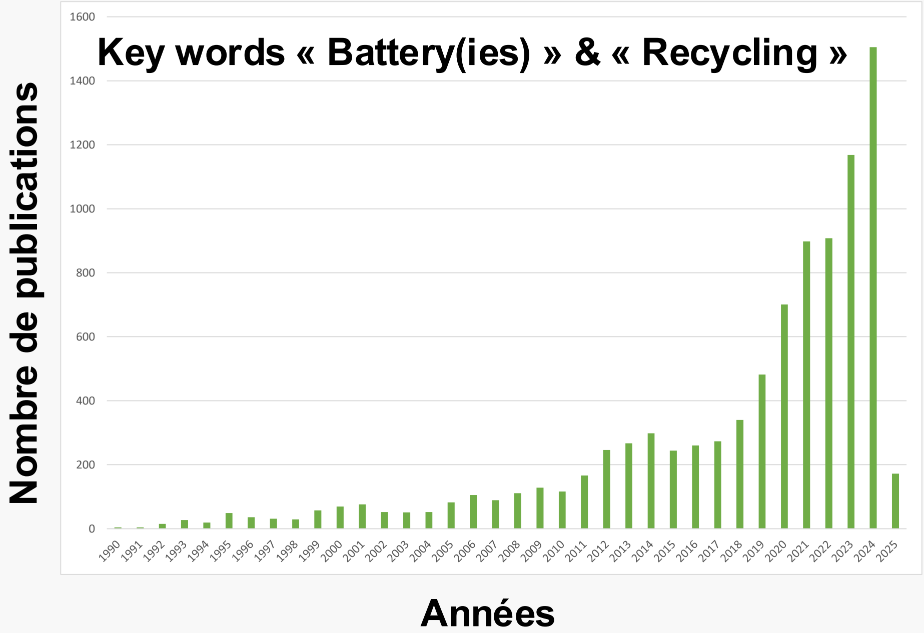
… nous allons consommer davantage de minerais durant la prochaine génération qu'au cours des 70000 dernières années, c'est-à-dire des deux mille cinq cent générations qui nous ont précédés. Nos 7,5 milliards de contemporains vont absorber plus de ressources minérales que les 108 milliards d'humains que la Terre a portés jusqu'à ce jour.

OUTLINE

I – A BRIEF INTRODUCTION TO SUB- AND SUPERCRITICAL FLUIDS

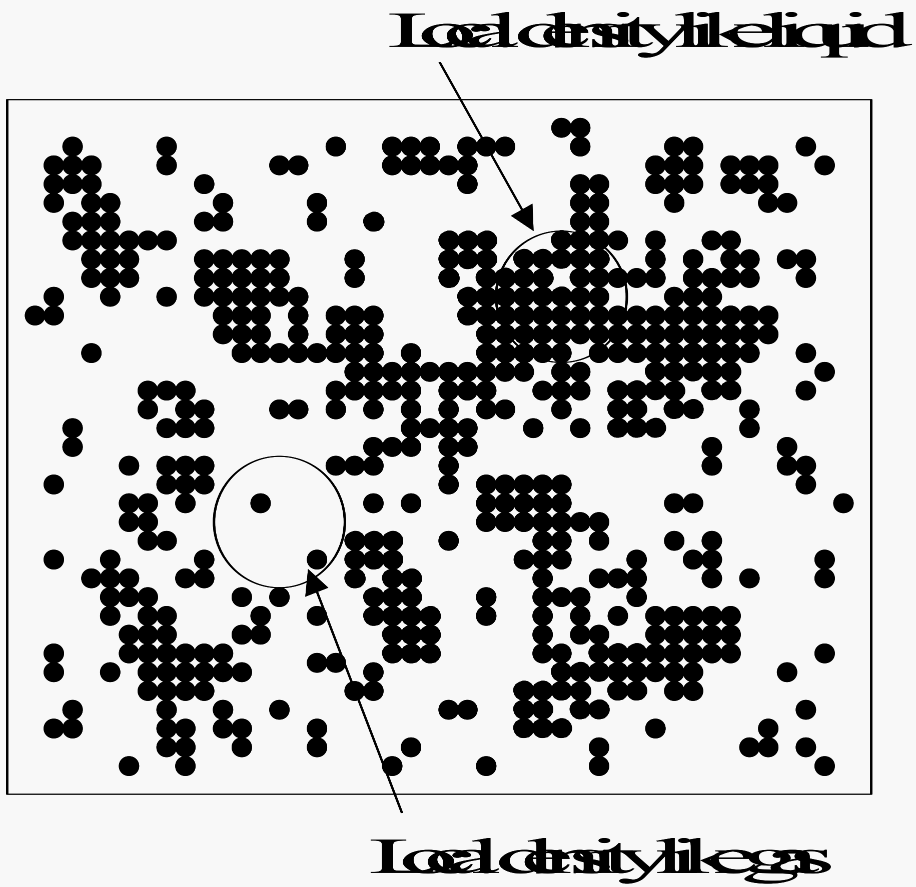
II - DIRECT RECYCLING OF BATTERIES USING PRESSURIZED CARBON DIOXIDE



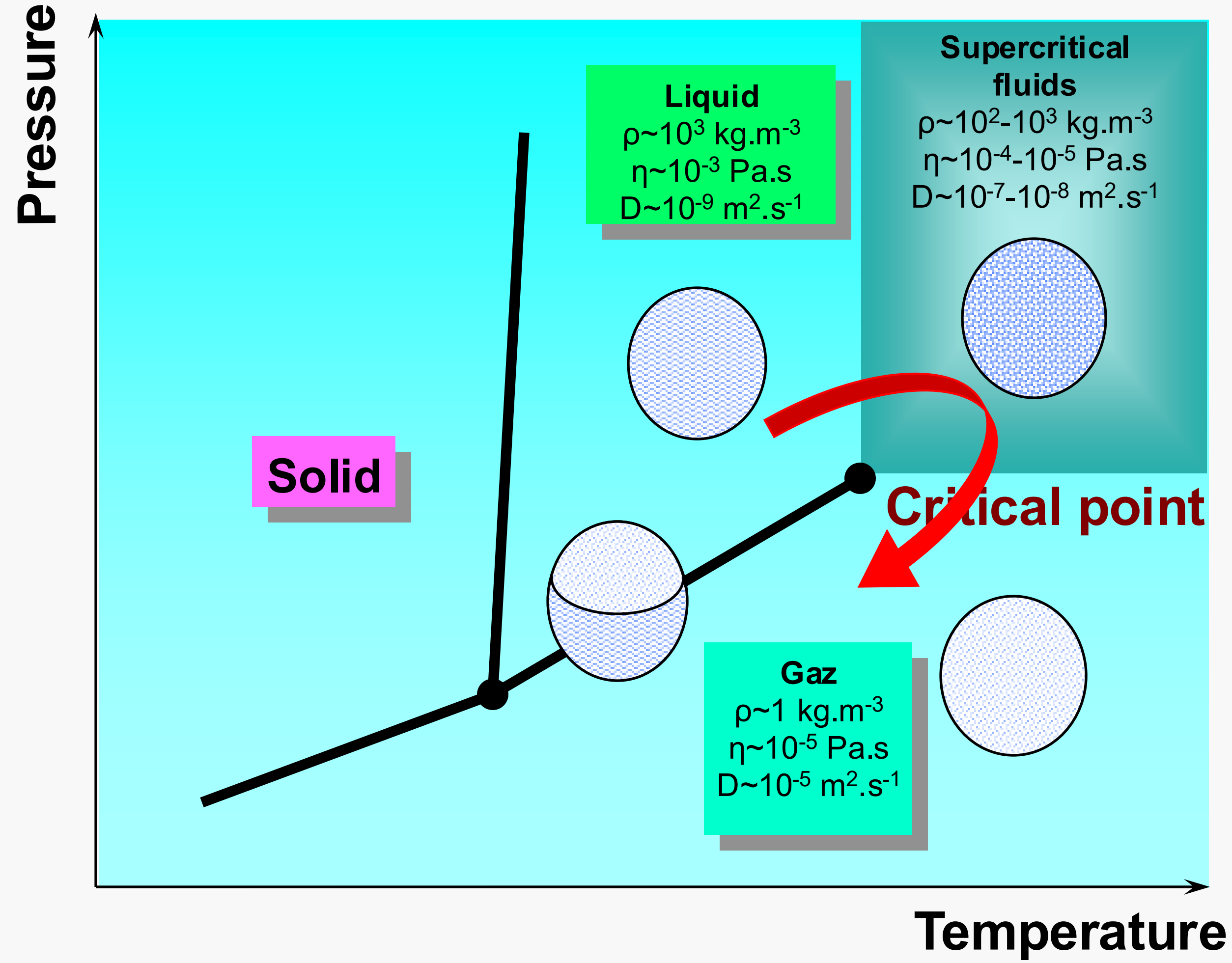


PART III

A BRIEF INTRODUCTION TO SUB- AND SUPERCRITICAL FLUIDS



SUPERCRITICAL FLUIDS ?



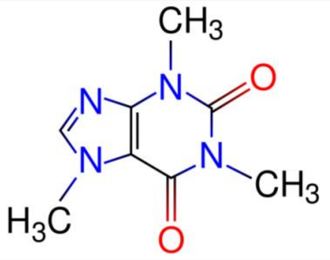
SUPERCRITICAL FLUIDS

Which ones?

Fluids	T_c (°C)	p_c (MPa)	ρ_c (kg.m^{-3})
CO_2	31.0	7.38	468
H_2O	374.0	22.10	322
NH_3	132.4	11.1	235
CH_3CH_3	32.4	4.88	207
$CH_3CH_2CH_3$	96.8	4.25	221
$CH_3(CH_2)_4CH_3$	234	2.90	233
CH_3OH	240	8.00	272
CH_3CH_2OH	243	6.39	276
$(CH_3)_2CHOH$	235.6	5.37	274
CH_3COCH_3	235.0	4.76	278

*Supercritical Fluids and Materials – ISBN 2-905267-55-0, **2007** – Institut National Polytechnique de Lorraine, Vandoeuvre, Eds C. Aymonier, F. Cansell, O. Fouassier.*

SUPERCRITICAL CO_2
Extraction



1er industrial development: extraction of cafein

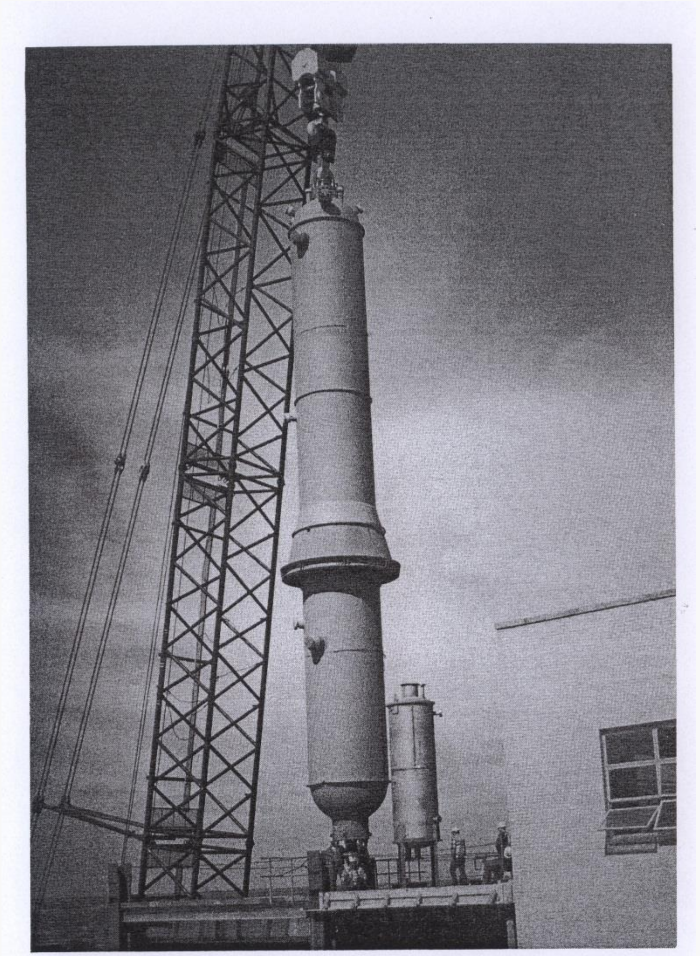
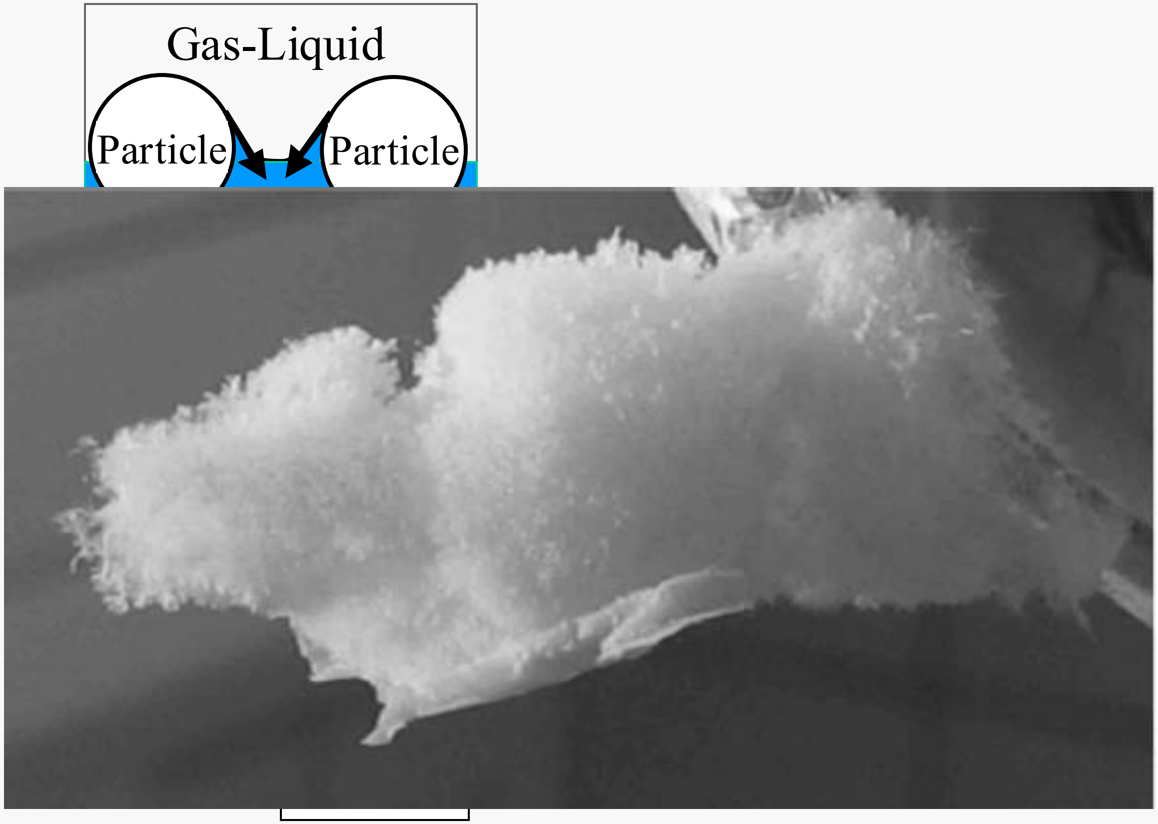


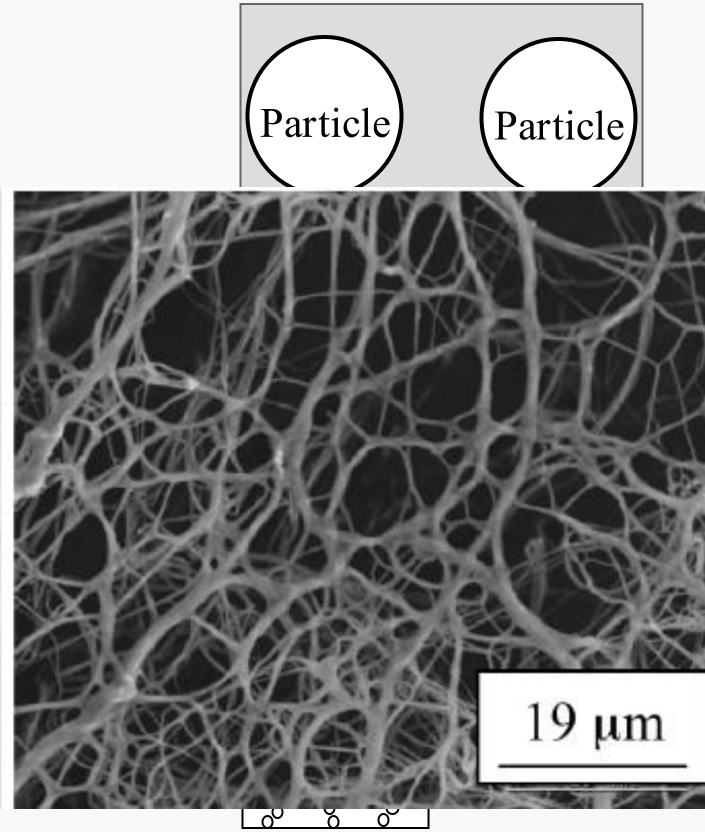
Figure 1.1 Extraction vessels used in the Maxwell House Coffee Company supercritical CO_2 decaffeination plant in Houston, Texas.

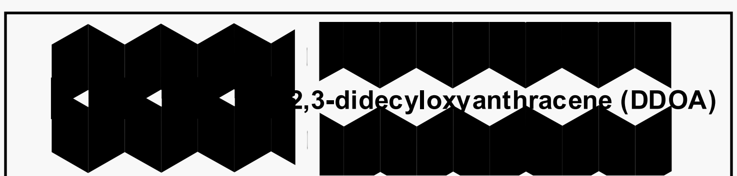
SUPERCRITICAL CARBON DIOXIDE

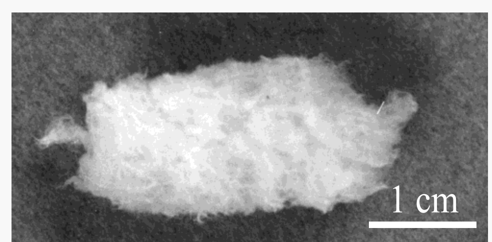
Specific properties

31°C – 73.8 bar









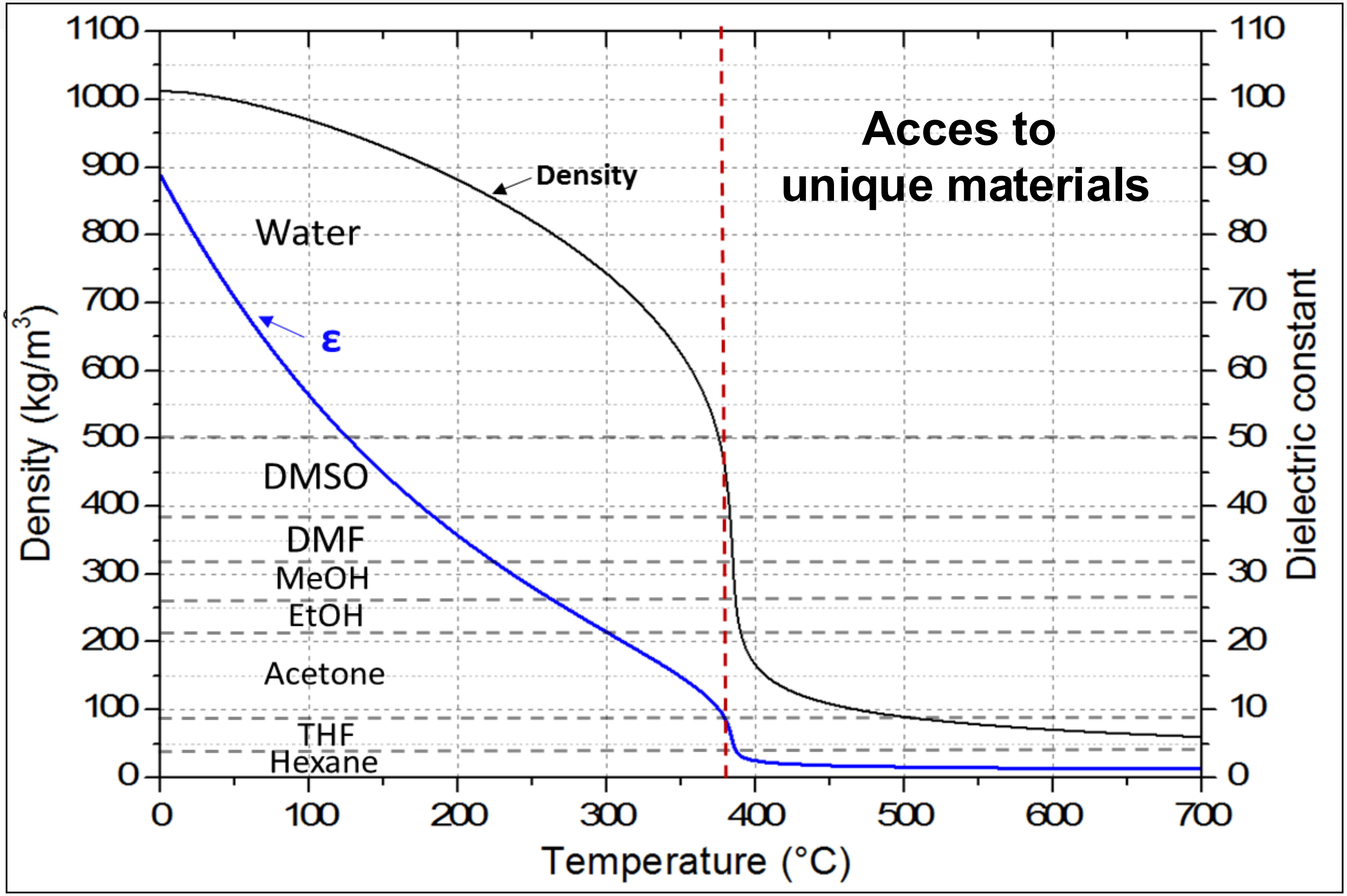
F. Cansell, C. Aymonier, A. Loppinet-Serani, Curr. Opin. Solid State Mater. Sci. 7 ***2003*** *331.*

FR2413709, ***2024***

SUPERCRITICAL WATER

Specific properties

374°C – 221 bar



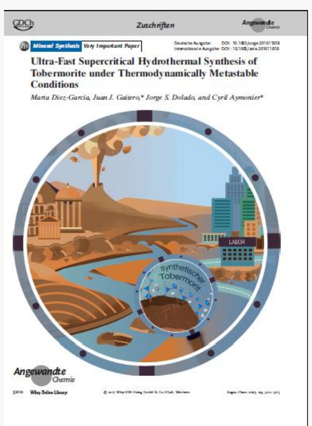
T. Voisin, A. Erriguible, D. Ballenghien, D. Mateos, A. Kunegel, F. Cansell, C. Aymonier, Solubility of inorganic salts in supercritical hydrothermal environment, J. Supercrit. Fluids, **2017,** 120, 18–31.

A NEW OPPORTUNITY FOR THE CONTINUOUS SUPERCRITICAL HYDRO-/SOLVOTHERMAL SYNTHESIS

THE CONTINUOUS PRODUCTION OF SYNTHETIC PHYLLOSILICATES AND IONOSILICATES

Angew. Chem. Int. Ed., **2016**, 55 (34), 9795–10149.
Angew. Chem. Int. Ed., **2017**, 56, 1-6.
ChemNanoMat, **2017**, 3, 614-619.
Chem. Eur. J., **2018**, 24, 519-542.
J. Supercrit. Fluids, **2018**, 134, 184-196.
J. Flow Chem., **2018**, 8(2), 89-95.
Clay Minerals, **2018**, 53(3), 497-503.
J. Geochem. Explor., **2019**, 200, 27-36.
Chem. Eur. J., **2019**, 25, 5814 – 5823.
Chem. Eur. J., **2021**, 27(44), 11309-11318.
ACS Sust. Chem. Eng., **2021**, 9, 49, 16597-16605.
Chem. Soc. Rev., **2022**, 51(11), 4828-4866.
J. Mater. Civ. Eng., **2022**, 34(12), 04022329 (10p).
ACS Sust. Chem. Eng., **2024**, 12, 5, 1911–1917.

11 patents – 2 licensings


Zuschriften
Mineral Synthesis Very Important Paper
Deutsche Ausgabe: DOI: 10.1002/ange.201611858
Internationale Ausgabe: DOI: 10.1002/anie.201611858
Ultra-Fast Supercritical Hydrothermal Synthesis of Tobermorite under Thermodynamically Metastable Conditions
Marta Diez-Garcia, Juan J. Gaitero,* Jorge S. Dolado, and Cyril Aymonier*

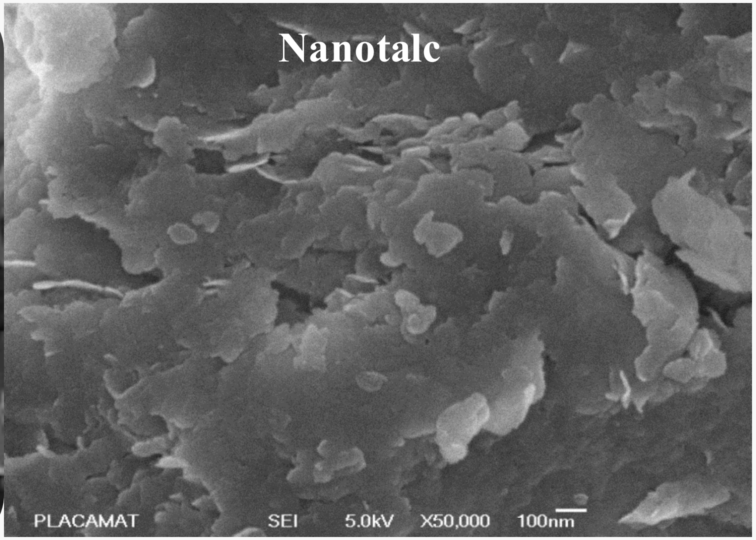
Coll. F. Martin (GET, Toulouse), F. Jouffret & C. Careme (IMERYS), J.S. Dolado (CFM, San Sebastian)

Green Concrete
Cross-Border Collaborative Laboratory

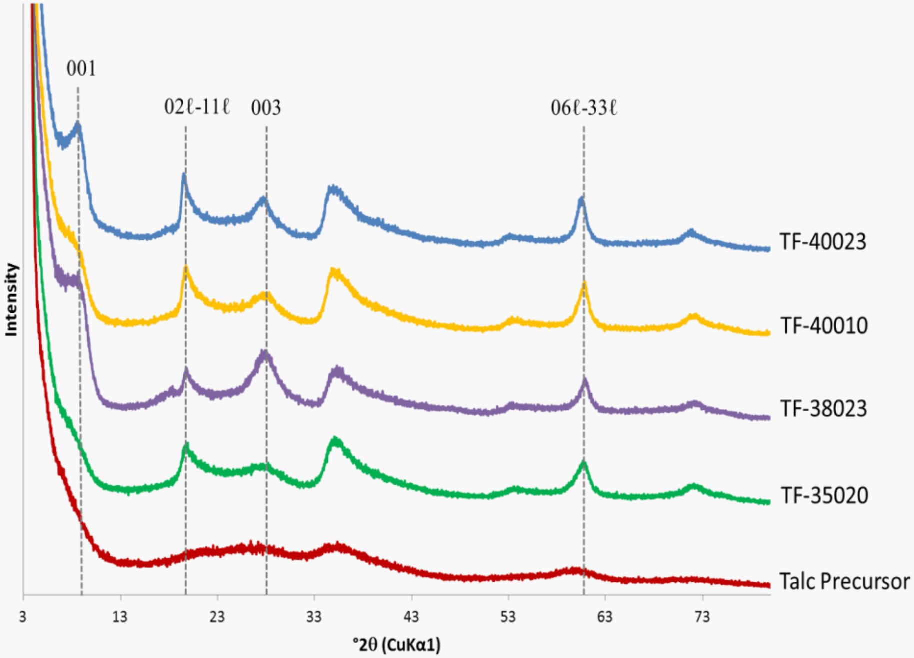
SYNTHETIC TALC AS AN ALTERNATIVE TO NATURAL ONE

NANOTALC

Natural talc
1 µm



Nanotalc
PLACAMAT
SEI
5.0kV
X50,000
100nm



001
02ℓ-11ℓ
003
06ℓ-33ℓ
Intensity
TF-40023
TF-40010
TF-38023
TF-35020
Talc Precursor
3
13
23
33
43
53
63
73
°2θ (CuKα1)

SYNTHESIS OF SYNTHETIC TALC

Towards a continuous and sustainable manufacturing at larger scale

New facility commissionned this year

2022

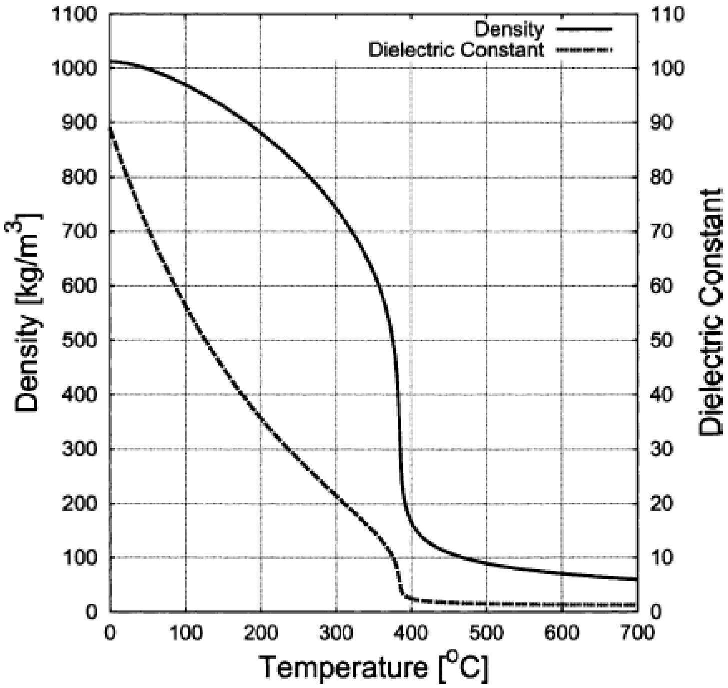
With the courtesy of the IMERYS company

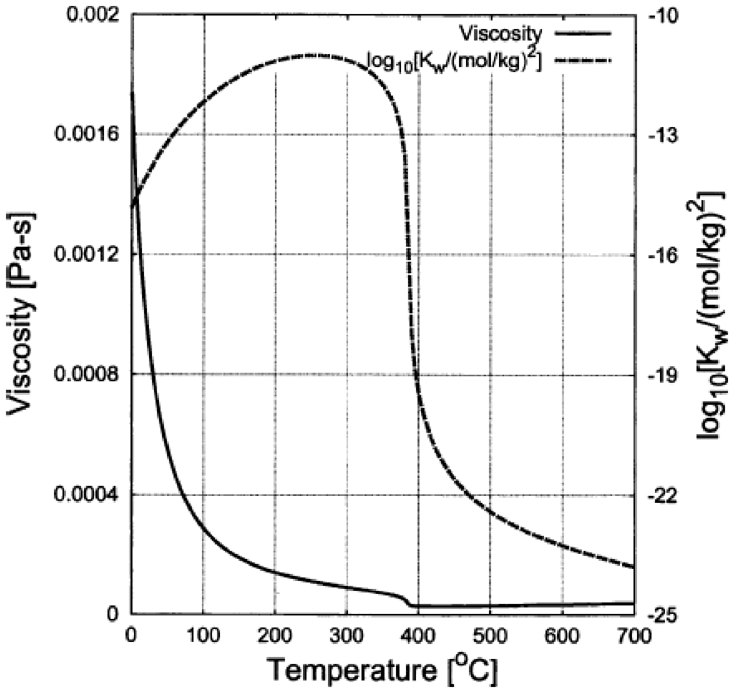
SUPERCRITICAL WATER

Specific properties

374°C – 221 bar

-288



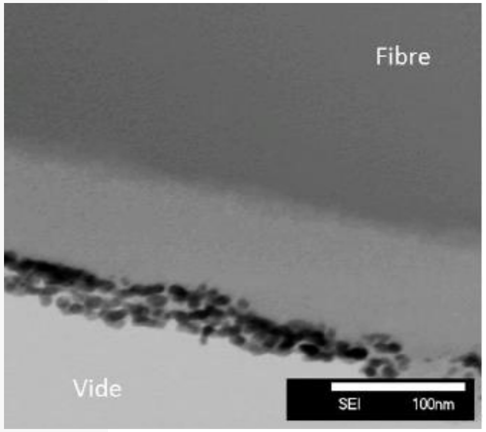


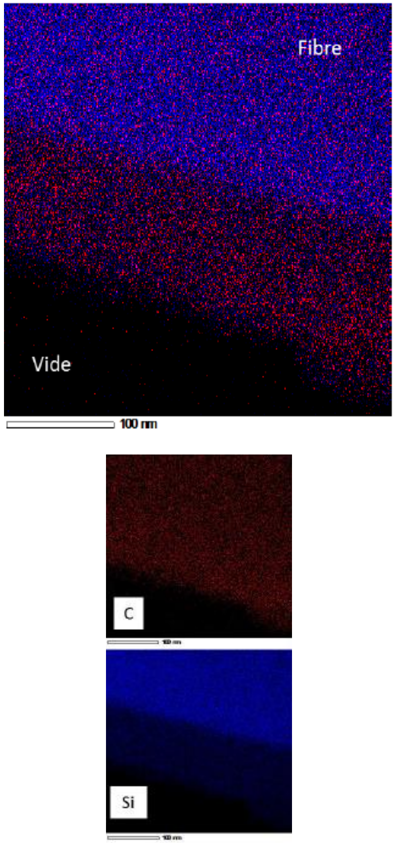
mperature

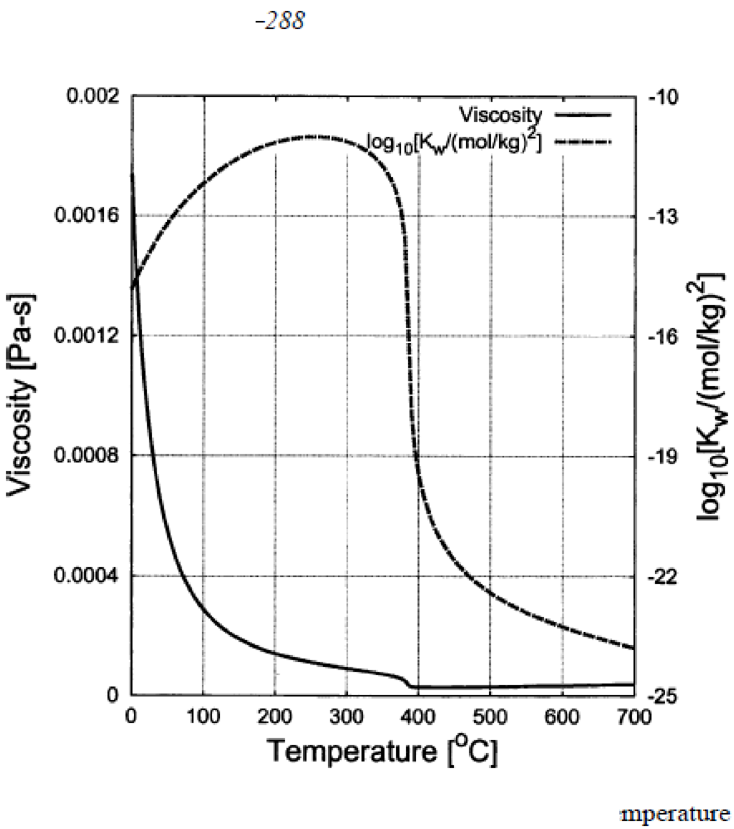
SUPERCRITICAL WATER

Specific properties

374°C – 221 bar







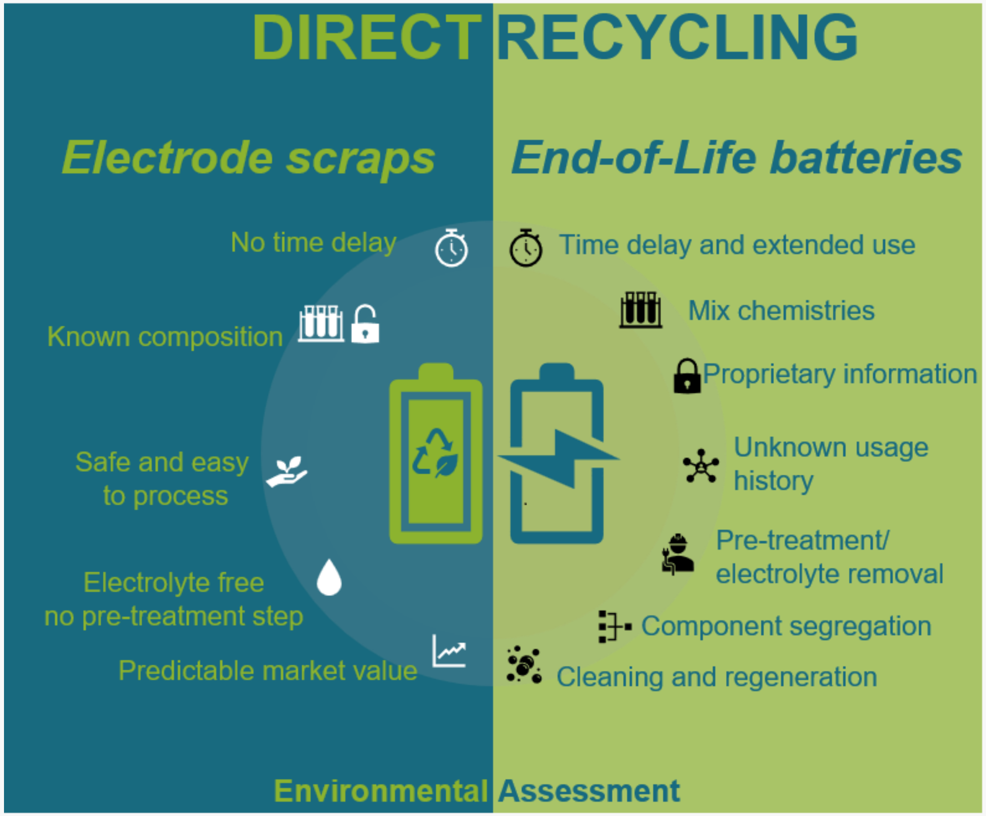
WO 2014114874
WO2019106257
FR2106670
FR2106671
Coll. Safran Ceramics

Acid or basic-based surface treatment with water !

L. Henry, N. Biscay, C. Huguet, S. Loison, C. Aymonier, A water-based process for the surface functionalization of ceramic fibres, Green Chem., **2020**, 22, 8308-8315.

PART II

DIRECT RECYCLING OF BATTERIES USING PRESSURIZED CARBON DIOXIDE

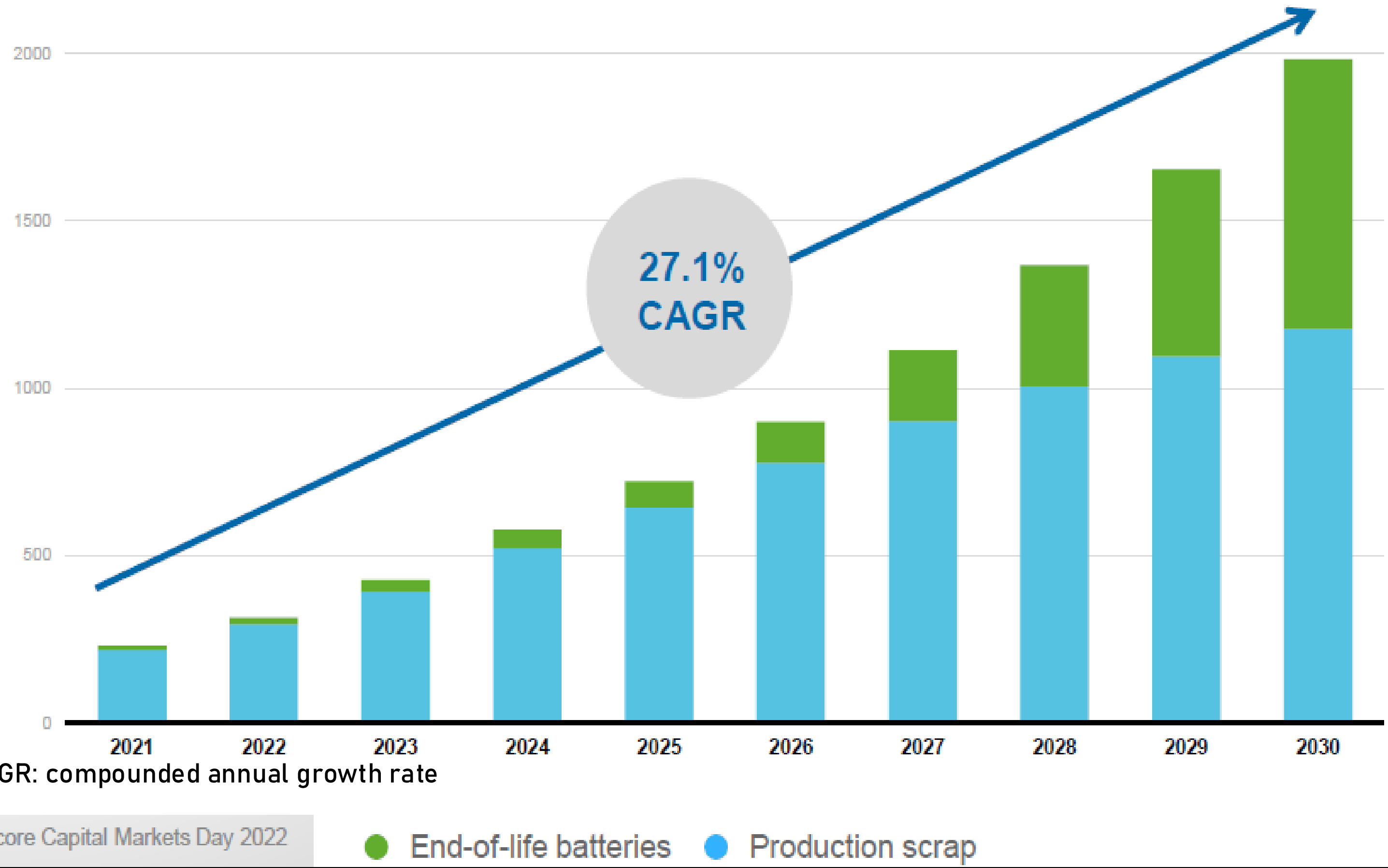


N. Hayagan et al., Batteries Supercaps, ***2024,*** *7, e202400120 (7).*

RECYCLING OF BATTERIES

Direct recycling: interest for production scrap

End-of-life EV batteries and production scrap available for recycling (kMT, global)[4]



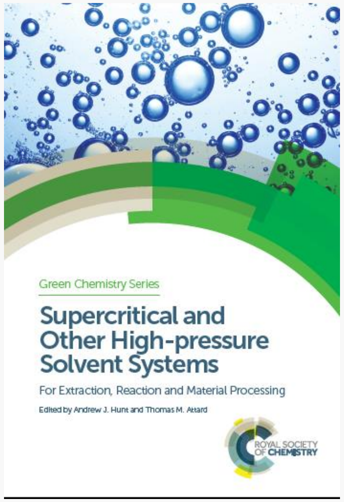
CAGR: compounded annual growth rate

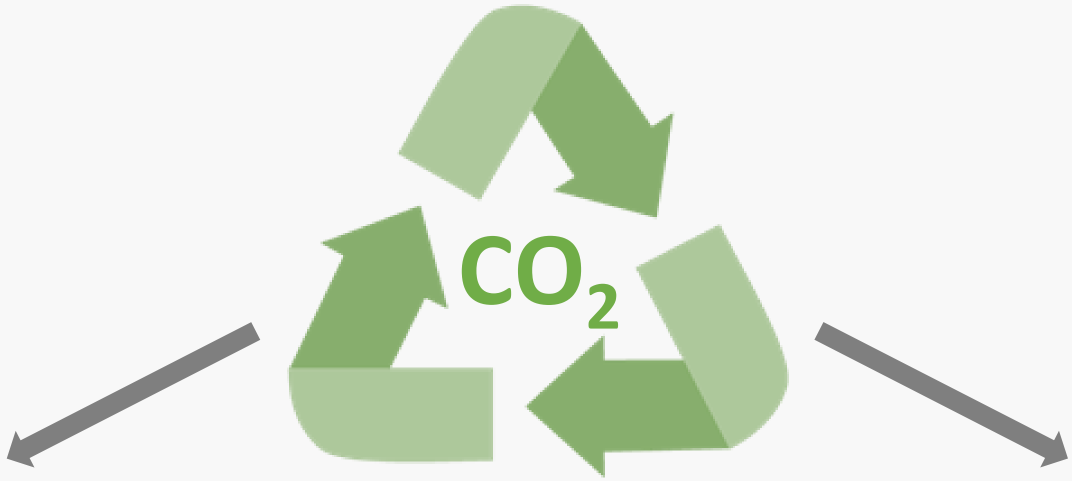
Umicore Capital Markets Day 2022

Focus on the sub- and supercritical fluid technologies

SUPERCRITICAL CO_2

Main fields of application of the $scCO_2$-based technologies in the field of material recycling





Extraction
- *LIB electrolyte*
- *Heavy metals*
- *Polymers*

Delamination
- *PCB*

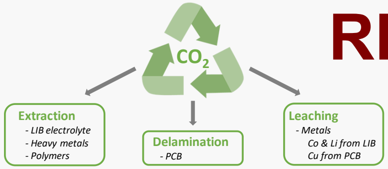
Leaching
- *Metals*

  Co & Li from LIB

  Cu from PCB

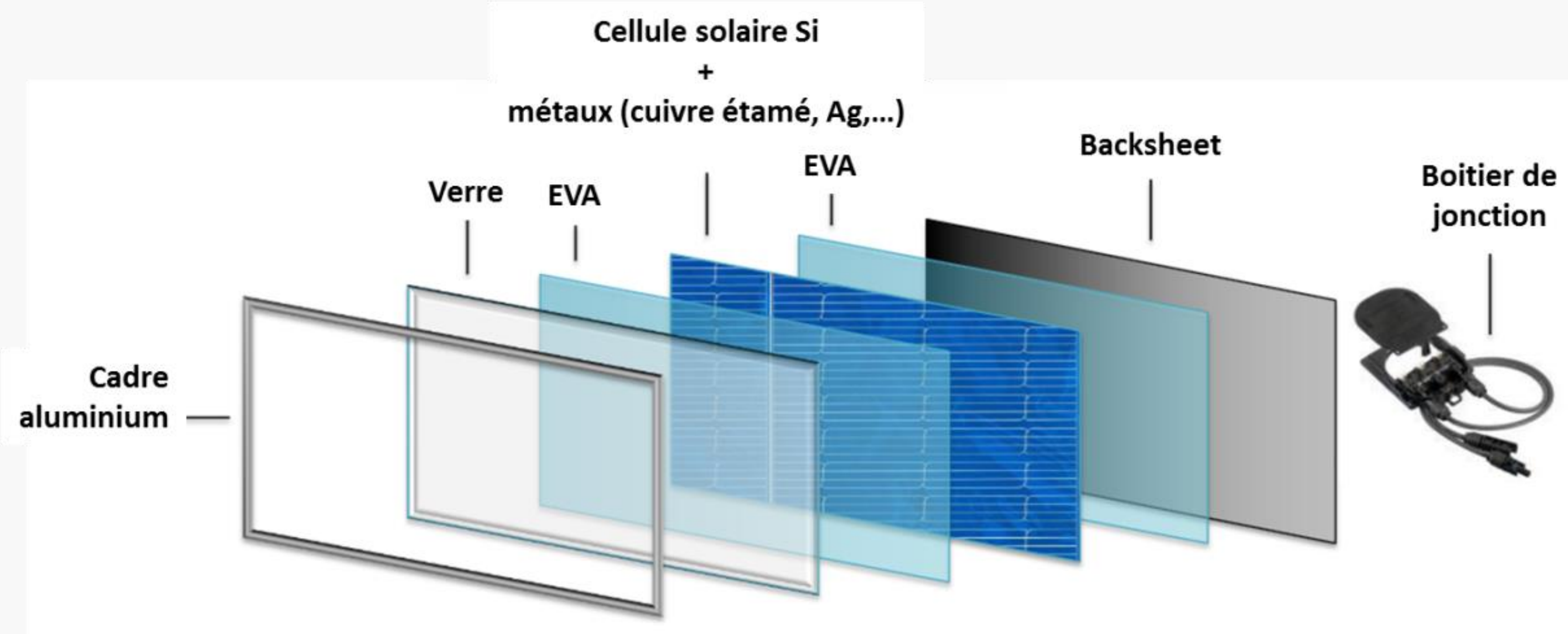
The use of supercritical CO_2 is of great interest for environmental considerations because it enables to turn a potential pollution, contributing to the global warming, into a tool for recycling.

C. Aymonier, G. Philippot, A. Erriguible, S. Marre, In Supercritical, High Pressure and Related Solvent systems, RSC, ***2018****.*



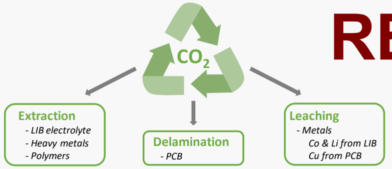
RECYCLING USING SUPERCRITICAL CO_2

Delamination of solar cells



Applied to the recycling of food packaging

WO 2017037260



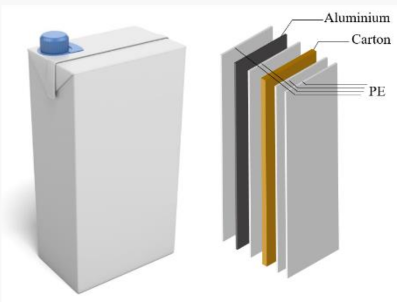
RECYCLING USING SUPERCRITICAL CO_2

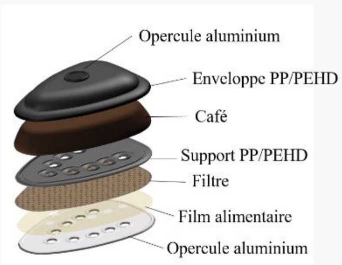
Delamination technology

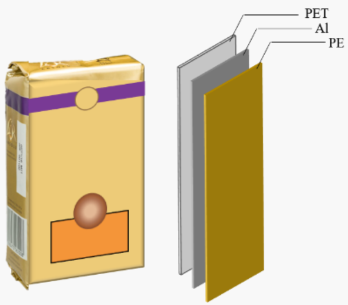
IDELAM Company: Applications

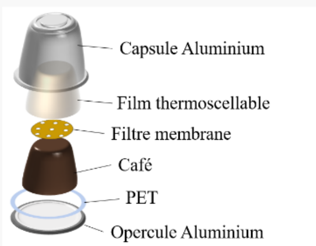
Shoes & Textiles

Food Packaging

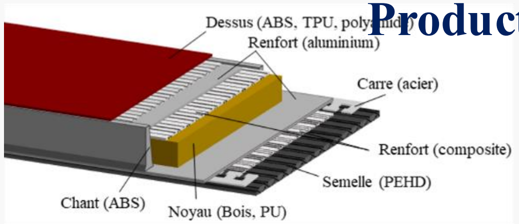


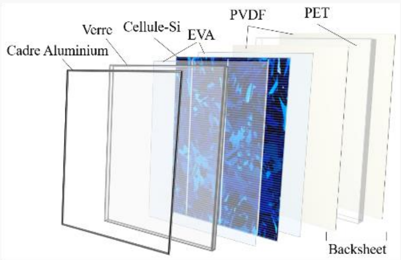


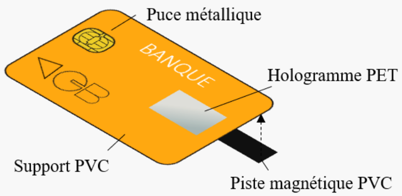


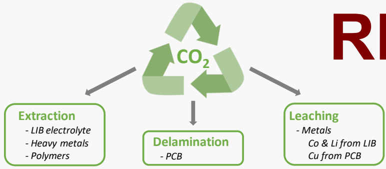


Complex Technical Products





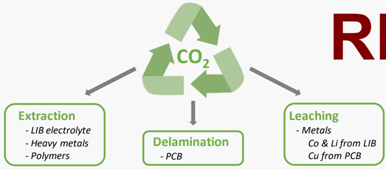




RECYCLING USING SUPERCRITICAL CO_2

Delamination technology

With the courtesy of the IDELAM company



RECYCLING USING SUPERCRITICAL CO_2

Delamination technology

ADN™

Programme de comaturation CNRS-ADN - 2025

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

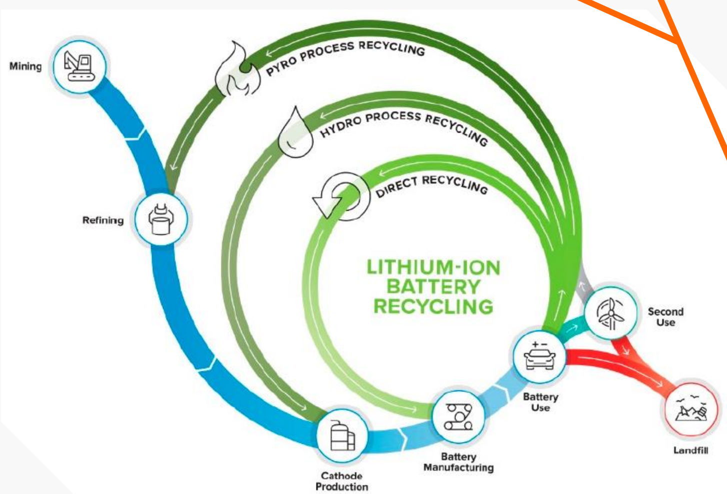
Gilles Philippot, Jacob Olchowka, Laurence Croguennec & Cyril Aymonier

Grand Programme de Recherche PPM | Post-Petroleum Materials
université de BORDEAUX
ppm

destiny
Région Nouvelle-Aquitaine
LRCS
IPREM

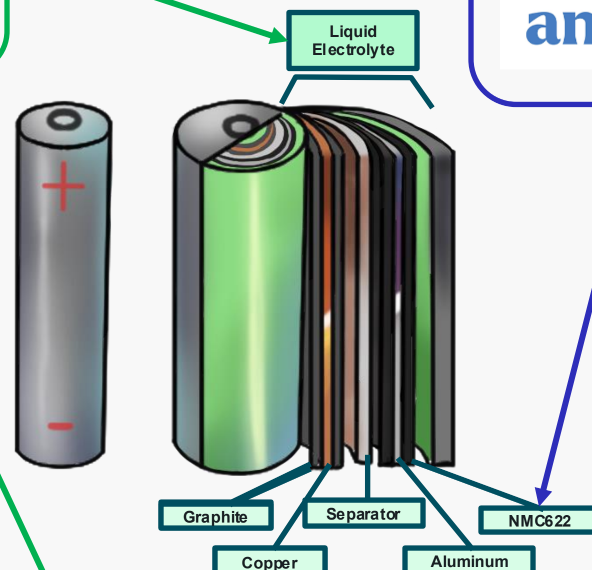
cnrs joint PhD programme
anr agence nationale de la recherche

Needs a multidimensional sustainability evaluation of the process



Need to be separated

Needs to be removed



Needs to be regenerated

Batteries Supercaps, **2024,** 7, e202400120 (7).
J. Mater. Chem. A, **2024**, 12 (46), 31685-31716.
ACS Sust. Chem. Eng., **2025**, 13(1), 105-118.
ACS Sust. Chem. Eng., **2025**, in press.

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

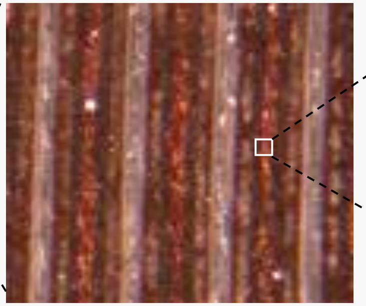
Inside of the 18650 LIB

Vertical cross section

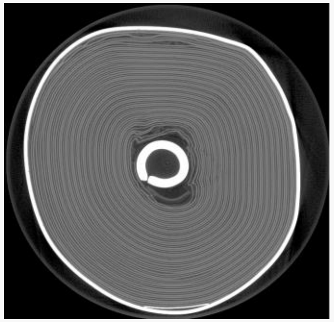
65mm

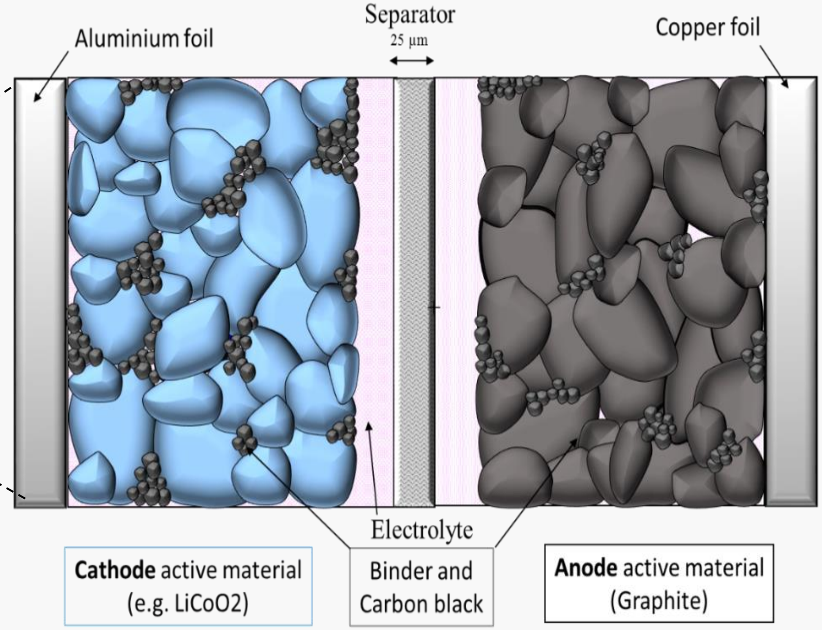
18mm

Zoom electrodes



Horizontal cross section



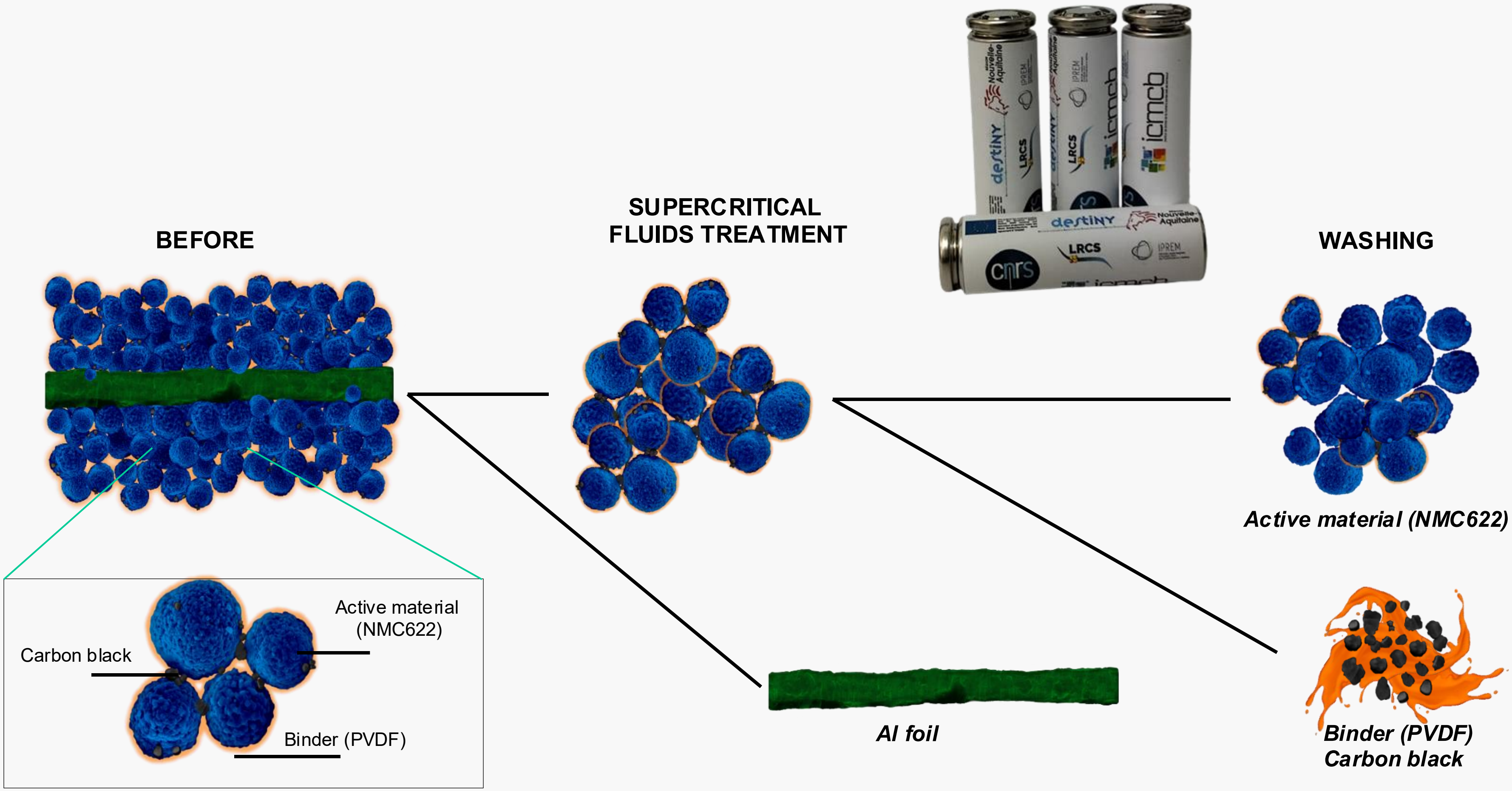


Anatomy of a LIB cell

Production scraps for Li ion batteries
EoL Li ion batteries

Vanderbruggen et al. (2021) doi.org/10.1016/j.mineng.2021.106924 || Figure reproduced with permission from Elsevier

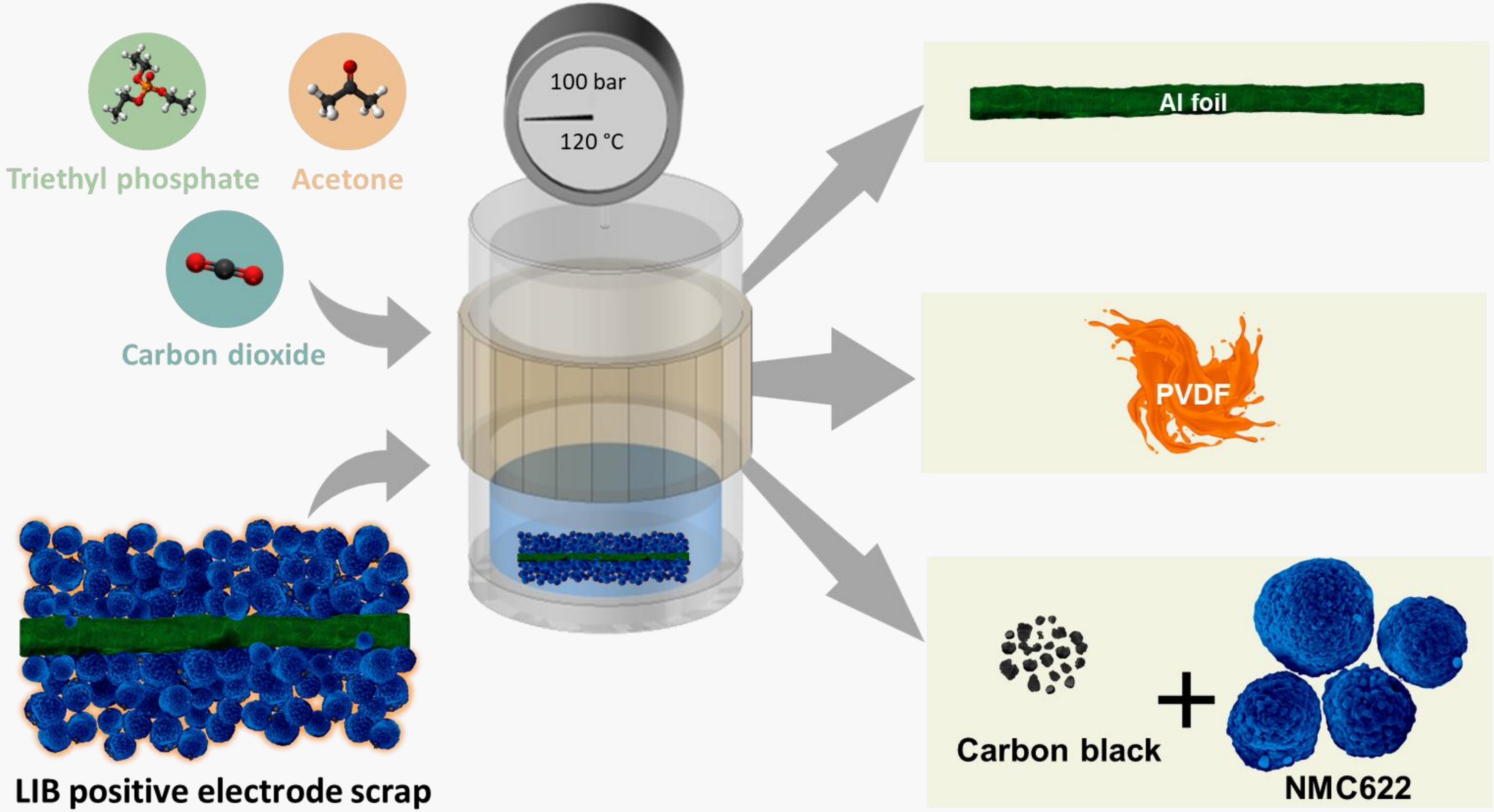
DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS



ACS Sust. Chem. Eng., **2025**, 13(1), 105-118.

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

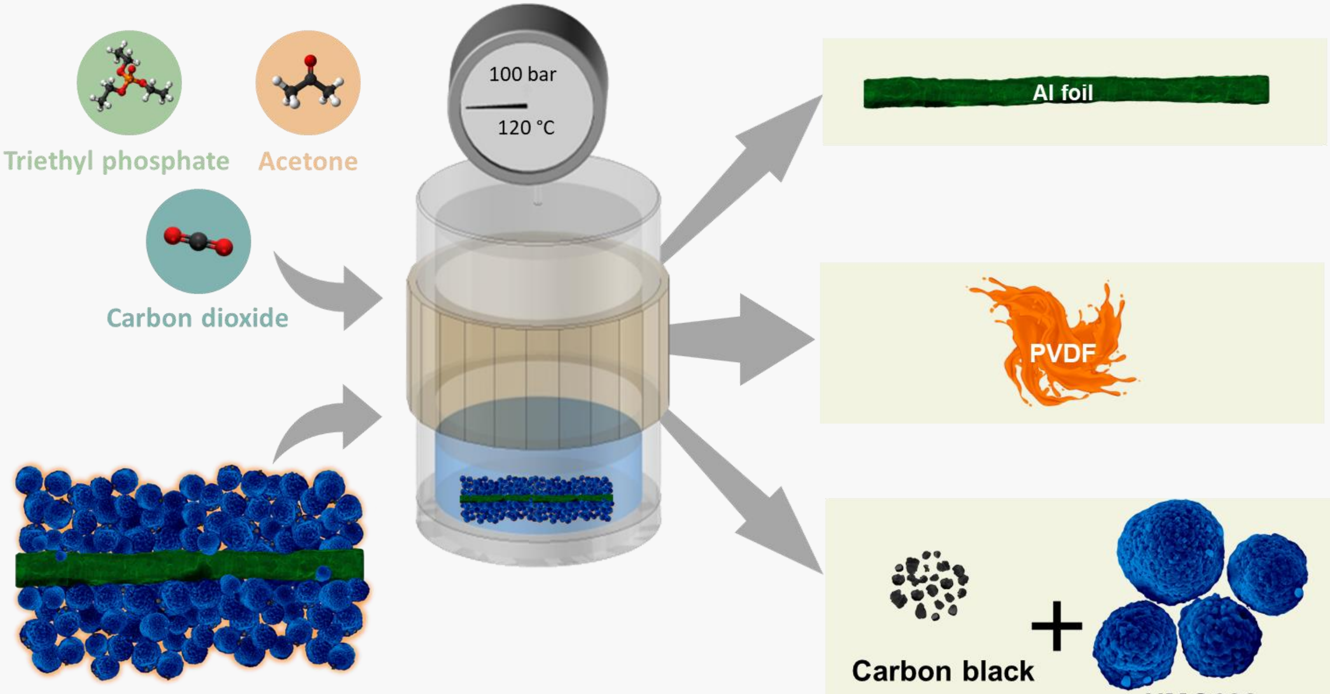
The delamination process

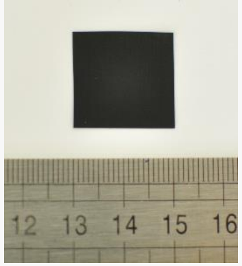


ACS Sust. Chem. Eng., **2025**, 13(1), 105-118.

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

The delamination process

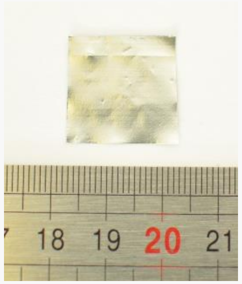




Before treatment

Process evaluation: key parameter indicator

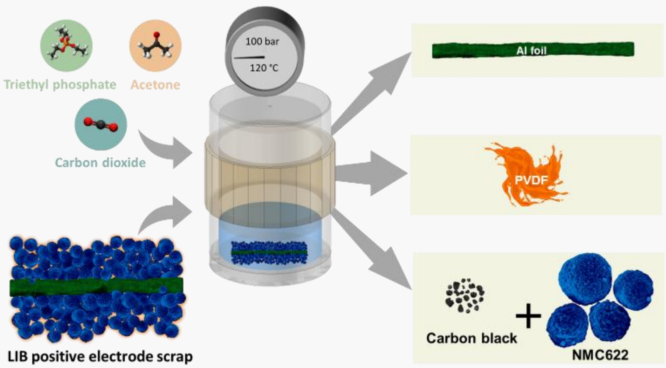
$$\text{Delamination efficiency (\%)} = 100 \times \frac{\text{Weight}_{\text{initial}} - \text{Weight}_{\text{final}}}{\text{Weight}_{\text{initial}} - \text{Weight}_{\text{Al foil}}}$$



After treatment

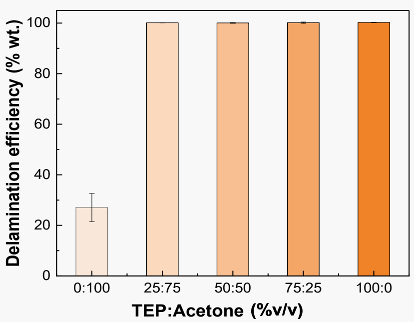
ACS Sust. Chem. Eng., **2025**, 13(1), 105-118.

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS



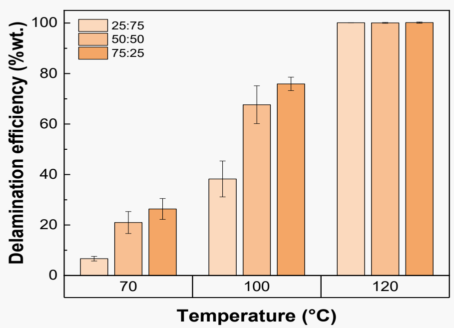
The delamination process: optimal parameters

100 bar



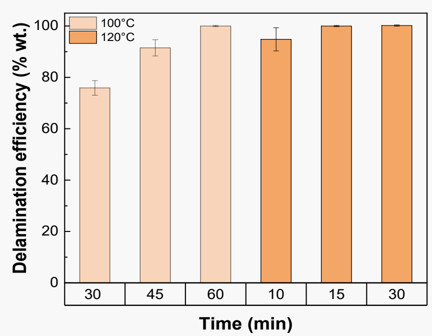
Cosolvent

75TEP : 25Acetone (vol.)



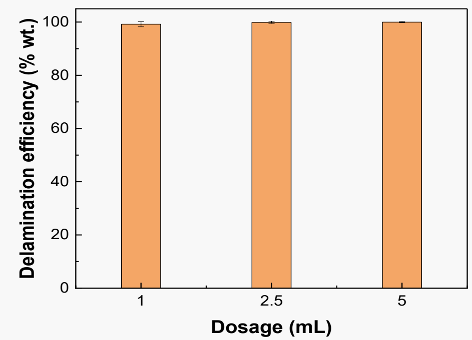
Temperature

120°C



Time

15 min



Dosage

<1.5 w/w TEP:electrode

Key parameter for scale up: loadind=g rate of the reactor

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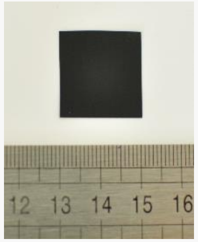
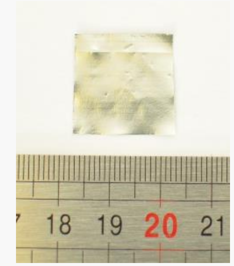
DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

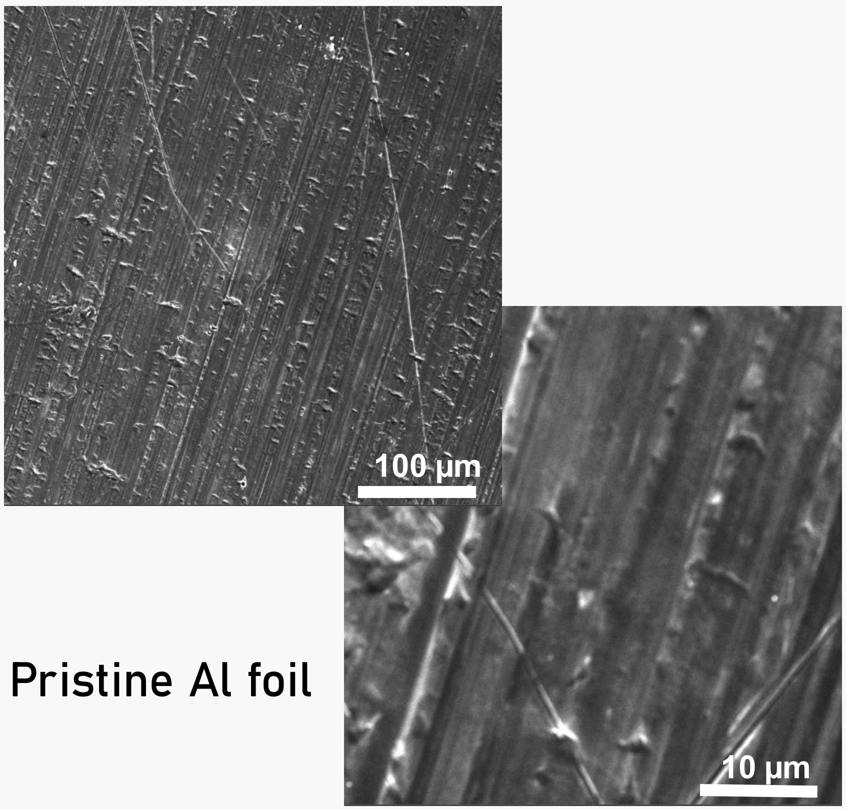
Recovered Al foil



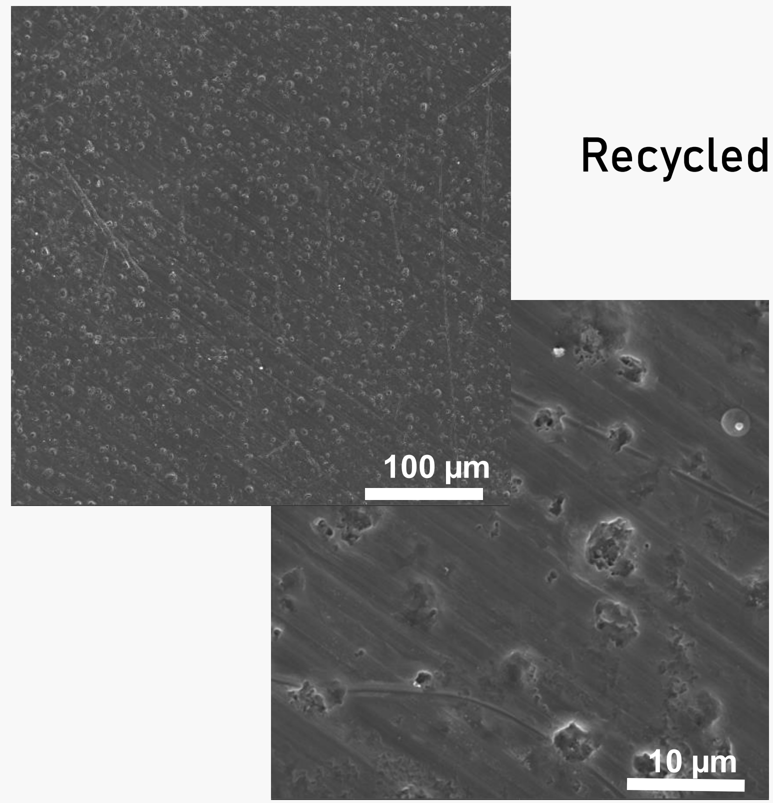
Before treatment



After treatment



Pristine Al foil



Recycled Al foil

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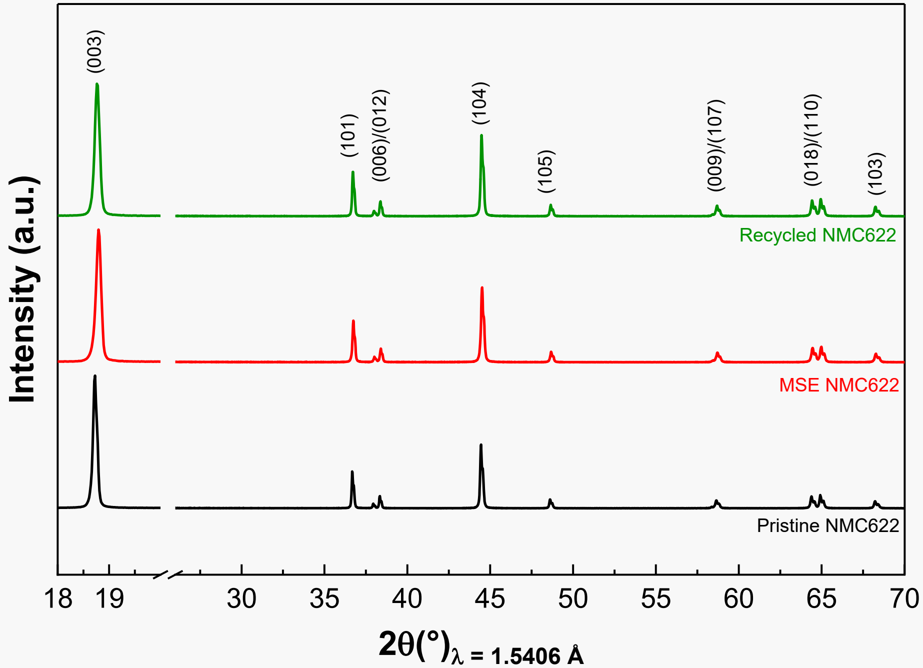
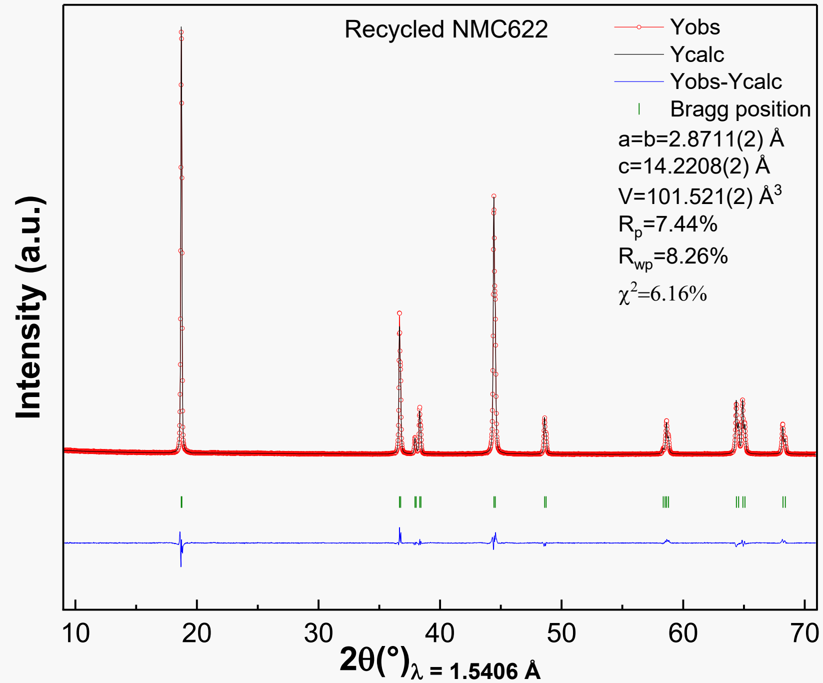
Direct recycling of lithium ion batteries assisted by supercritical fluids

Preservation of the crystal structure (XRD)





Sample	a=b (Å)	c (Å)	Vol. ($Å^3$)
Pristine NMC622	2.8704(2)	14.2218(3)	101.474(2)
MSE NMC622	2.8712(3)	14.2211(3)	101.529(3)
Recycled NMC622	2.8711(2)	14.2208(2)	101.521(2)

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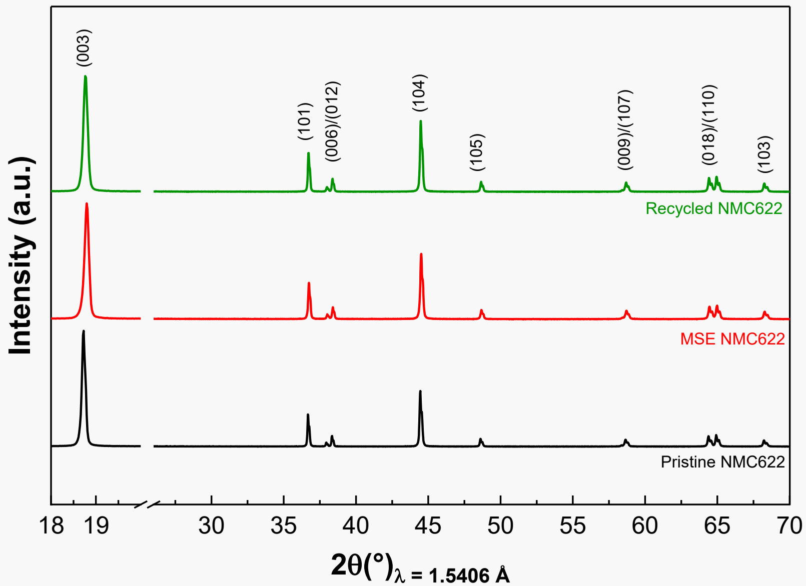
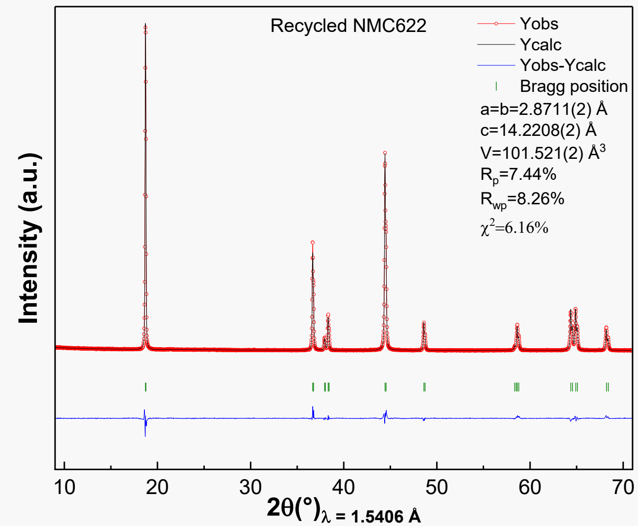
MSE: Manually scraped electrode

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Preservation of the crystal structure (XRD)





Preservation of chemical composition (ICP-OES)

Sample	Li/Ni	Li/Mn	Li/Co	Li/TM
Pristine NMC622	1.59 ± 0.04	4.96 ± 0.05	5.07 ± 0.03	0.97 ± 0.04
MSE NMC622	1.57 ± 0.04	4.89 ± 0.05	5.00 ± 0.03	0.96 ± 0.04
Recycled NMC622	1.57 ± 0.04	4.88 ± 0.05	4.99 ± 0.03	0.96 ± 0.04

Process has no impact on material structure and composition

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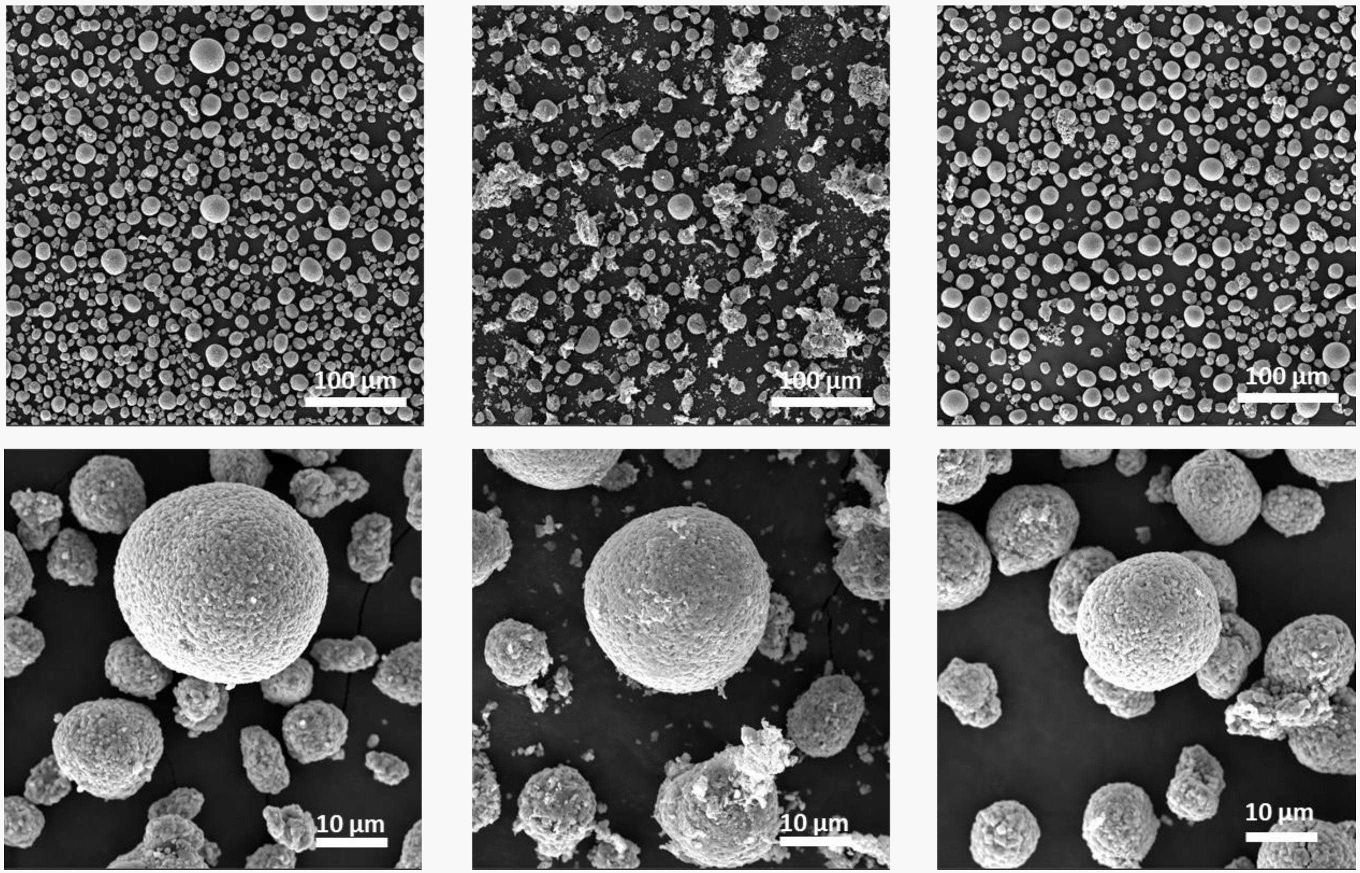
MSE: Manually scraped electrode

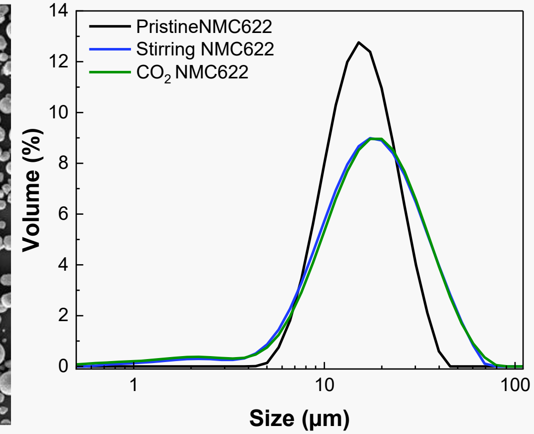
DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

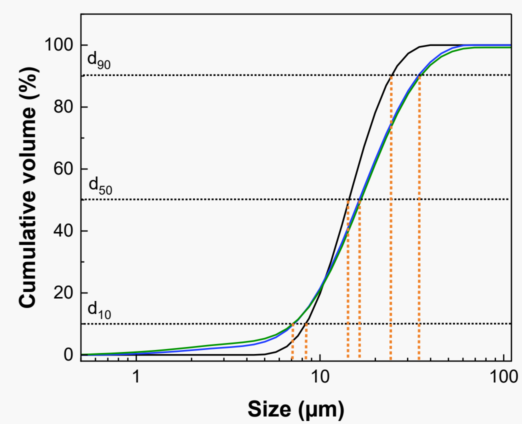
Preservation of particle morphology (SEM)

Pristine NMC622 | **MSE NMC622** | **Recycled NMC622**



Preservation of particle size (granulometry)





Process has no impact on particle size and morphology!

ACS Sust. Chem. Eng., ***2025***, *13(1), 105-118.*

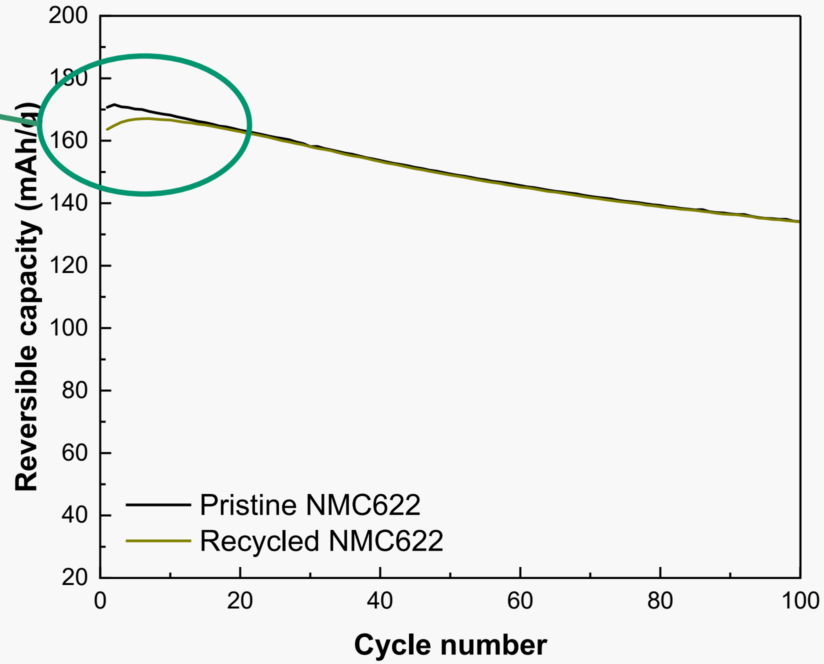
MSE: Manually scraped electrode

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Capacity evolution up to 100 cycles at C/5 (2.5 – 4.3 V)

CAM geometry
PVDF traces
Surface property evolution

Electrode formulation
to be revisited with
the recycled raw material



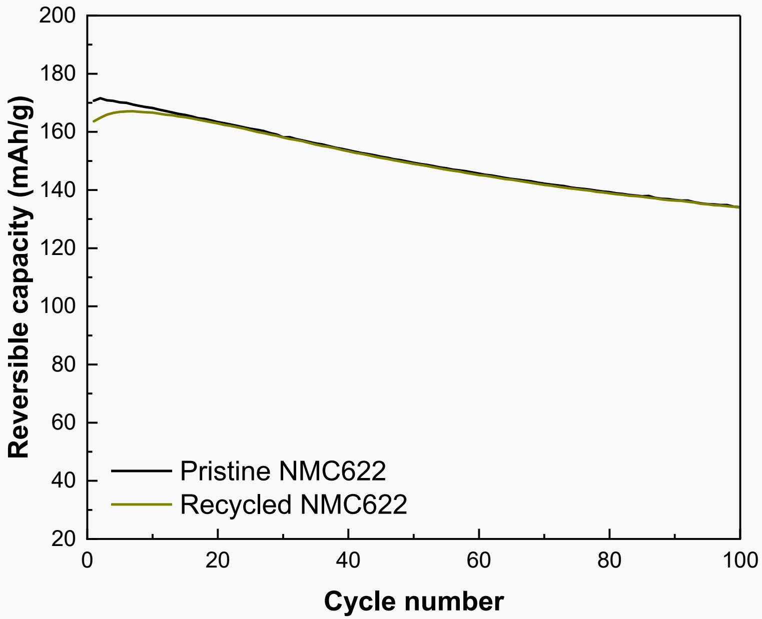
80:10:10 || 1M LiPF6 in (1:1 wt.%) EC: DMC

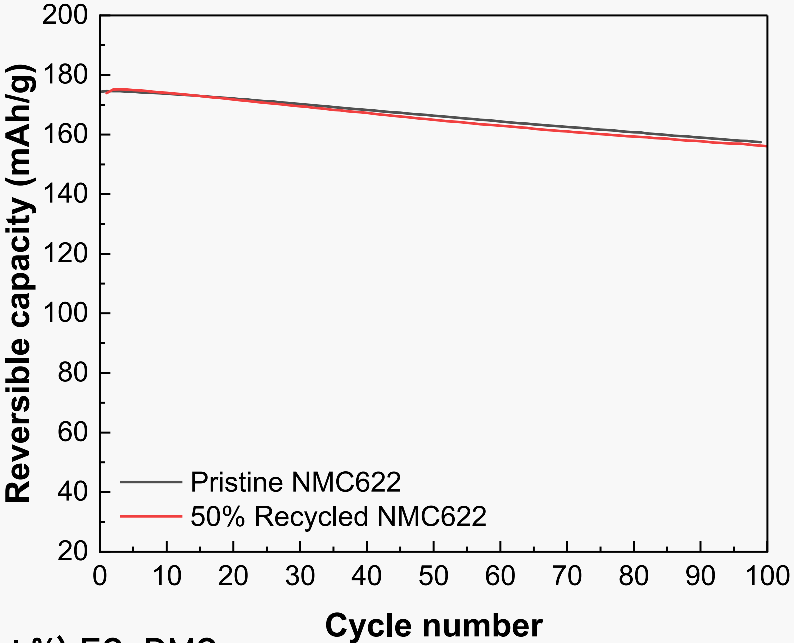
Quasi similar performance

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Capacity evolution up to 100 cycles at C/5 (2.5 – 4.3 V)

From 100 wt.% recycled CAM to 50 wt.%





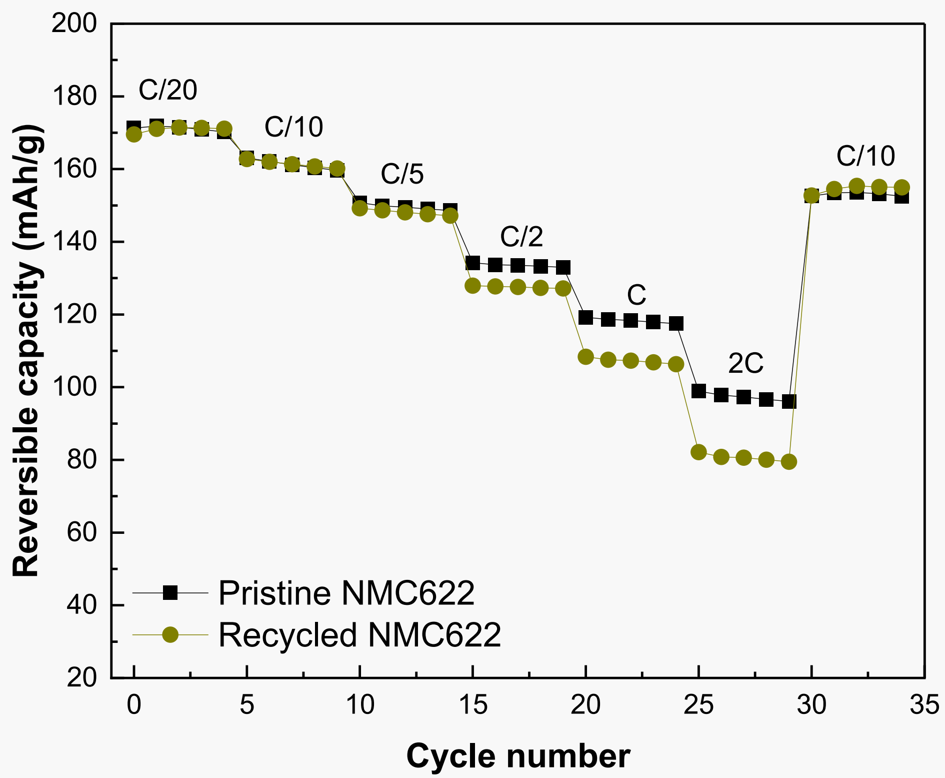
80:10:10 || 1M LiPF6 in (1:1 wt.%) EC: DMC

Quasi similar performance

Same Performance

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Rate capability test at varied C-rates

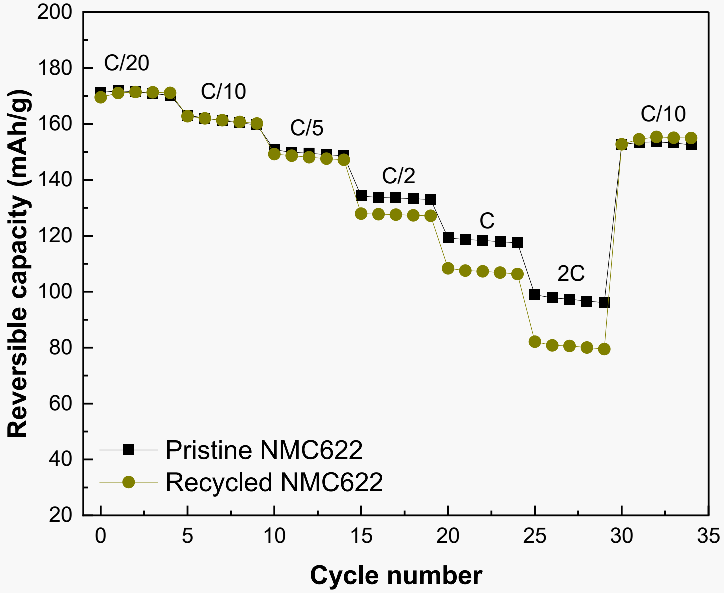


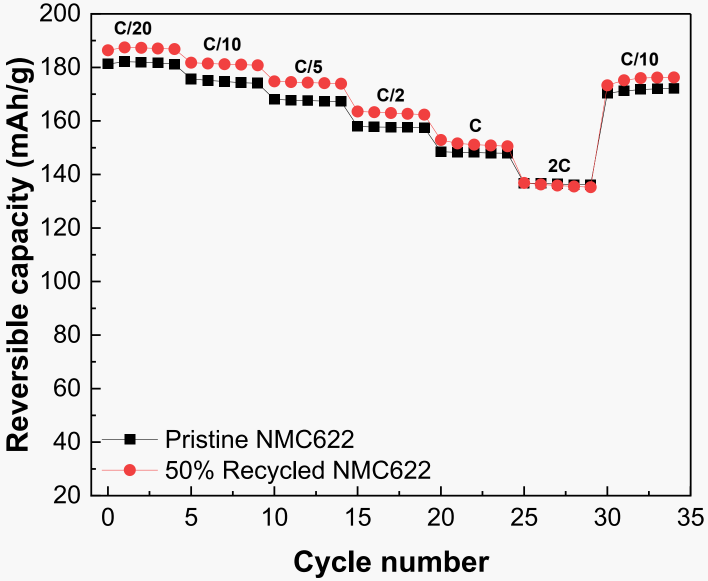
Performance degradation at high rate

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Rate capability test at varied C-rates

From 100 wt.% recycled CAM to 50 wt.%





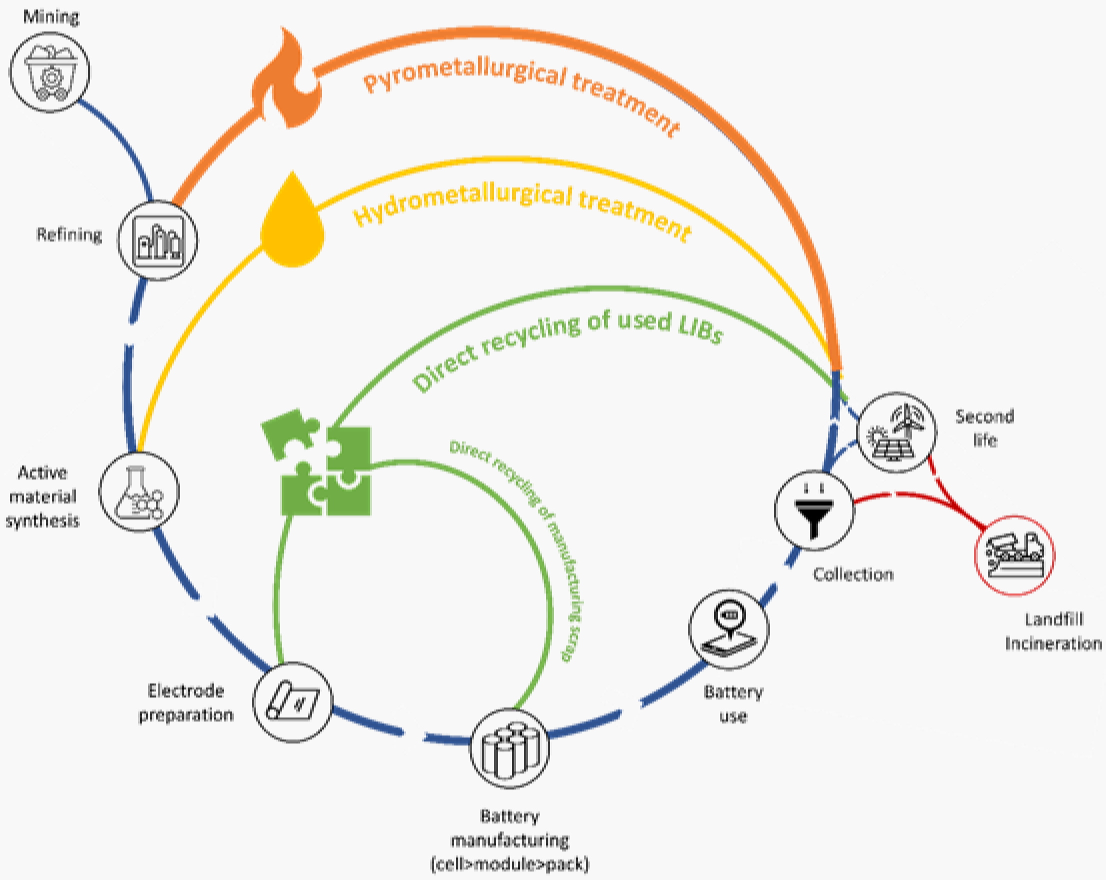
Performance degradation at high rate

Same performance as pristine NMC622

An injection between 10 to 30 wt.% would be maximum !

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Evaluation of the environmental impact



Pyrometallurgy

- High temperature (> 1400°C)
- Energy intensive
- High GHGs direct emissions
- Mature technology

Hydrometallurgy

- Pre-treatment (black mass)
- High-concentrated acid effluents
- Battery-grade metal salts

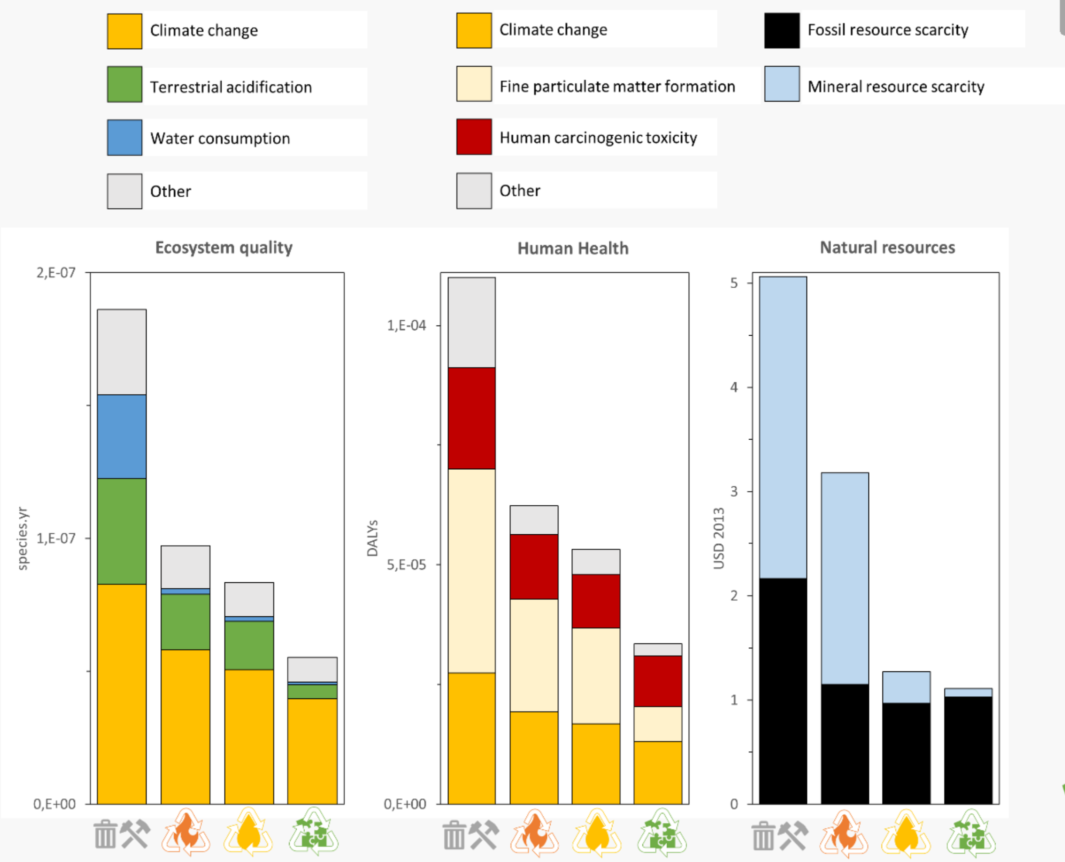
Direct Recycling

- Laboratory scale
- Homogenous input
- Adapted to production scrap
- Recovery of active materials

ACS Sust. Chem. Eng., ***2025***, *13(12), 4717-4728.*

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

Evaluation of the environmental impact



Can still be improved !

Incineration without recovery
Treat 1 kg of scrap by incineration and produce a 0.96 kg (+) electrode with primary NMC622 (137 Ah)

Pyrometallurgy
*Treat 1 kg of scrap by pyro and produce a 0.96 kg (+) electrode with NMC622 synthesized with recycled precursors (**Ni, Co**) (137 Ah)*

Hydrometallurgy
*Treat 1 kg of scrap by hydro and produce a 0.96 kg (+) electrode with NMC622 synthesized with recycled precursors (**Ni, Mn, Co and Li**) (137 Ah)*

Direct Recycling
*Treat 1 kg of scrap and produce a 1 kg (+) electrode with **recycled NMC622** (137 Ah)*

ACS Sust. Chem. Eng., ***2025***, *13(12), 4717-4728.*

DIRECT RECYCLING OF LITHIUM ION BATTERIES ASSISTED BY SUPERCRITICAL FLUIDS

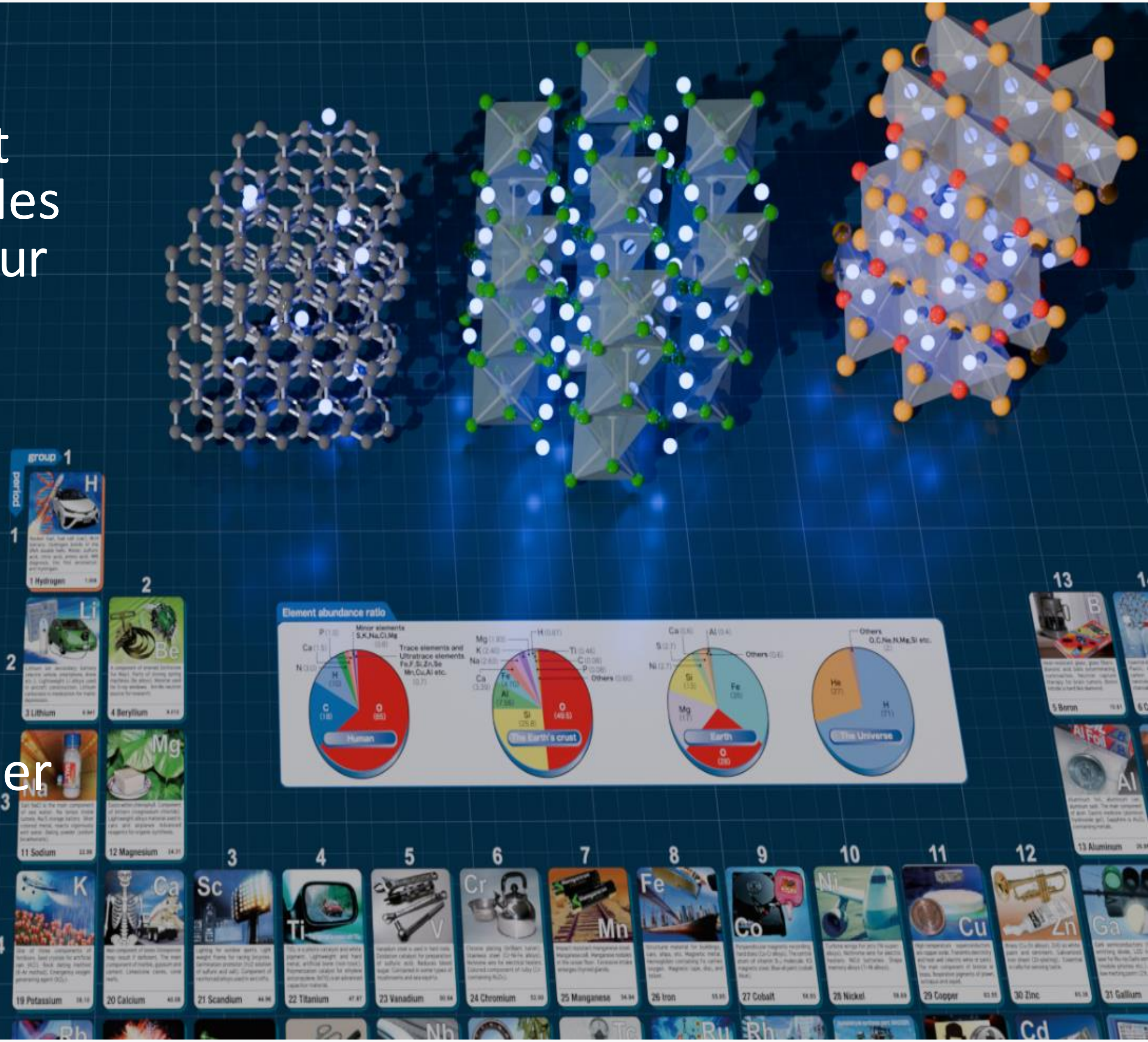
Conclusions and perspectives

- Development of a new pressurized CO_2-based process for the direct recycling of Li-ion batteries
- Applied to production scraps on the positive and negative electrodes
- Applied to EoL Li-ion batteries

- Investigation of the recycling of $LiFePO_4$
- Transfer of the technology to industry
- Recycling avoiding black mass → Recyclability

CHESS

Durabilité et Recyclabilité des Matériaux pour l'Energie (DREAME)



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Bordeaux INP
CoPI Cyril Aymonier
ICMCB

MANY THANKS TO MY COLLABORATORS