Économie circulaire des batteries et recyclage

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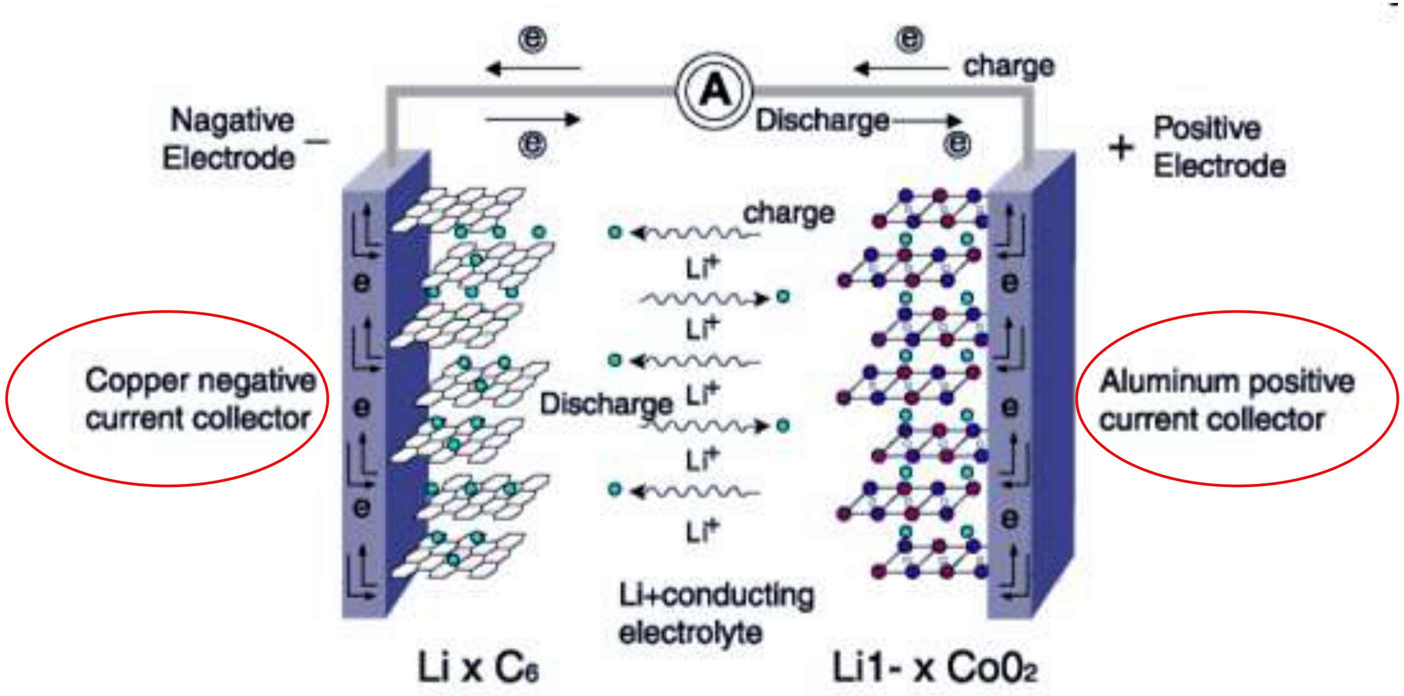
Collège de France 6 février 2023

Quoi recycler dans une batterie ?
Pourquoi le recyclage ?
Comment le recyclage ?

La batterie lithium- ion



décharge $Li_xC_6 \rightarrow x\ Li^+ + C_6 + x\ e$ $x\ Li^+ + MO_2 + x\ e \rightarrow Li_xMO_2$

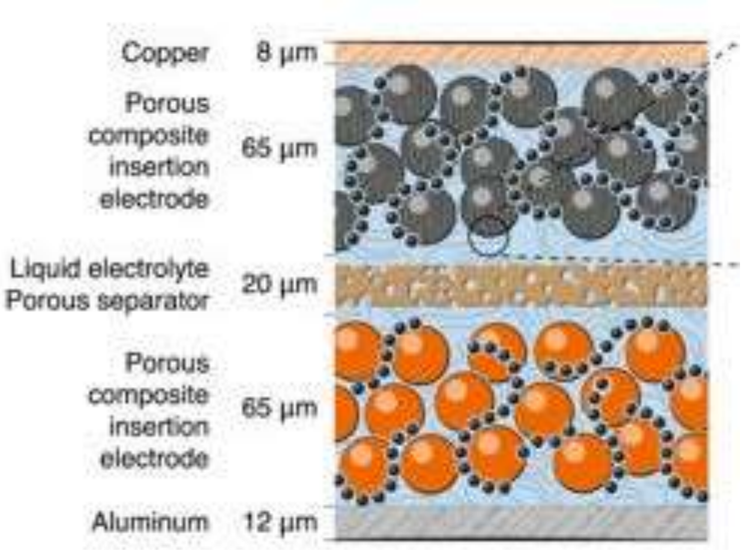
charge $x\ Li^+ + C_6 + x\ e \rightarrow Li_xC_6$ $Li_xMO_2 \rightarrow x\ Li^+ + MO_2 + x\ e$

S. Whittingham
1970’
Sulfides vs Li

J. B. Goodenough
1980’
oxides vs Li

A. Yoshino
End 1980’
oxides vs graphite

composants



copper on negative Li

separators : porous polymer
Kynar PVDF (CH_2CF_2)
polyéthylène

aluminium on positive
forms alloys with Li

$Li(NMC)O_2$

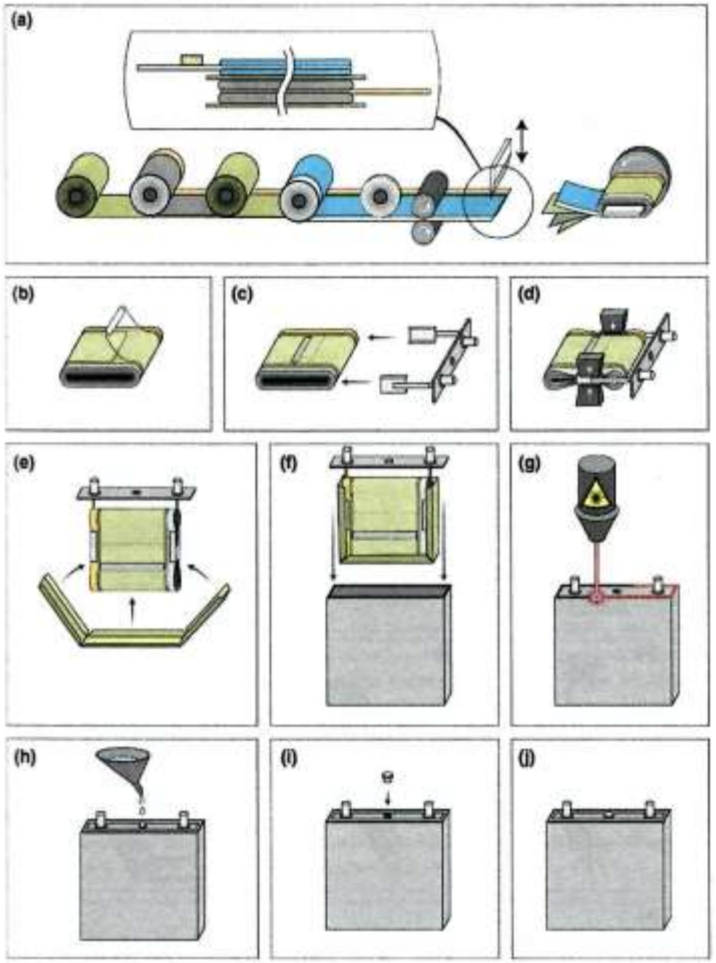
graphite

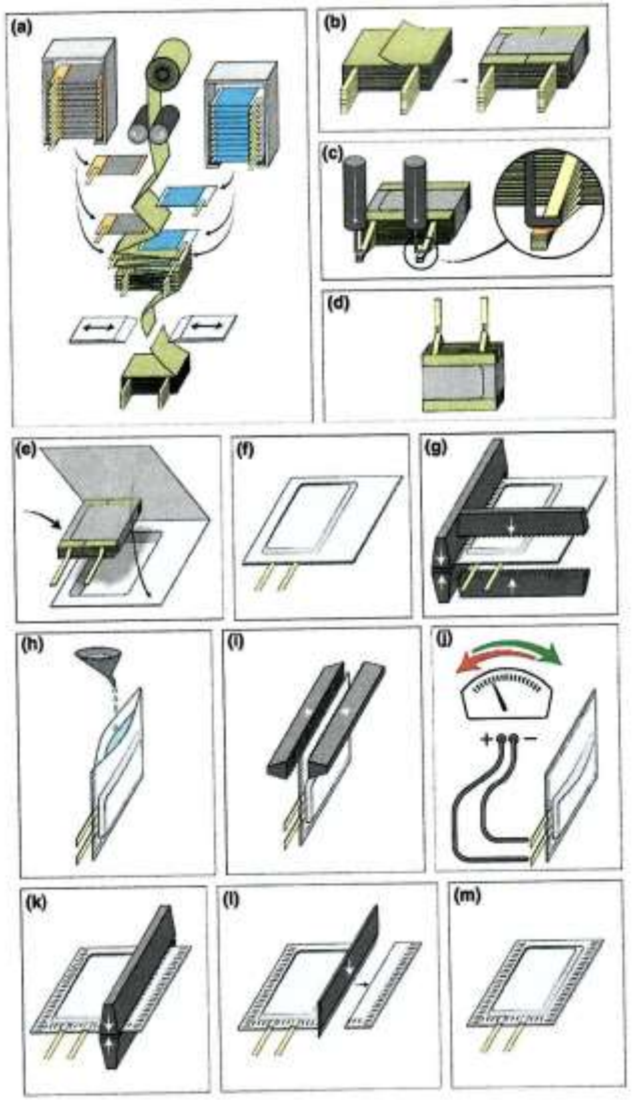
Batteries are built Discharged:

not dangerous
Not air sensitive

2% binder : PVDF or CMC or cellulose
2% carbon black additive (not graphite !)
95% electrode material

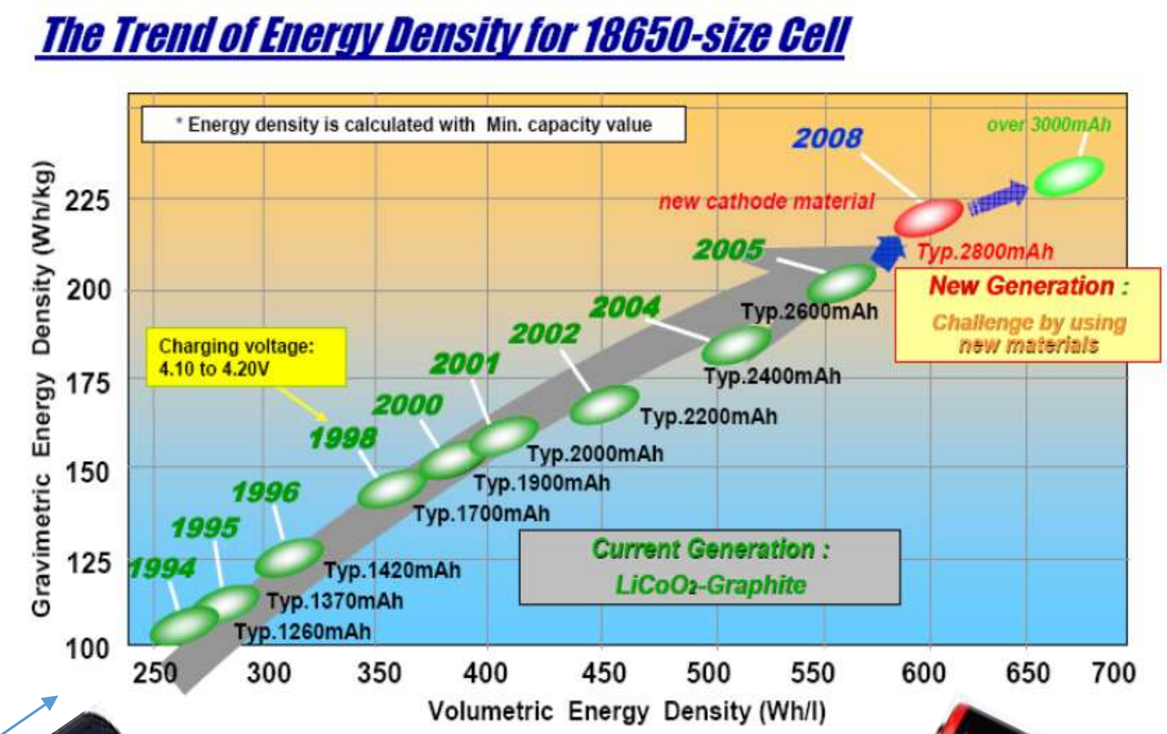
Géométries

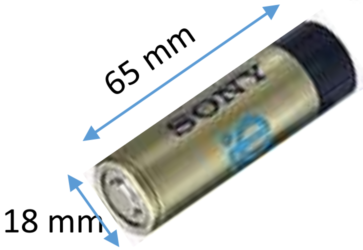




Cylindriques
Prismatiques
Cellule pouch (plates)

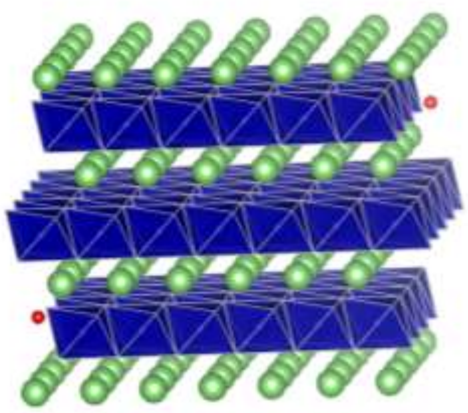
Progrès de la technologie

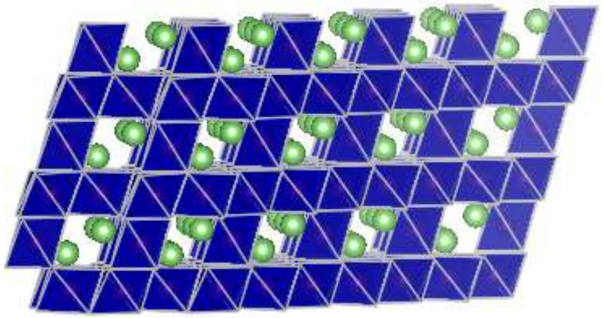


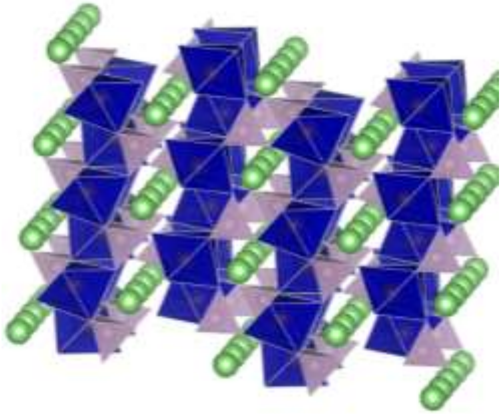


1991 Sony
1000 mAh

40 ans de recherche sur les cathodes







2D Structures
$LiCoO_2$ (LCO)
4.2V vs Li

+ densité d'énergie
- Sécurité à haute puissance
- Coût du Cobalt

→ Premiers téléphones

$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA)
$Ni_{8/10}Mn_{1/10}Co_{1/10}$ = NMC811

→ Véhicules et téléphones

Structures 3D spinelles
$LiMn_2O_4$ (LMO)
4.2 V vs Li

+ Peu cher
+ Sécurité
- Cyclage faible

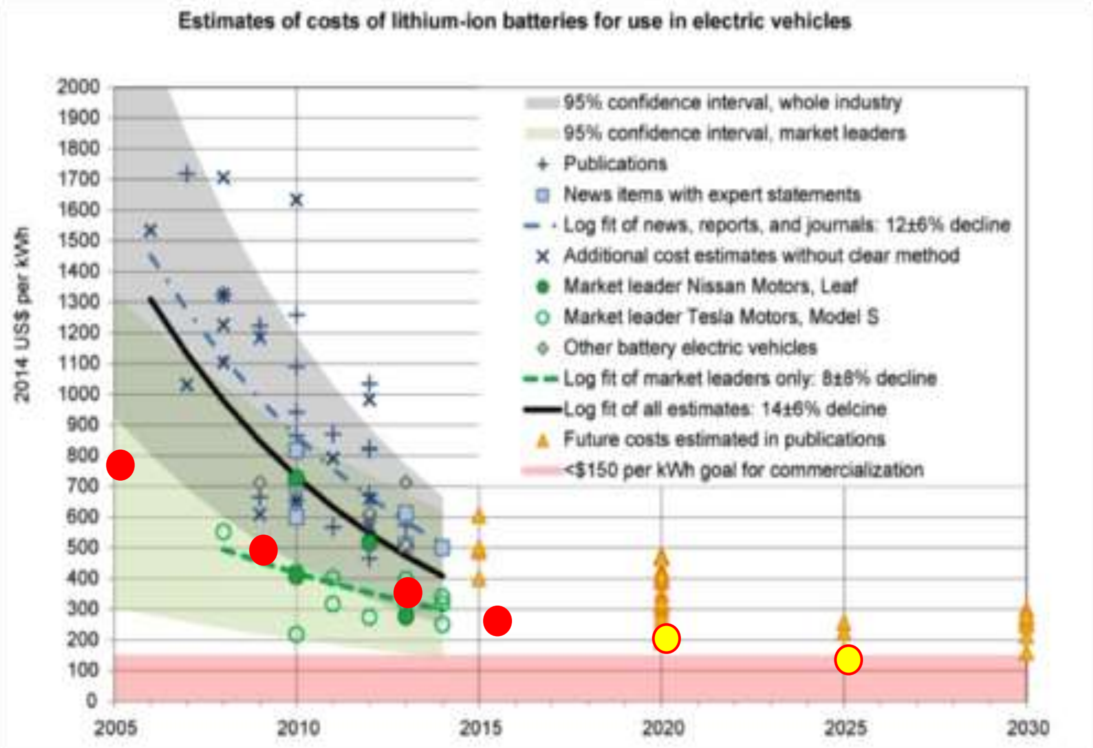
→ Outils portatifs

Structures olivine ou anioniques
$LiFePO_4$ (LFP)
3,5 V vs Li

Faible densité d'énergie
fiable
Peu couteux

→ Voitures (Chine BYD)
→ Petite mobilité
→ Stationnaire

Le coût des batteries Co → Ni



● Données Yann Laot Saft-Total

2018 = 150 $/kWh

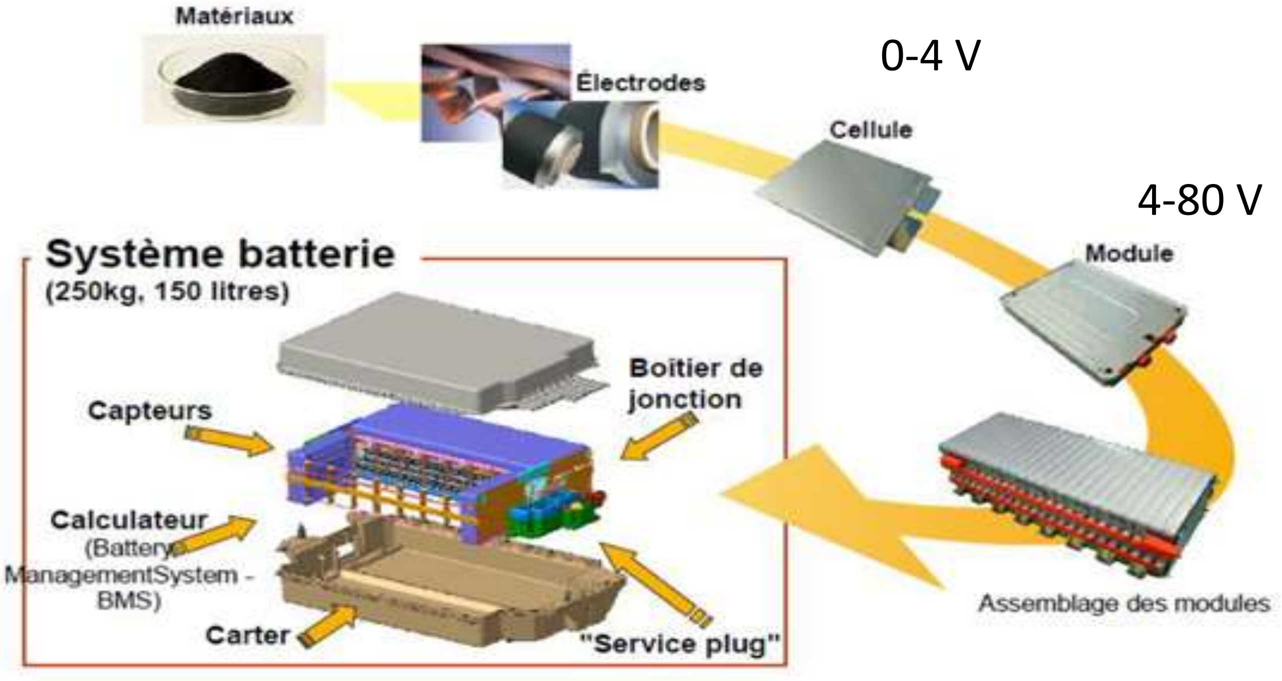
1 Véhicule électrique = 40 kWh = 6000 € batterie

$LiCoO_2$

$LiCoO_2$ → $Ni_{1/3}Mn_{1/3}Co_{1/3}$ → $Ni_{0.6}Mn_{0.2}Co_{0.2}$ → $Ni_{0.8}Mn_{0.1}Co_{0.1}$

NMC333 NMC622 NMC811

Construction additive



0-4 V

4-80 V

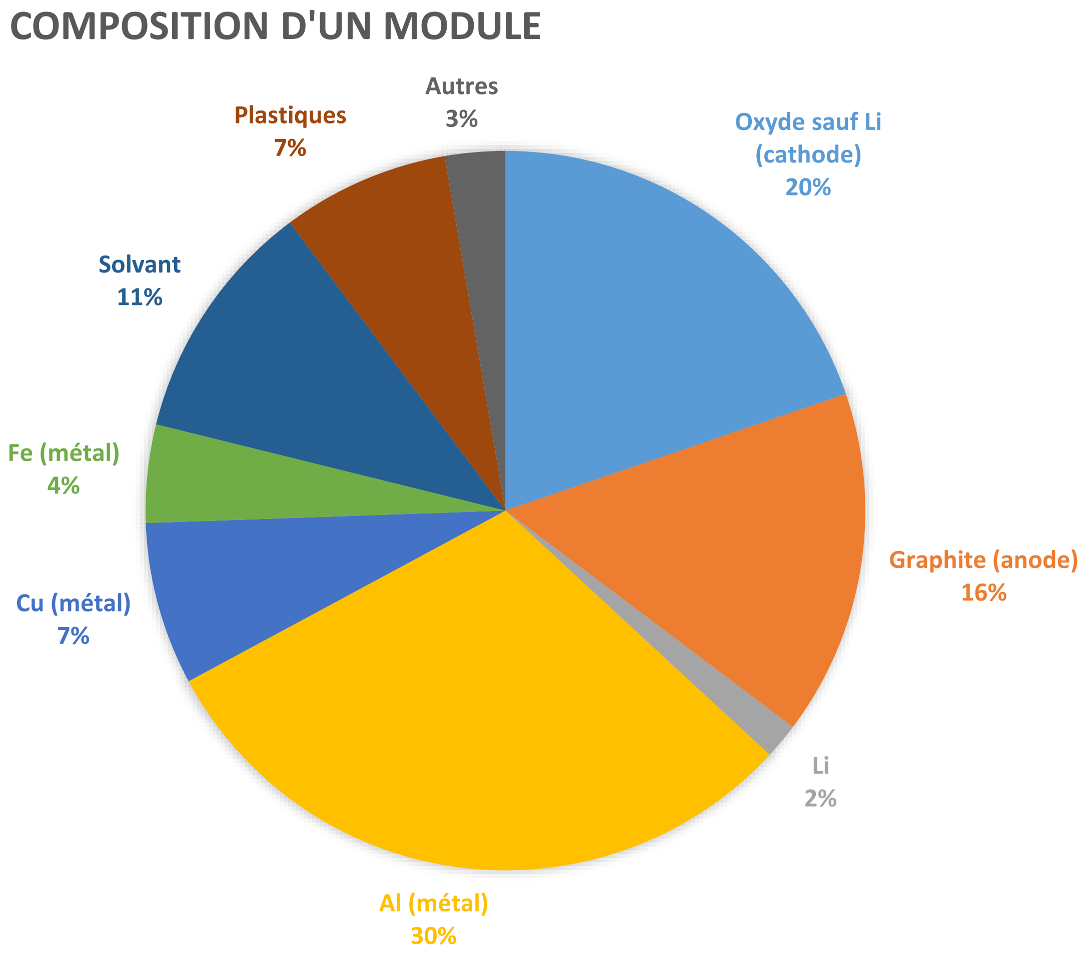
80-400 V

RENAULT

Cellule →	Module →	Batterie
3.8 V	48 V	400 V
250 Wh/kg	→	150 Wh/kg

2018 Collège de l'X François Orsini (Renault)

Composition d'une batterie



1,6% de Li
1,3% de Co (NMC 811)

Etat de l'art 2018

Automaker	Battery supplier	Cell chemistry
Nissan-Renault-Mitsubishi	AESC + LG Chem → AESC? + LG Chem + CATL	MNC/NCA
BYD	BYD	LFP → LFP+NMC
BAIC	CATL, Lishen, others	LFP → LFP+NMC
Geely	CATL, Lishen, others	LFP → LFP+NMC
Tesla	Panasonic + Tesla gigafactory	MNC/NCA
BMW	Samsung SDI → Samsung SDI + CATL	MNC/NCA
VW	Samsung SDI→ Samsung SDI + CATL	MNC/NCA
SAIC	CATL, Lishen, others	LFP → LFP+NMC
GM	LG Chem	MNC/NCA
Toyota	Panasonic	MNC/NCA

Technologie dominante NMC

Mélanges utilisés
- Cyclabilité
- Puissance

Utilisation du LFP
- Chine
- Micro-mobilité
- Bas de gamme
- Tesla Chine
- Stationnaire

Pelegov, D. V.; Pontes, J. Main Drivers of Battery Industry Changes: Electric Vehicles—A Market Overview. *Batteries* **2018**, *4* (4), 65. https://doi.org/10.3390/batteries4040065.

Quoi recycler dans une batterie ?
Pourquoi le recyclage ?
Comment le recyclage ?

Un aspect éthique

Ressources primaires

Around 70% of cobalt is mined in the Democratic Republic of Congo, where workers include children and families and conditions are unsafe.

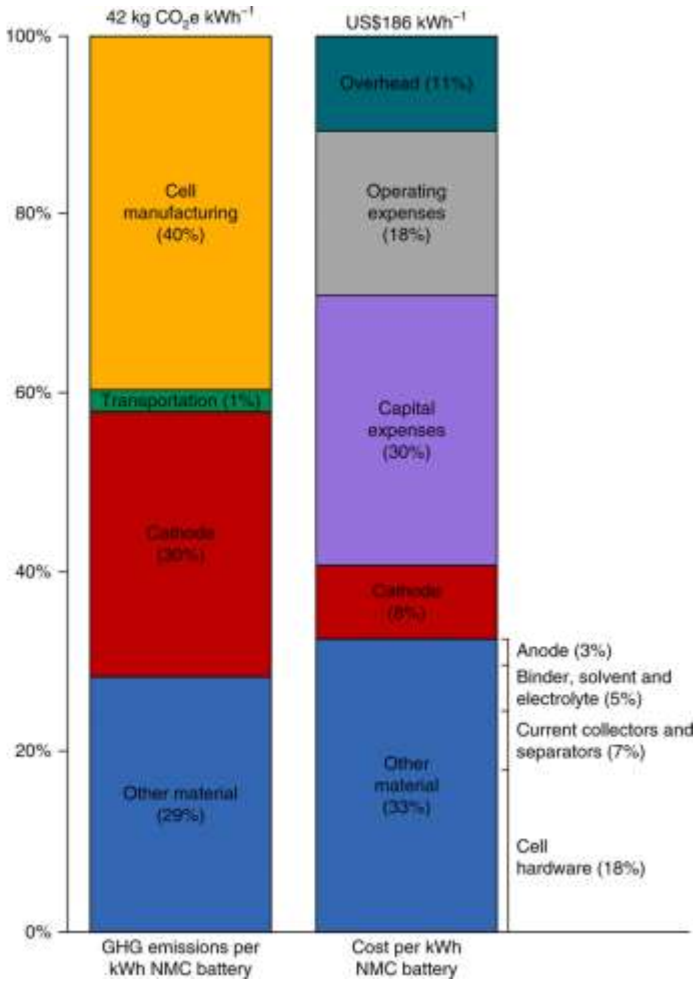
Credit: Sebastian Meyer/Corbis News/Getty

Ressources secondaires

Pure Earth 2016 World worst Pollution Problems

Ballantyne AD, Hallett JP, Riley DJ, Shah N, Payne DJ. 2018 Lead acid battery recycling for the twenty-first century. R. Soc. open sci. ***5***

émissions

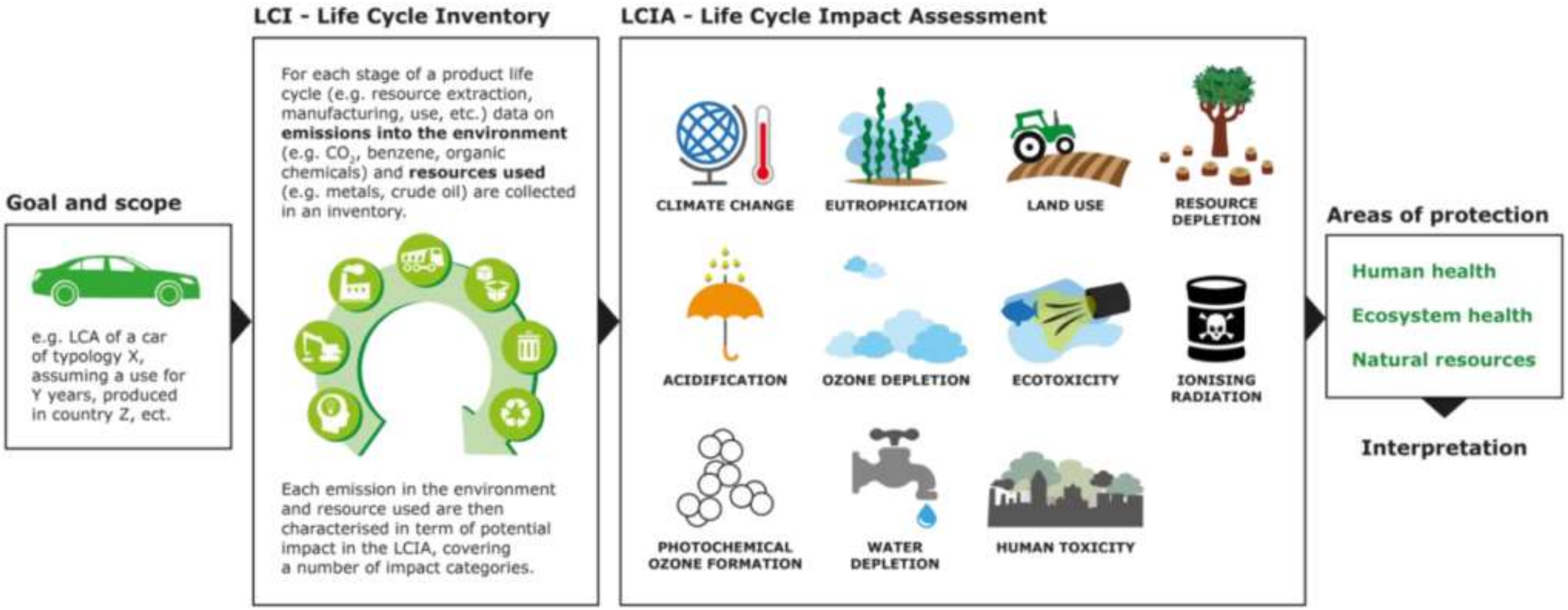


Ademe 2013: production
Véhicule thermique 3,74 tonnes CO_2
Véhicule électrique 6,57 tonnes CO_2

Emissions GHS:
40% fabrication de la batterie
60% matériaux

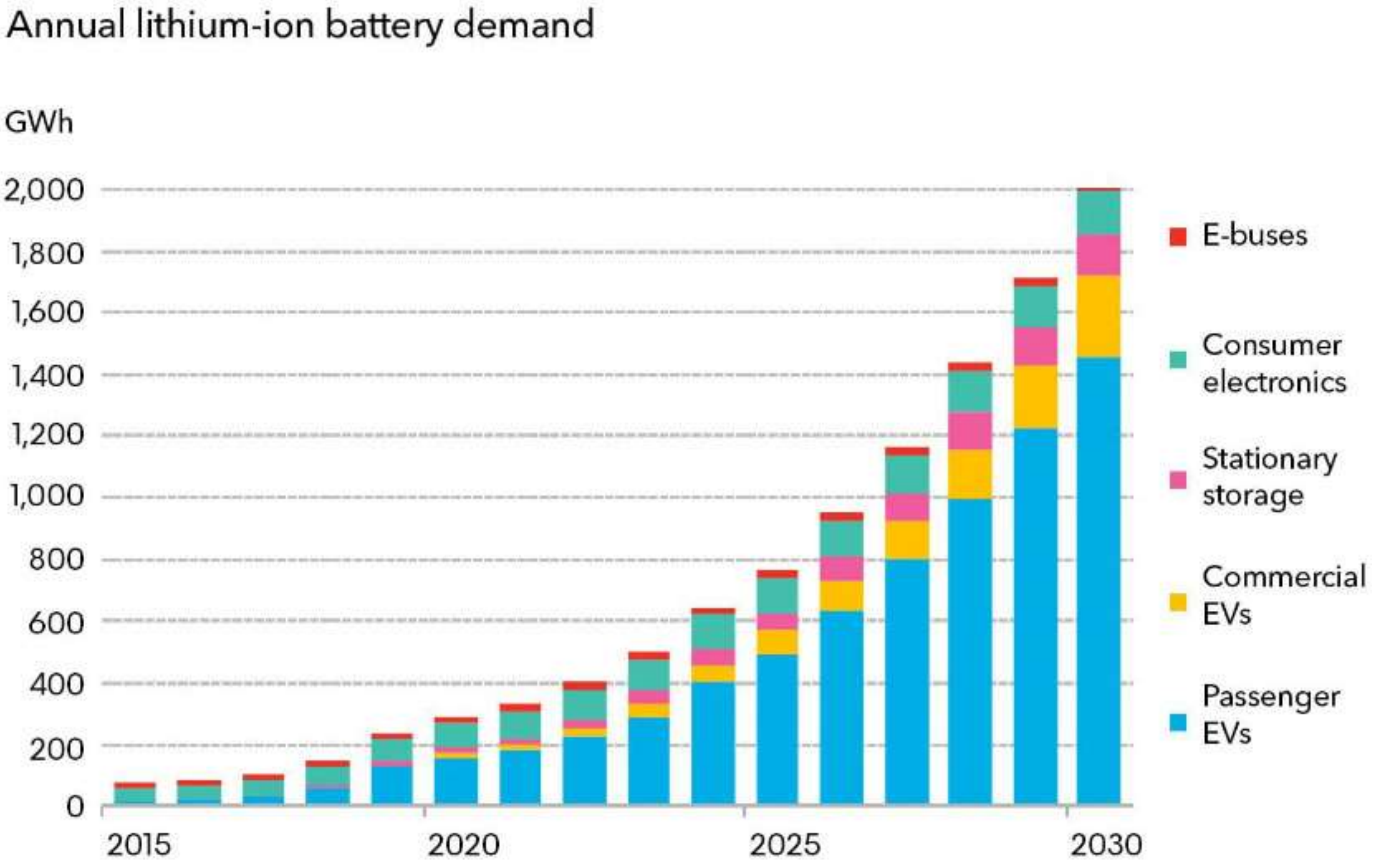
BMS 30% des émissions (électronique)

Analyse de cycle de vie



Sala, S., Reale, F., Cristobal-Garcia J., Marelli, L., Pant R.;
Life cycle assessment for the impact assessment of policies
Technical report by the Joint Research Centre (JRC), the European Commission's science and knowledge service 2016

Prédiction de demande mondiale



Expansion mondiale

50 % électrification

1% réserves mondiales/an

1 véhicule pour 9 humains
66 millions de nouveaux véhicules / an
15 % électrique (2022)

A terme:
1 milliard de véhicules / 9 milliards humains
50 % électrique (2030)
6 millions de tonnes Li immobilisés dans les véhicules
15-30 millions de tonnes Réserves mondiales

Ressources de lithium

16- 30 Mt Li

Saumures

Sel → LiCl
500 mg/L

65% LiCl

Roches

Minéraux → Spodumène ….
$LiO_2.Al_2O_3.4SiO_2$ 3-4 %

35%

Commerce lithium Battery Grade

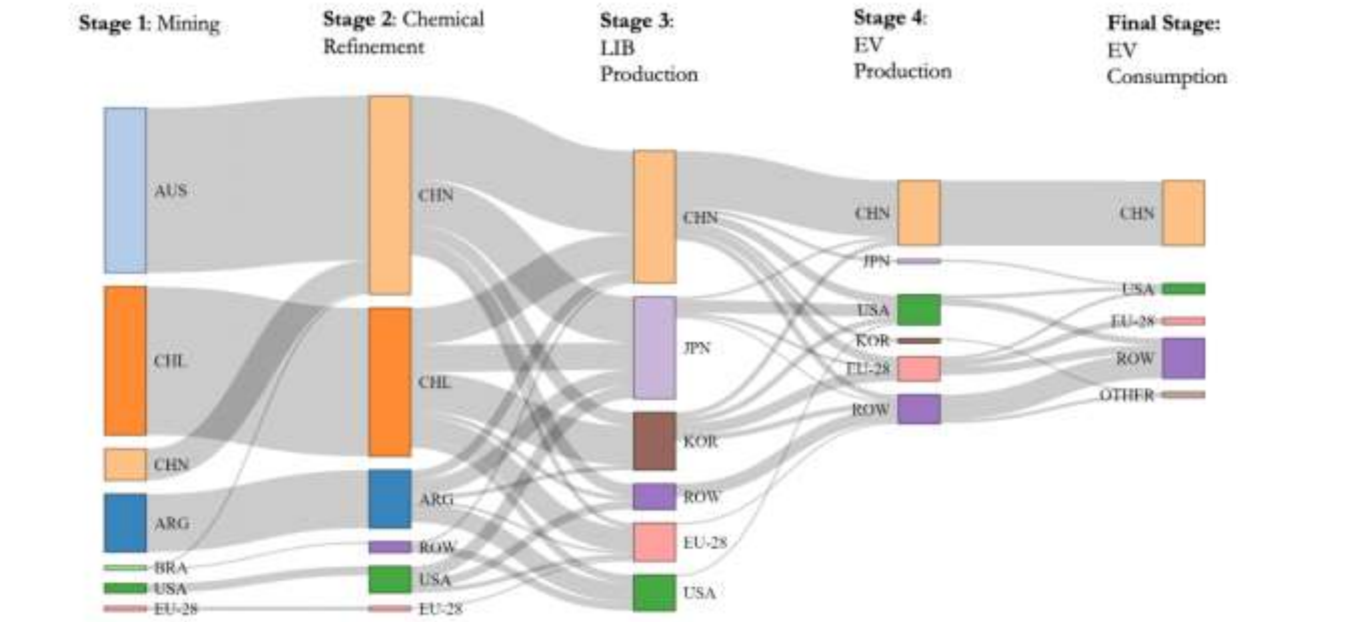
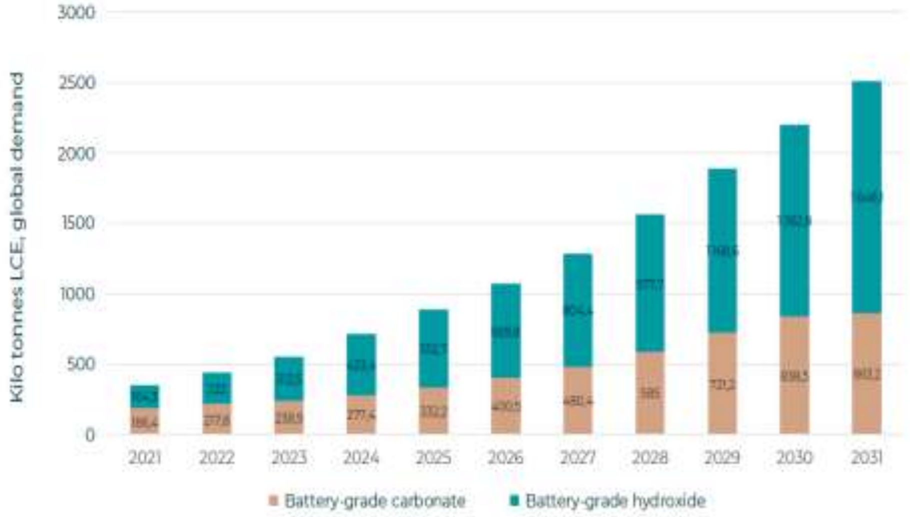


Diagramme Sankey Lithium en 2017

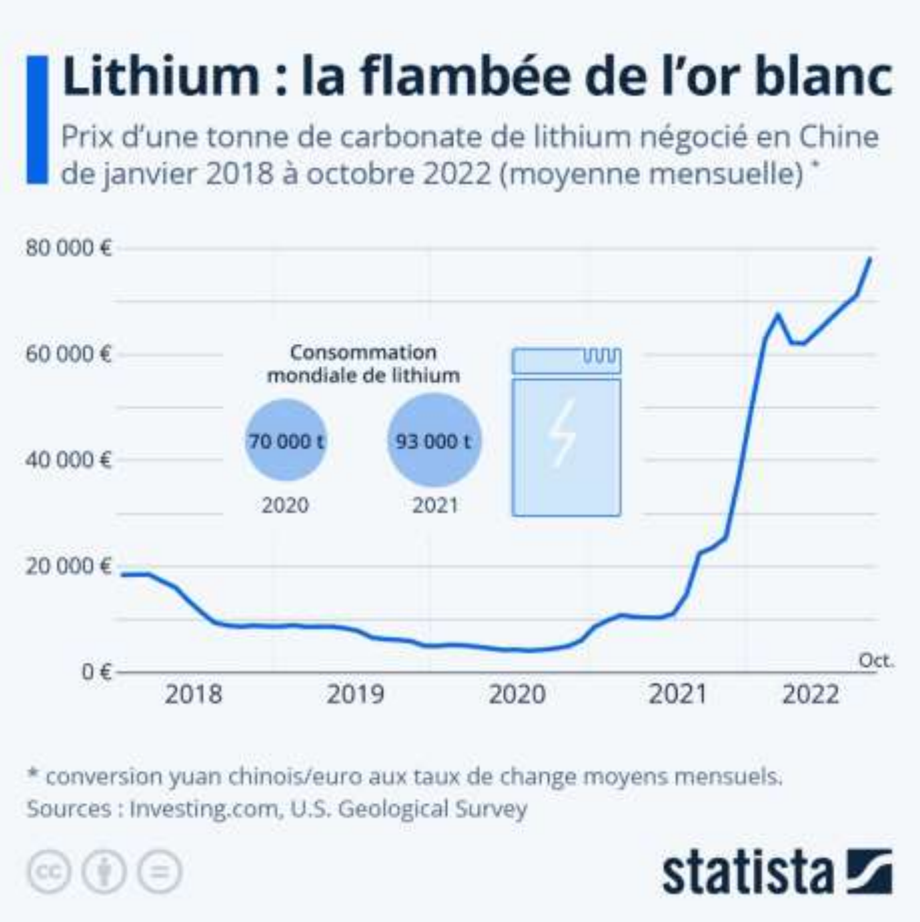


Hao, H.; Liu, Z.; Zhao, F.; Geng, Y.; Sarkis, J. Material Flow Analysis of Lithium in China. *Resour. Policy* **2017**, *51*, 100–106. https://doi.org/10.1016/j.resourpol.2016.12.005

Prix du lithium

Prix marché en octobre 2022

Material	**Price (USD $/Ton)**	**Y2Y**
Cobalt	51955	-2,6 %
Nickel	22366	+16,3 %
Lithium	70470	+ 190,5%
Copper	7580	-20,4 %
Aluminium	2290	-22%
Manganese	2500 (?)*	-7,9%
Iron	551	-33%



https://tradingeconomics.com/commodities (accessed on 08/10/2022).

* Except manganese

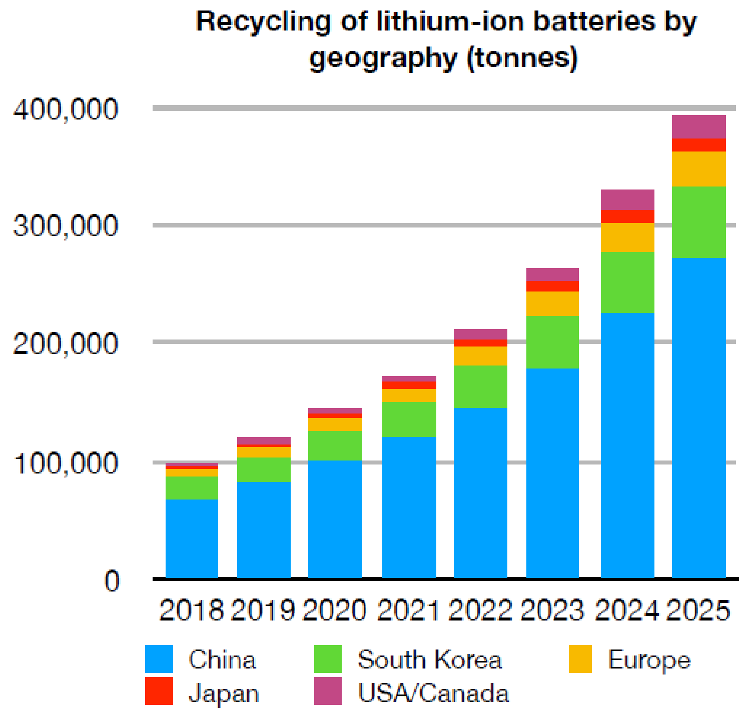
Un aspect économique

2016 Closed loop lithium battery recycling still not economical

“But with only 3% of lithium in the material mix in batteries, the current economic viability of recycling lithium-ion batteries is low.
Speaking at the meeting, Alain Vassart, secretary general of the European Battery Recycling Association (EBRA), said at the present point in time conditions for a closed loop system had not yet been met.
The conditions include: a sufficient, constant flow of recyclable material; completion of tests on various recycling processes; and establishing the price of lithium at a high level for a stable period of time.”

2016 **bestmag.co.uk**

Un aspect économique



Hans Eric Melin, Circular Energy Storage, global battery alliance 2020

Cycle fermé !

Gain d'efficacité
Cycle plus vertueux

…..due to the current low volumes, recyclers struggle to find the best balance between economics and meeting the recovery targets, resulting in the industry not yet focussing enough on high efficiency and low emissions.

Et l'Europe règlemente:

Opérateurs

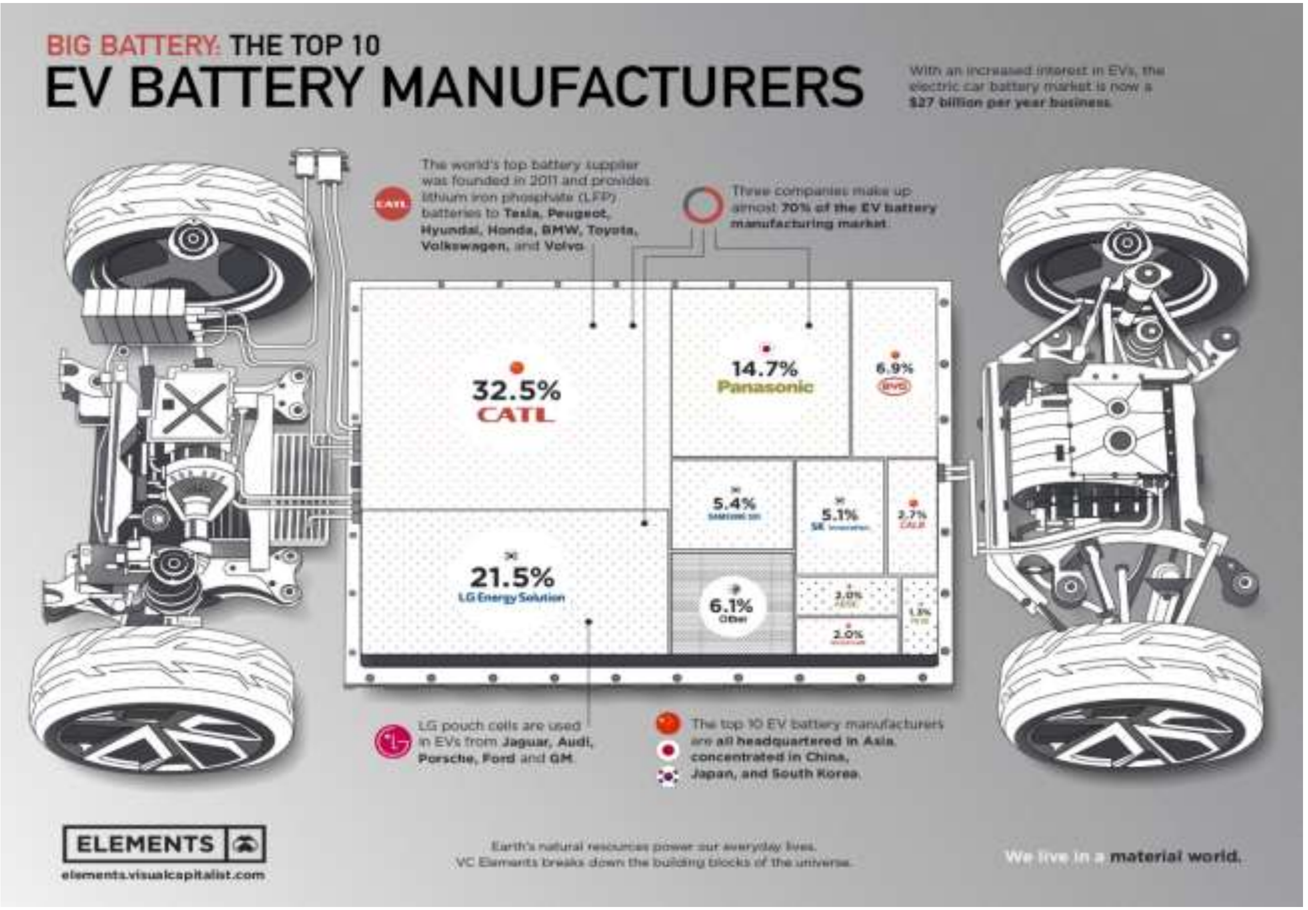
Opérateur	Pays	Traitements spécifique	Capacité (tonne/an)
EuroDieuze	France	Tri/broyage	-
SNAM	France	Broyage/pyrolyse Blackmass	300 (2014)
Solvay	France	Hydrométallurgie	?
Eramet	France	Hydrométallurgie	Pilote
Orano	France	Hydrométallurgie	?
Umicore	Belgique	Hydrométallurgie	7000
Batrec (@Veolia)	Suisse	Hydrométallurgie	
Hydrovolt- Northvolt	Norvège	Hydrométallurgie	8000 t/an 2021
Boliden/Accurec	Finlande	Pyro Cuivre, Blackmass	4000
Fortum	Suède	Hydrométallurgie	
Accurec	Allemagne	Tri/pyrolyse	6000
Duesenfeld (Lithorec)	Allemagne	Hydrométallurgie	3000
Retriev (ex Toxco)	Canada	Hydrométallurgie	
Xstrata	Canada	Pyrométallurgie	
GEM	Chine/Corée	Hydrométallurgie	30000 (2021)
Brunp	Chine	Hydrométallurgie	6000 t (2021)

50 000 t Dunkerque

300 000 t 2025

2028 300000 t/an de batterie à recycler
15% en Europe
Gigafactory = 10% de rebut (scrap)

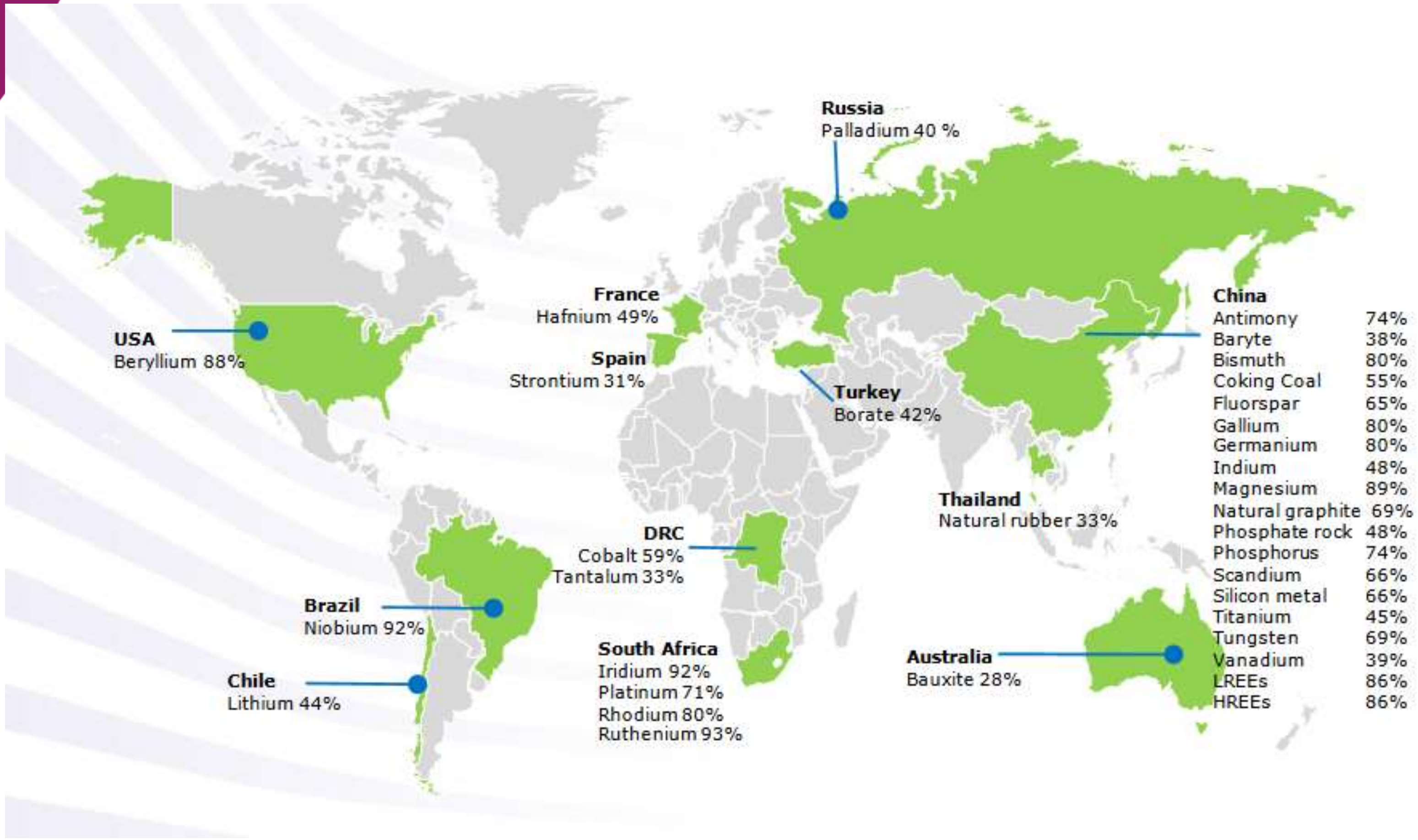
Un aspect géo-politique



According to data from SNE Research, the top three battery makers—CATL, LG, and, Panasonic—combine for nearly 70% of the EV battery manufacturing market.

Gigafactories européennes

Matériaux critiques Europe



2020 CRMs vs. 2017 CRMs		
Antimony	LREEs	Tungsten
Baryte	Indium	Vanadium
Beryllium	Magnesium	
Bismuth	Natural Graphite	Bauxite
Borate	Natural Rubber	Lithium
Cobalt	Niobium	Titanium
Coking Coal	PGMs	
Fluorspar	Phosphate rock	Strontium
Gallium	Phosphorus	
Germanium	Scandium	~~Helium~~
Hafnium	Silicon metal	
HREEs	Tantalum	

Lithium
Cobalt
Graphite (naturel)

Nickel ?

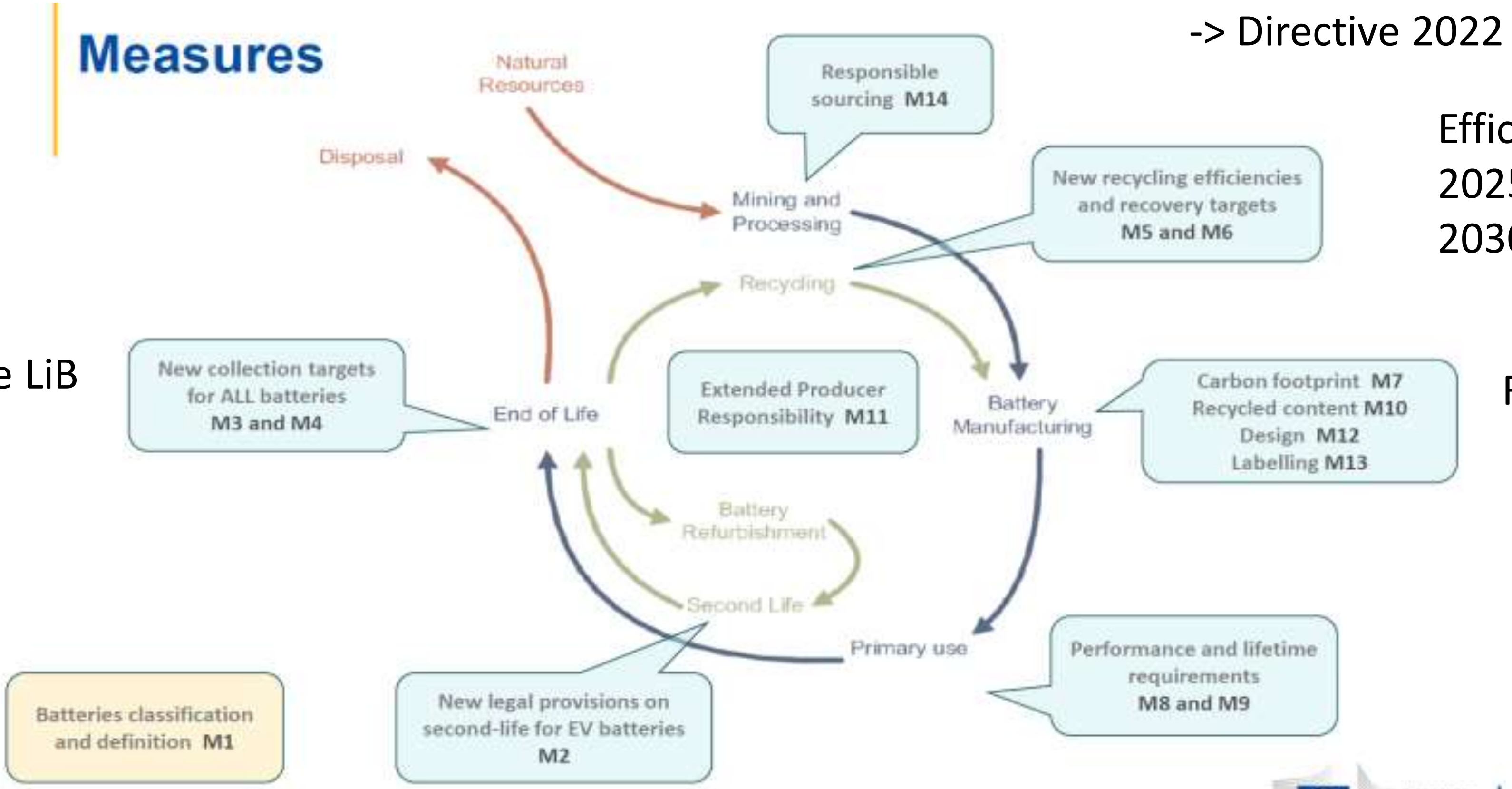
European Commission, Study on the EU's list of critical raw materials – Final reports 2020

Nouvelles directives européennes 2022 (14 Mesures)

Directive 2006/66/CE
-> Directive 2022

Projection 2027
50 000 t batteries

Taux de collecte LiB
2006 45%
2025 65%
2030 70%



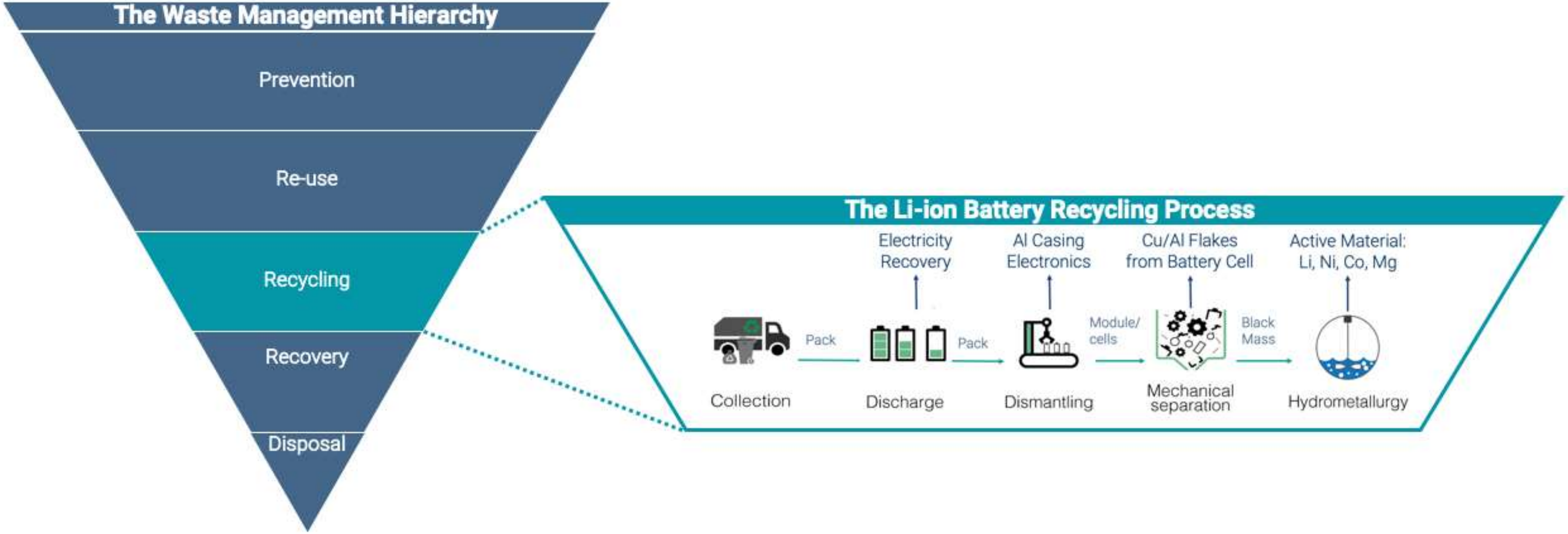
Efficacité du recyclage
2025 65%
2030 70%

Re-Introduction 2030
Co 12%
Li 4%

Passeport de la batterie

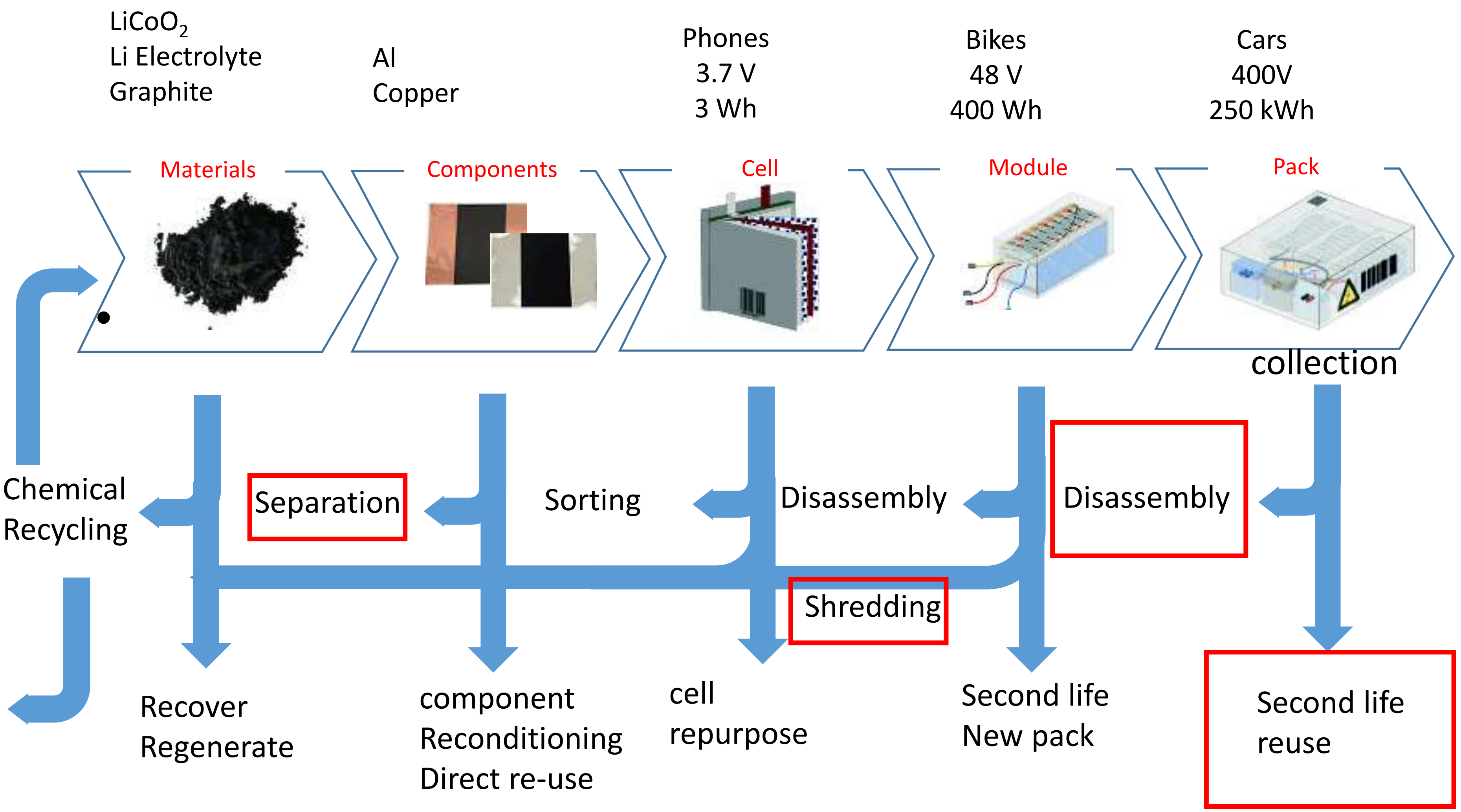
Emmanuel Toussaint Dauvergne, Screlec

Quoi recycler dans une batterie ?
Pourquoi le recyclage ?
Comment le recyclage ?



G. Harper et al. , “Recycling lithium-ion batteries from electric vehicles,” Nature , vol. 575, no. 7781, pp. 75–86, Nov. 2019.

Re- Use



$LiCoO_2$
Li Electrolyte
Graphite
Al
Copper
Phones
3.7 V
3 Wh
Bikes
48 V
400 Wh
Cars
400V
250 kWh
Materials
Components
Cell
Module
Pack
collection
Chemical
Recycling
Separation
Sorting
Disassembly
Disassembly
Shredding
Recover
Regenerate
component
Reconditioning
Direct re-use
cell
repurpose
Second life
New pack
Second life
reuse

Re- Use
Re- Purpose

MOB- ENERGIE

3 kW

CHARLES

LE ROBOT CHARGEUR

Mob-Energy développe des robots chargeurs, baptisés «Charles», qui intègrent des batteries de seconde vie.

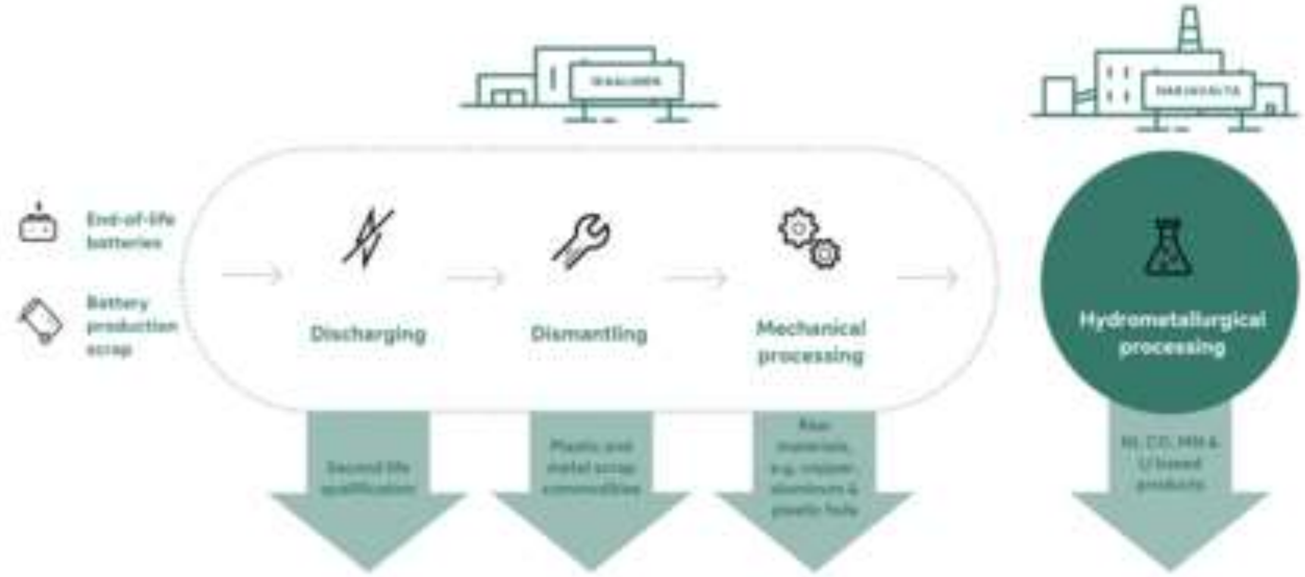
Une fois installé dans un parking, le robot **stocke l'énergie** et **se déplace de manière autonome** vers les véhicules qui ont commandé une charge pour leur donner le kilométrage souhaité.

https://www.mob-energy.com/

RE- USE ?

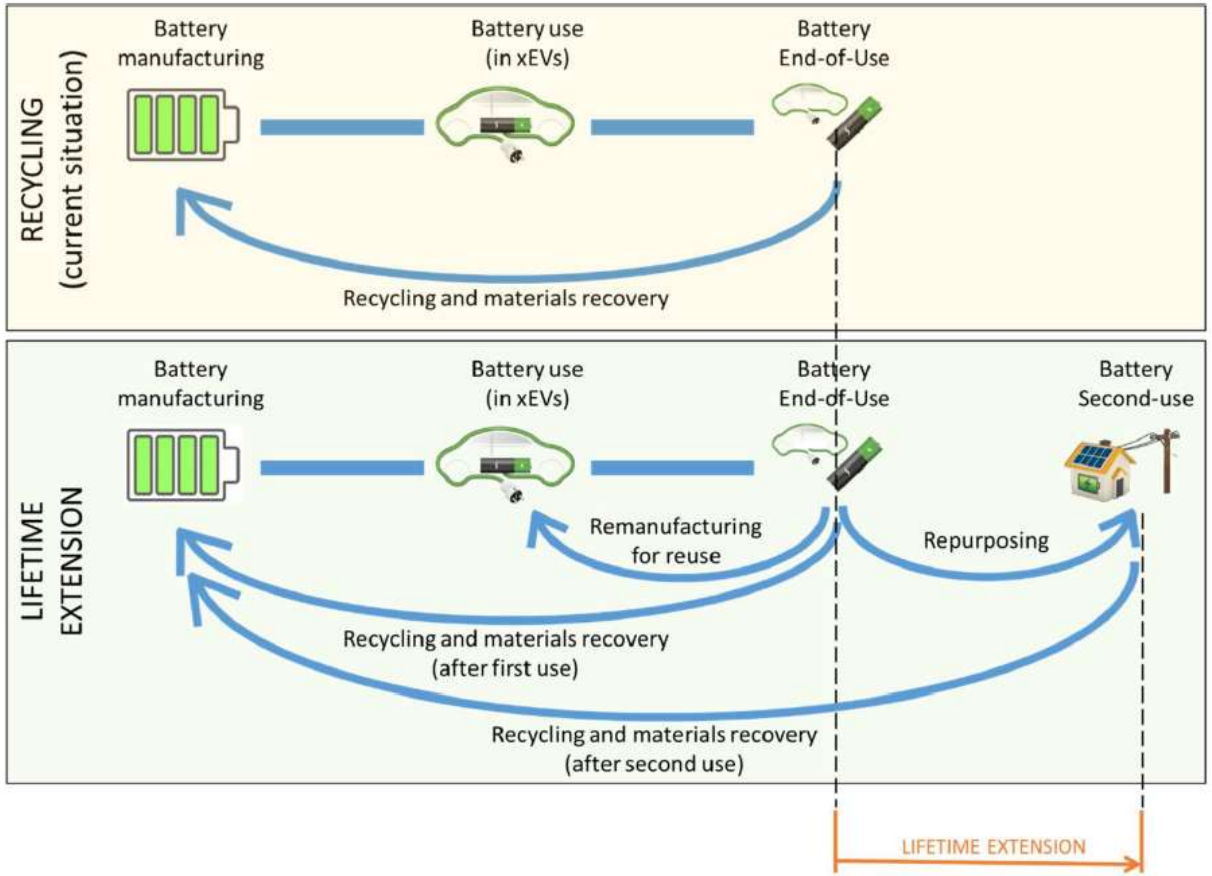
Collaboration Volvo (Suède)
Cleantech company Comsys
Fortum (Finlande)

500 kW



Usines de recylage de Harjavalta (hydrométallurgie)

Refurbish- reuse- recycle



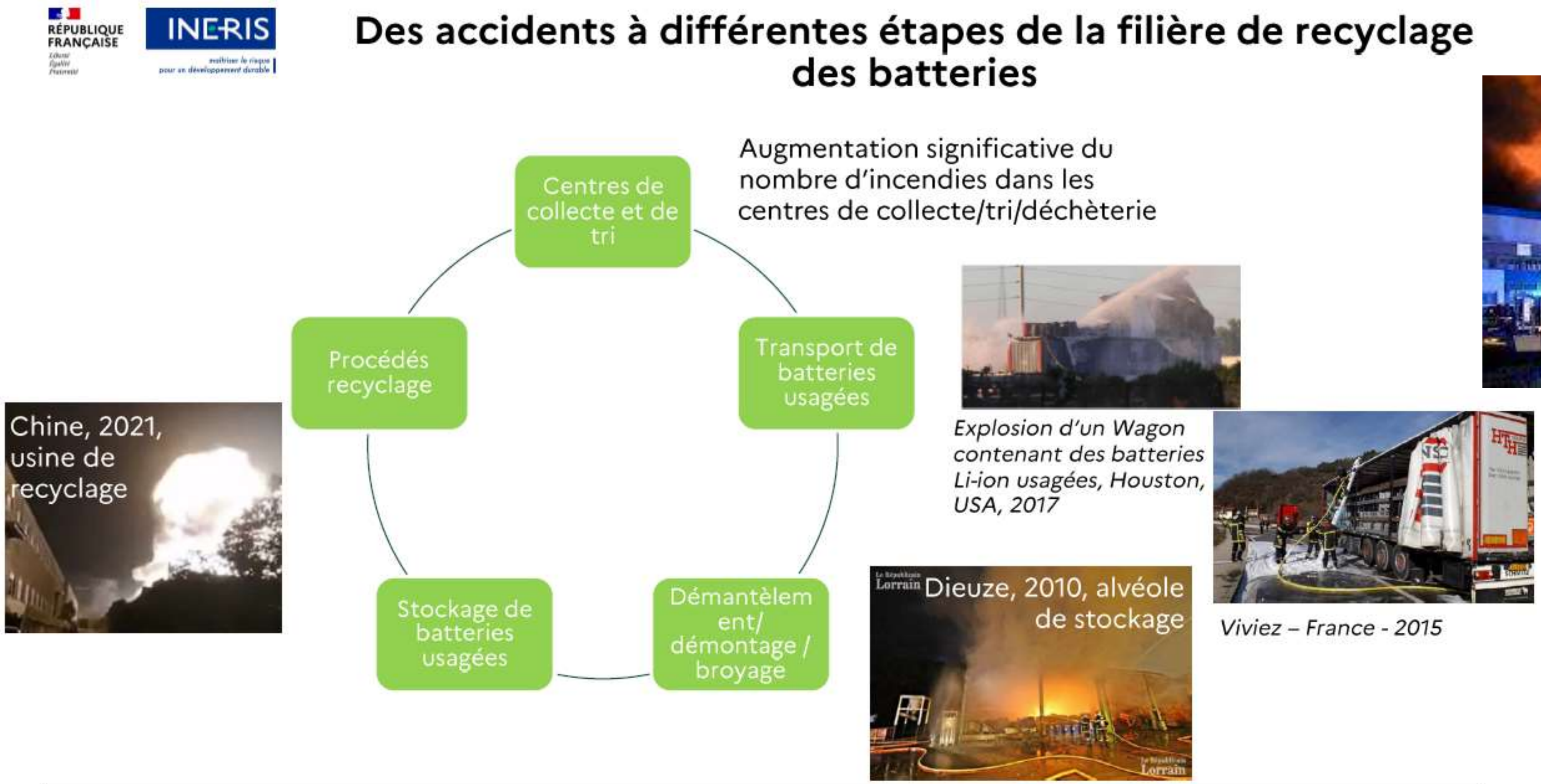
3 MW

Depending on re- use help the amount of Co available for recycling in 2030 ranges between 9% and 15% of Co demand and between 7 and 16% for Li.

S. Bobba et al. Resources, Conservation and recycling 145 (2019) 279-291
M. Pagliaro, M. Meneguzzo, Heliyon 5 (2019) e01866

Pyrométallurgie

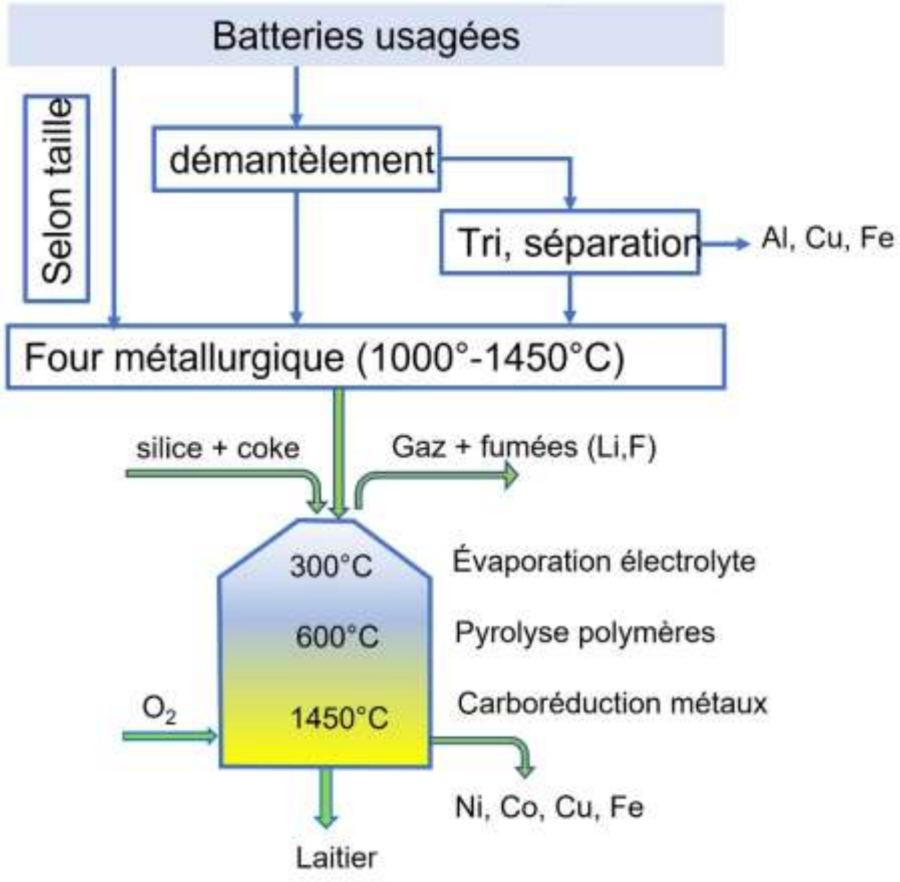
Les enjeux à venir du recyclage en terme de sécurité



Rouen 16/01/2023

C. Dupuis, A. Lecocq, T. Delbaere, La gestion des risques liés au recyclage des batteries et le lien avec les règlementations Présentation RS2E Oct 2022

Smelting = fonderie



Umicore ValÉas process (Belgique et Suède).
Méthode haut foruneau pour récupérer Ni et Co

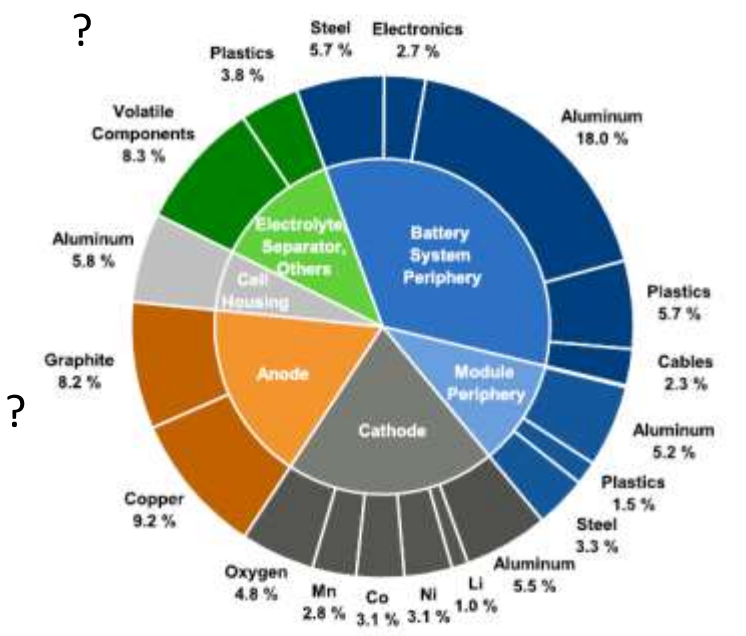
Fonderie en Suède/
Fonderie et hydrométallurgie en Belgique
Dissolution et purification acide sulfurique et récupération $NiSO_4$ and $CoCl_2$

Sécurisé et versatile (Ni-Mh, Pb)
Perte des organiques et graphite
Perte du Li (%) et Al oxydé

Emissions de CO_2

Schéma par Liu, C.; Lin, J.; Cao, H.; Zhang, Y.; Sun, Z. Recycling of Spent Lithium-Ion Batteries in View of Lithium Recovery: A Critical Review. *J. Clean. Prod.* **2019**, *228*, 801–813.

Module	LiCoO2	Cours $ /t	ratio %	LiCoO2/t
		$ 2022	%	$\ tonne
Li	1,6	40000	70,00%	448
Co	12,5	51500	70,00%	4506
Ni		22470	70,00%	0
Mn		2200	70,00%	0
O	7,2	0	70,00%	0
LiPF6	1,8	0	70,00%	0
DMC	10,9	0	70,00%	0
Graphite	15,5	1300	70,00%	141
Al (métal)	30,2	2290	70,00%	484
Cu (métal)	7,3	7580	70,00%	387
Fe chassis(métal)	4,4	550	70,00%	17
Plastique	7,5	0	70,00%	0
Autres (ou FePO4)	0,7	0	70,00%	0
TOTAL	100		RECUPERE	4893
Diagnostic				343
Logistique				400
Broyage				-
Pyrométallurgie				643
Bénéfice $ / ton				3507



Pyrométallurgie:

Sécurisé
Mix batteries (Pb, NiCd, NiMH)
Peu d'étapes

Pas si énergétique

Boucle non fermée (non BG)
Perte Li
Émissions CO_2

Estimations coûts du recyclage:
Roland Berger estimates accessed oct 2021 https://www.rolandberger.com/en/Insights/Publications

Procédés en cours

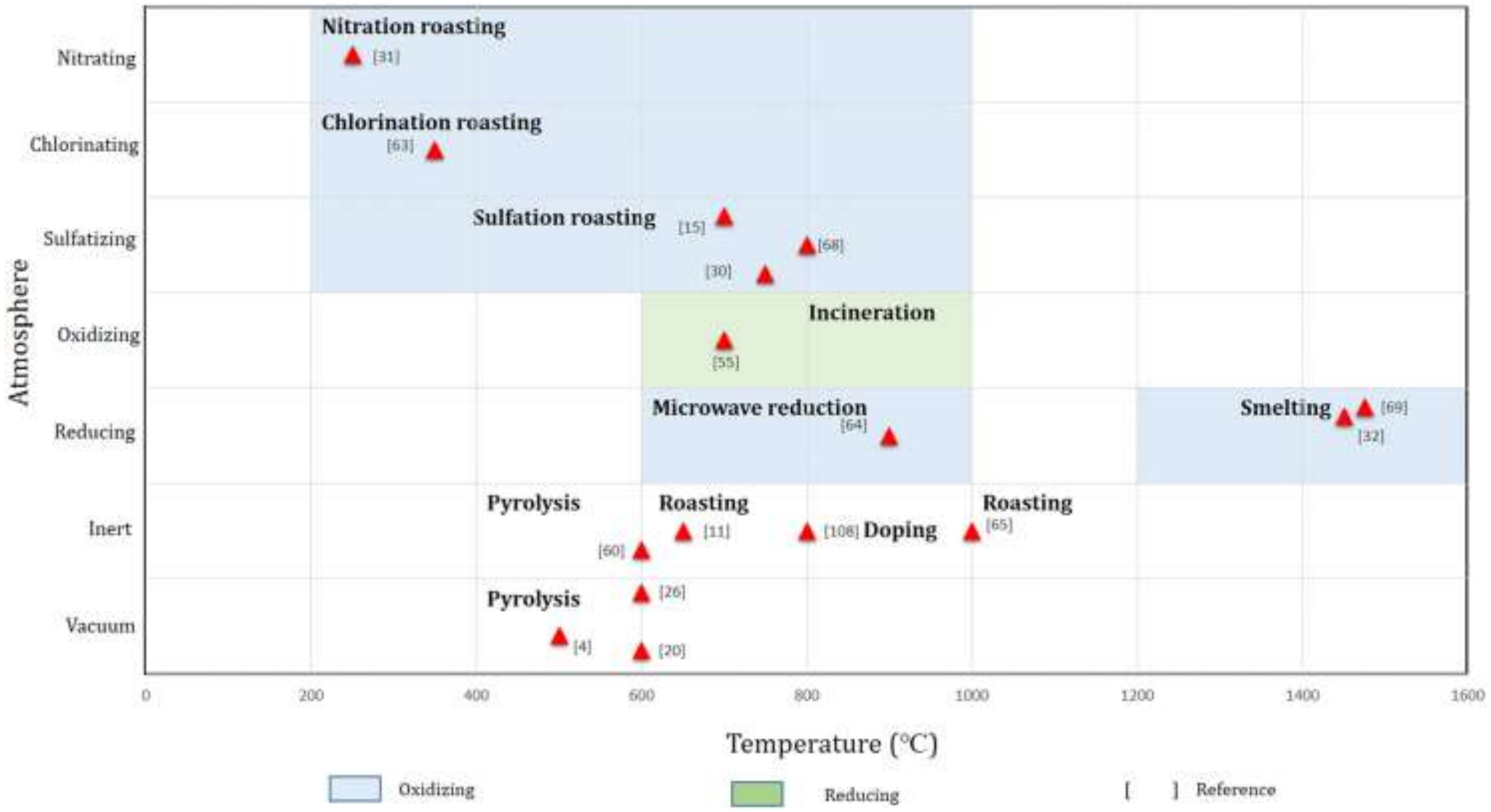
Table 3
Current major commercial processes for recycling spent LIBs (2018a; 2018b; 2018c; 2018d; 2018e; 2018f; Knights and Saloojee, 2015; Lv et al., 2018; Pistoia et al., 2001).

Company/process	Capacity (tonnes/year)	Main products	Technology	Li recovery
TOXCO (Retriev)	4500	Li_2CO_3, mixed metal oxides	Hydro-dominant	Yes
Accurec GmbH	6000	Co alloy, Li_2CO_3	Pyro-dominant	Yes
Inmetco	6000	Co alloy	Pyro-dominant	No
Green Eco-Manufacture Hi-Tech Co	20,000	NiCo alloy, Ni, Co, Co_3O_4	Hydro-dominant	No
Akkuser Ltd	4000	Metal powder	Pyro-dominant	No
Bangpu Ni/Co High-Tech Co.	3600	Cathode materials, Co_3O_4	Hydro-dominant	No
Sumitomo-Sony	150	Co alloy, Co metal	Pyro-dominant	No
Batrec AG	200	Battery scraps	Pyro-dominant	No
SNAM	300	NR	Pyro-dominant	No
ERAMET (Valdi)	20,000	Raw materials for special steel	Pyro-dominant	No
Nippon Recycle Center Co.	5000	Raw materials for special steel	Pyro-dominant	No
DK Recycling und Roheisen GmbH	NR	NR	Pyro-dominant	NR
Umicore	7000	Ni-Co alloy, $NiCO_3$, $NiSO_4$, $CoCO_3$, $CoSO_4$	Pyro-dominant	No
Glencore plc. (Xstrata)	7000	Co alloy	Pyro-dominant	No

NR: not reported.

Compilation: Liu, C.; Lin, J.; Cao, H.; Zhang, Y.; Sun, Z. Recycling of Spent Lithium-Ion Batteries in View of Lithium Recovery: A Critical Review. *J. Clean. Prod.* **2019**, *228*, 801–813.

Recyclage Traitements thermiques

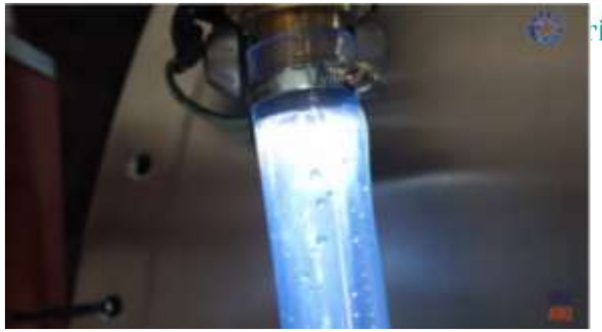


Makuza, B.; Tian, Q.; Guo, X.; Chattopadhyay, K.; Yu, D. Pyrometallurgical Options for Recycling Spent Lithium-Ion Batteries: A Comprehensive Review. *J. Power Sources* **2021**, *491*, 229622.

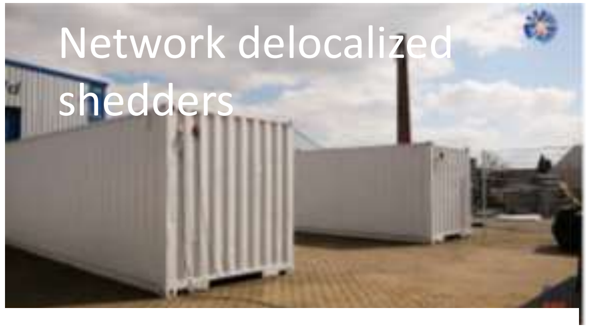
Traitements physiques

Traitement mécanique







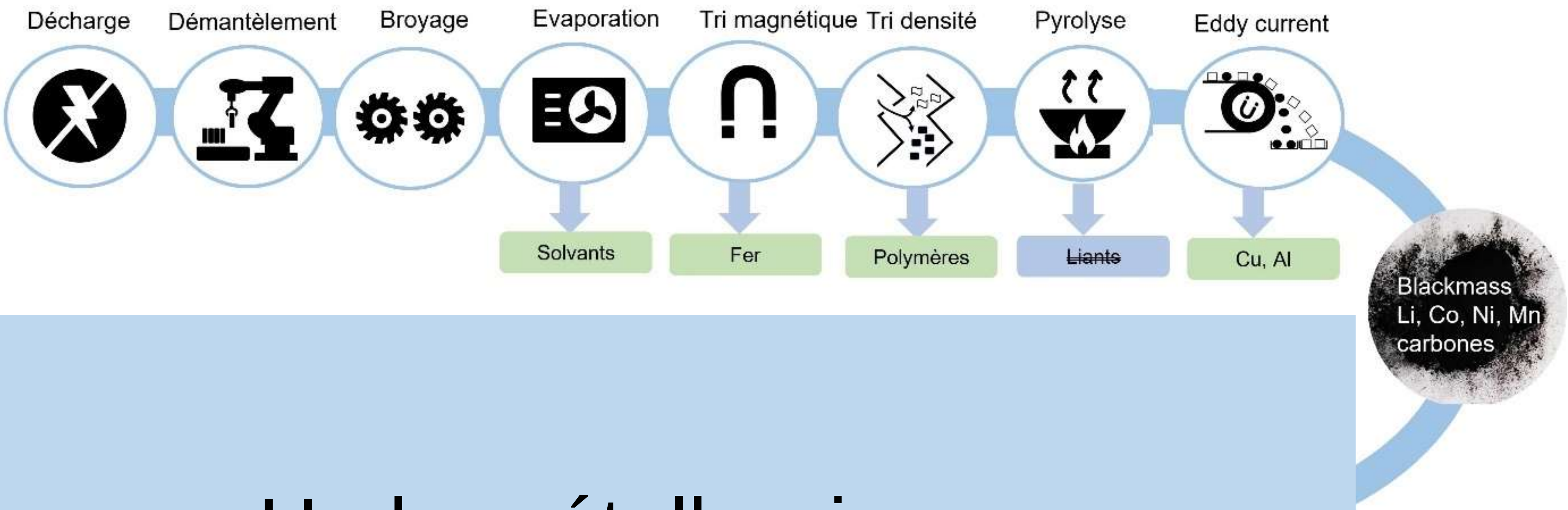
Duesenfeld https://www.youtube.com/watch?v=pwoRxee97Rs

Robotisation

Veolia

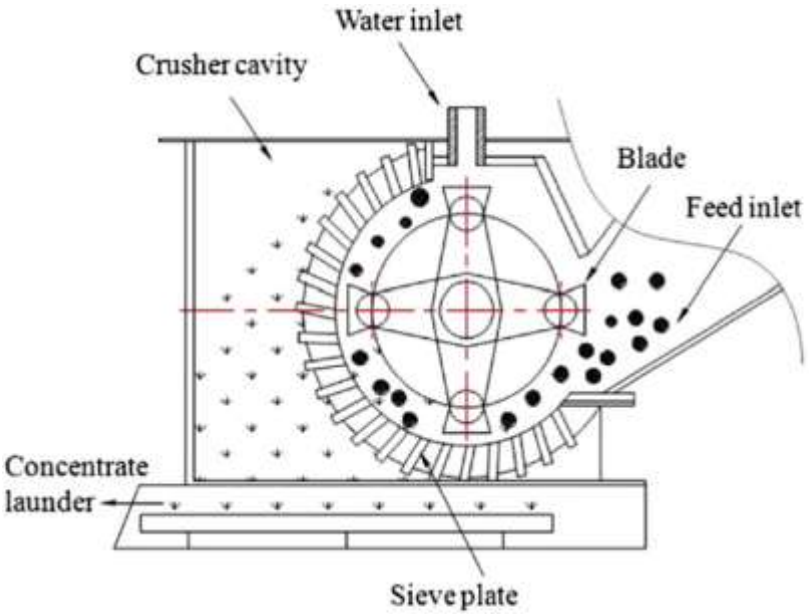
https://www.youtube.com/watch?v=xPDkiwoq6Vg

Tri mécanique



Hydrométallurgie

Séparation mécanique poussée



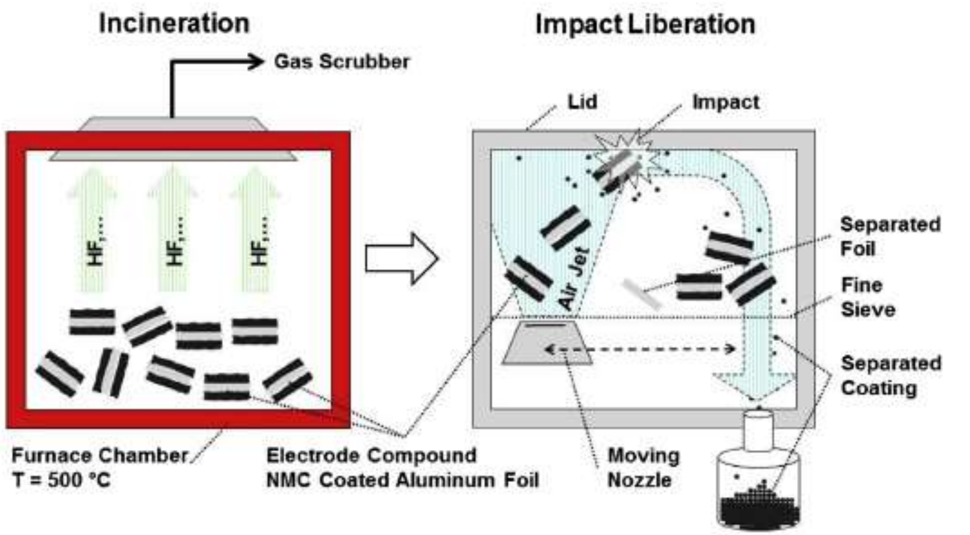


Fig. 2. Experimental set-up for the ANVIIL (adhesion neutralization via incineration and impact liberation) process.

Zhang, T.; He, Y.; Ge, L.; Fu, R.; Zhang, X.; Huang, Y. Characteristics of Wet and Dry Crushing Methods in the Recycling Process of Spent Lithium-Ion Batteries. *J. Power Sources* **2013**, *240*, 766–771

Hanisch, C.; Loellhoeffel, T.; Diekmann, J.; Markley, K. J.; Haselrieder, W.; Kwade, A. Recycling of Lithium-Ion Batteries: A Novel Method to Separate Coating and Foil of Electrodes. *J. Clean. Prod.* **2015**, *108*, 301–311

Machines de triage- broyage

Dry cell box pour le scrap sec
Batteries usagées

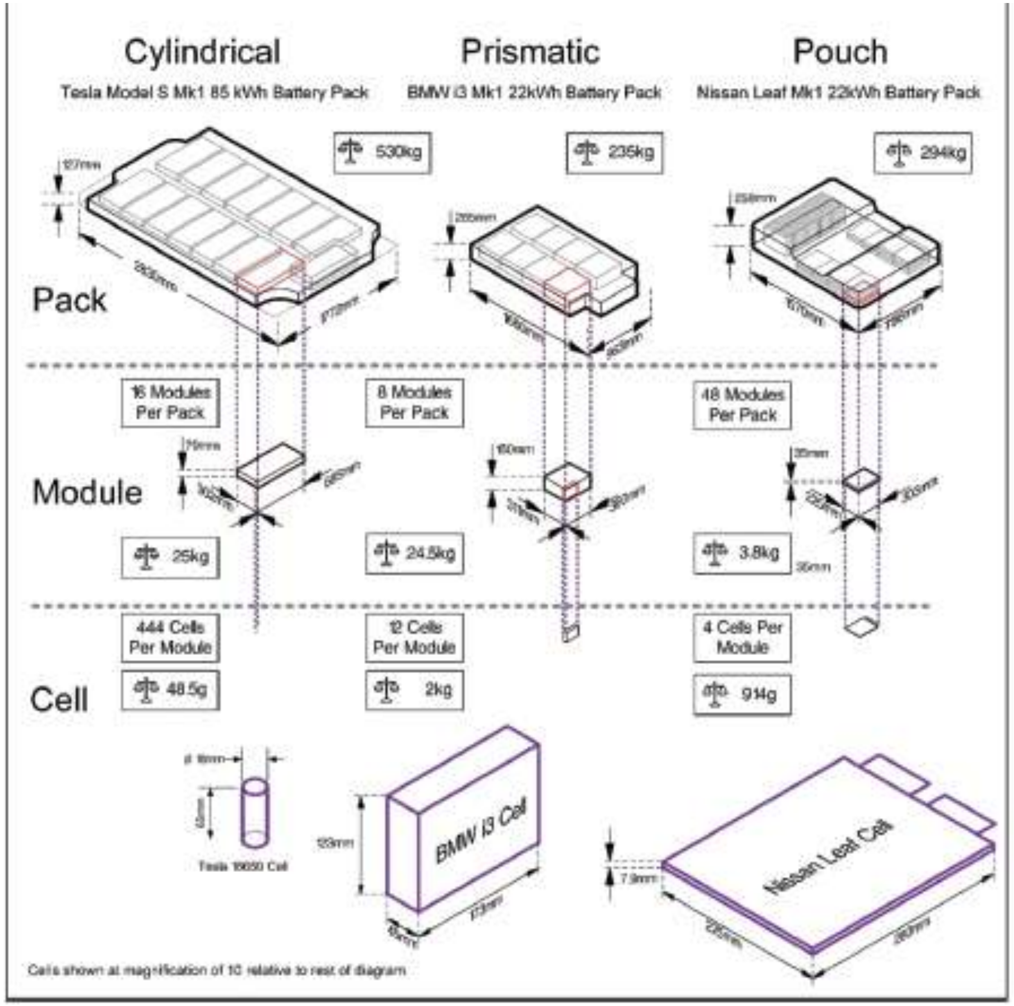
Robotisation = Standardisation

Cell to module to pack

Cell to pack

Cell to chassis

Quid de l'écoconception ?



Bilan traitement physique

Améliorer le rendement de séparation collecteur blackmass
Séparations mécaniques poussées (jets)
Dissolution solvants NMP/DMF
Dissolution sels fondus

Pyrolyse 500-600°C destruction des liants

Desaggréger les particules (régénération)
Nettoyer la surface des particules
Accélérer leur dissolution et augmenter le rendement

He, Y.; Yuan, X.; Zhang, G.; Wang, H.; Zhang, T.; Xie, W.; Li, L. A Critical Review of Current Technologies for the Liberation of Electrode Materials from Foils in the Recycling Process of Spent Lithium-Ion Batteries. *Sci. Total Environ.* **2021**, *766*, 142382

Hydrométallurgie

Module	LiCoO2	NMC811	Cours $ /t	Ratio V %	LiCoO2/t	NMC811	NMC
			$ 2022	%	$\ tonne	$\ tonne	$ / 40 kWh
Li	1,6	1,6	40000	70,00%	448	448	125,4
Co	12,5	1,3	51500	70,00%	4506	469	131,2
Ni		10,5	22470	70,00%	0	1652	462,4
Mn		1,2	2200	70,00%	0	18	5,2
O	7,2	7,2	0	70,00%	0	0	0,0
LiPF6	1,8	1,8	0	70,00%	0	0	0,0
DMC	10,9	10,9	0	70,00%	0	0	0,0
Graphite	15,5	15,5	1300	70,00%	141	141	39,5
Al (métal)	30,2	30,2	2290	70,00%	484	484	135,5
Cu (métal)	7,3	7,3	7580	70,00%	387	387	108,5
Fe chassis(métal)	4,4	4,4	550	70,00%	17	17	4,7
Plastique	7,5	7,5	0	70,00%	0	0	0,0
Autres (ou FePO4)	0,7	0,7	0	70,00%	0	0	0,0
RECYCLE	51,6 %w	51,6%w		$	5842	3442	985,2
Diagnostic					343	343	96,0
Logistique					400	400	112,0
Broyage					157	157	44,0
Hydrométallurgie					643	643	180,0
Bénéfice $ / ton					4299	1932	553,2

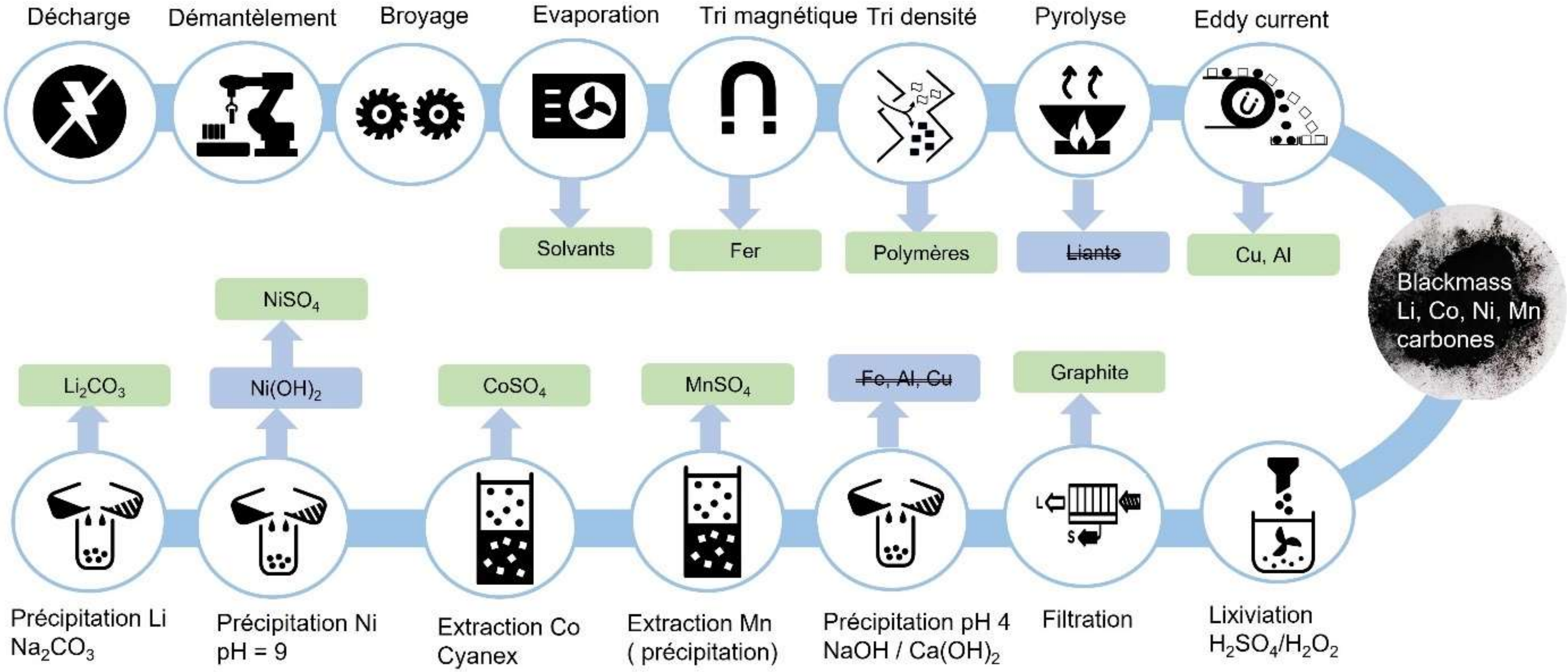
Ferait les 70% (2030)

Diminue le CO_2

Estimations coûts du recyclage:
Roland Berger estimates accessed oct 2021 https://www.rolandberger.com/en/Insights/Publications

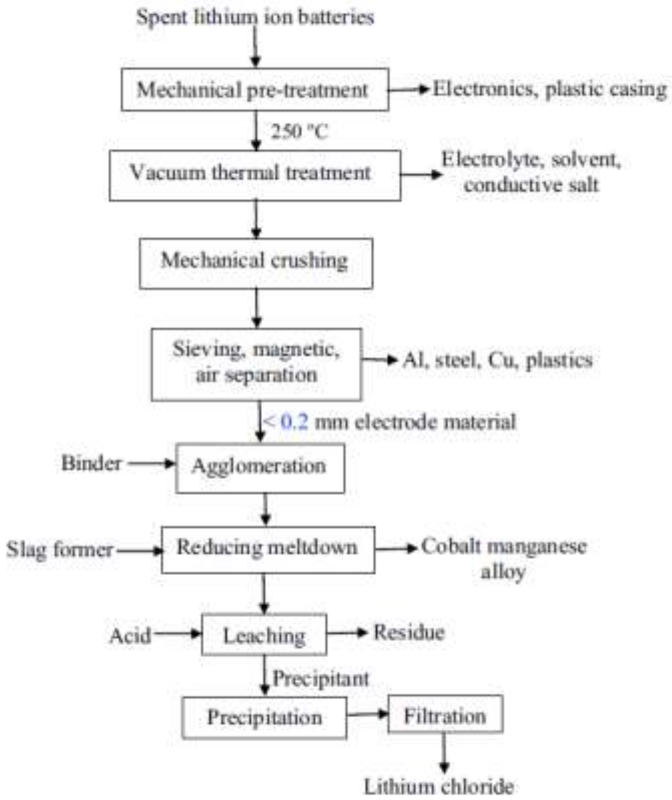
1 kWh ≈ 7 kg

Hydrométallurgie

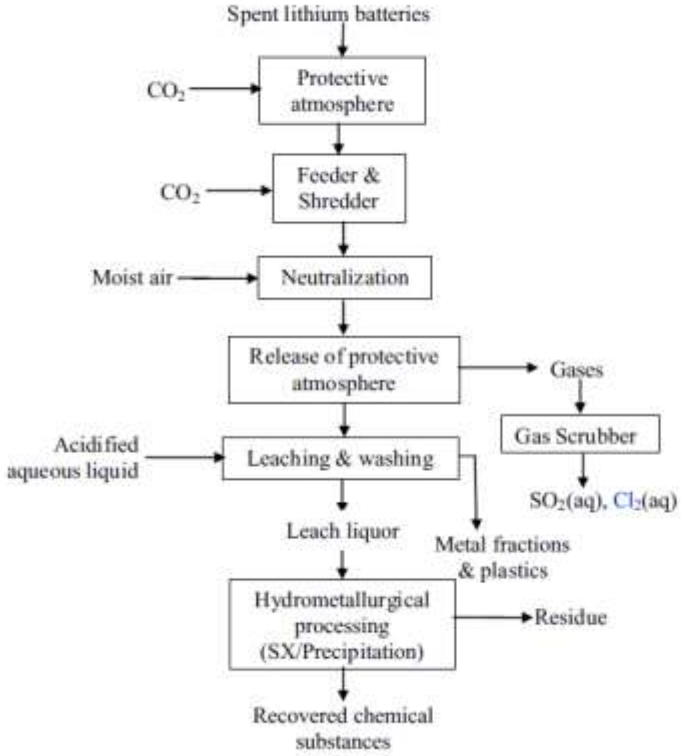


Sélection de procédés

Accurec (Allemagne)



BATREC AG (Veolia Suisse)



RECUPYL (France)

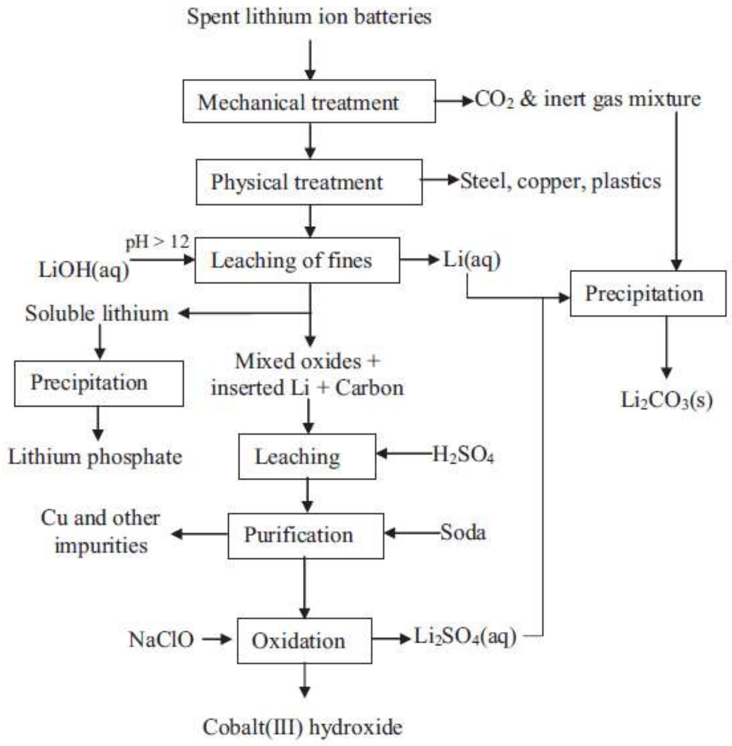


Fig. 5. Recupyl process for LIBs recycling.

Meshram, P.; Pandey, B. D.; Mankhand, T. R. Extraction of Lithium from Primary and Secondary Sources by Pre-Treatment, Leaching and Separation: A Comprehensive Review. *Hydrometallurgy* **2014**, *150*, 192–208. https://doi.org/10.1016/j.hydromet.2014.10.012.

Leaching/ lixiviation

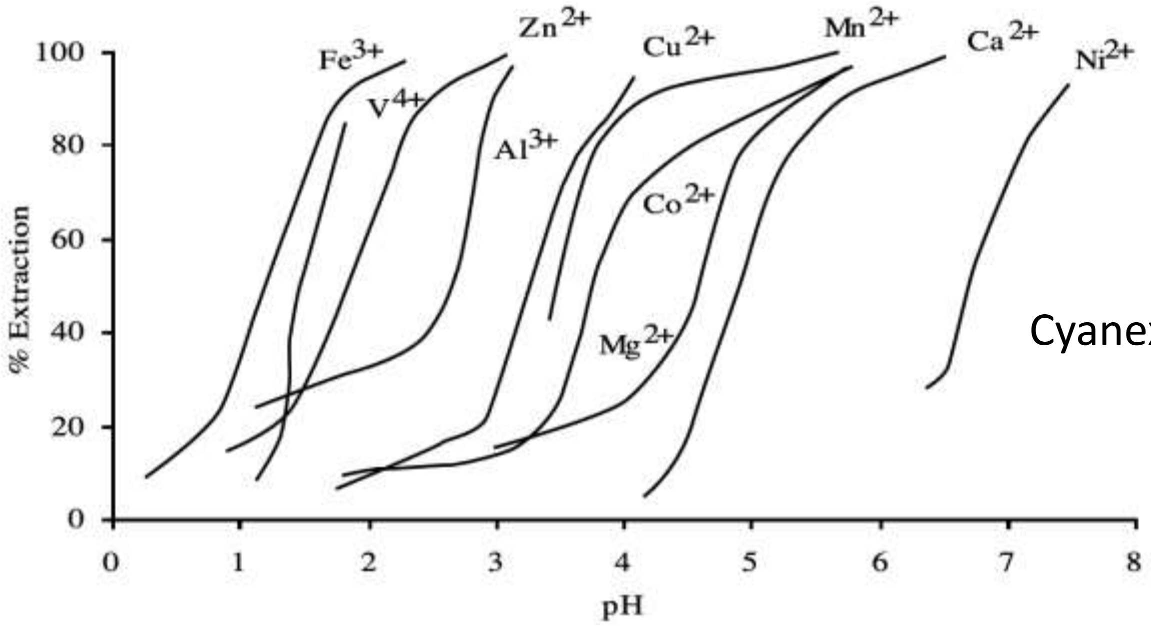
Table 3 Leaching conditions of 8 hydrometallurgical processes with various acids and redox agents in the literature showing temperature time and solid/liquid (S/L) ratio. See ESI† for methods and data

Literature reference	Input material	Acid (M)	Redox agent (M)	T (°C)	t (h)	S/L (g L^{-1})	Relative cost	Relative value
Kim *et al.*[92]	Cathode black mass	H_2SO_4 (2)	H_2O_2 (2.13)	60	2	100	10	2.9
Dutta *et al.*[93]	Cathode black mass	H_2SO_4 (2)	H_2O_2 (4.26)	30	3	75	22	0.36
Gao *et al.*[94]	Cathode black mass	Formic (1)	H_2O_2 (6)	60	1	50	55	1.6
Huang *et al.*[95]	Cathode black mass	HCl (6.5)	H_2O_2 (6.4)	60	2	200	14	1.5
Prabaharan *et al.*[96]	Calcined black mass	H_2SO_4 (2)	Electrolysis, 400 A m^{-2}	25	3	75	10	1.1
Hu *et al.*[97]	Calcined black mass	H_2SO_4 (3.5)	—	85	3	200	2	2.5
Yang *et al.*[98]	Calcined black mass	H_2SO_4 (4)	H_2O_2 (2)	90	2	25	43	3.0
Barik *et al.*[99]	Calcined black mass	HCl (1.8)	—	50	1.5	200	1	1

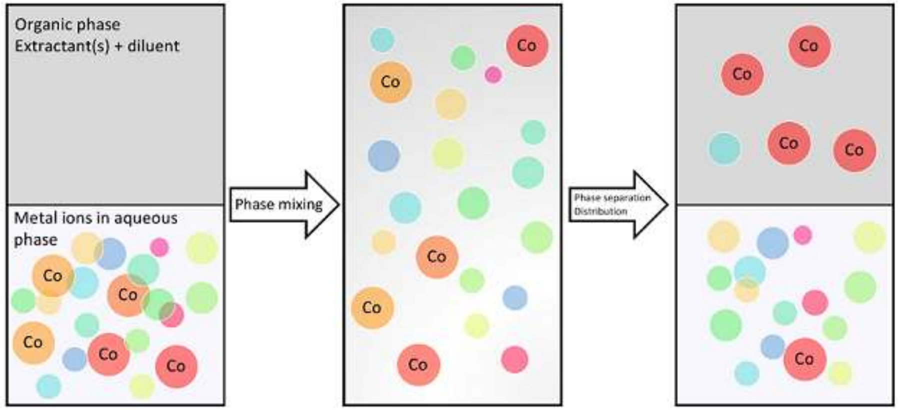
$$2LiMO_{2(s)} + 3H_2SO_4 + H_2O_{2(aq)} \rightarrow 2MSO_{4(aq)} + Li_2SO_{4(aq)} + 4H_2O + O_{2(g)}$$

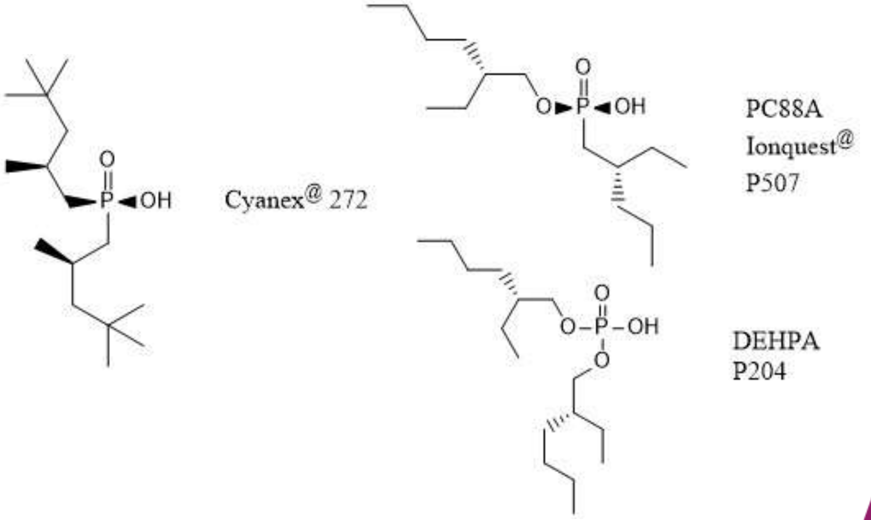
Thompson, D. L.; Hartley, J. M.; Lambert, S. M.; Shiref, M.; Harper, G. D. J.; Kendrick, E.; Anderson, P.; Ryder, K. S.; Gaines, L.; Abbott, A. P. The Importance of Design in Lithium Ion Battery Recycling – a Critical Review. *Green Chem.* **2020**, *22* (22), 7585–7603

Solvent separation SX



Cyanex@272



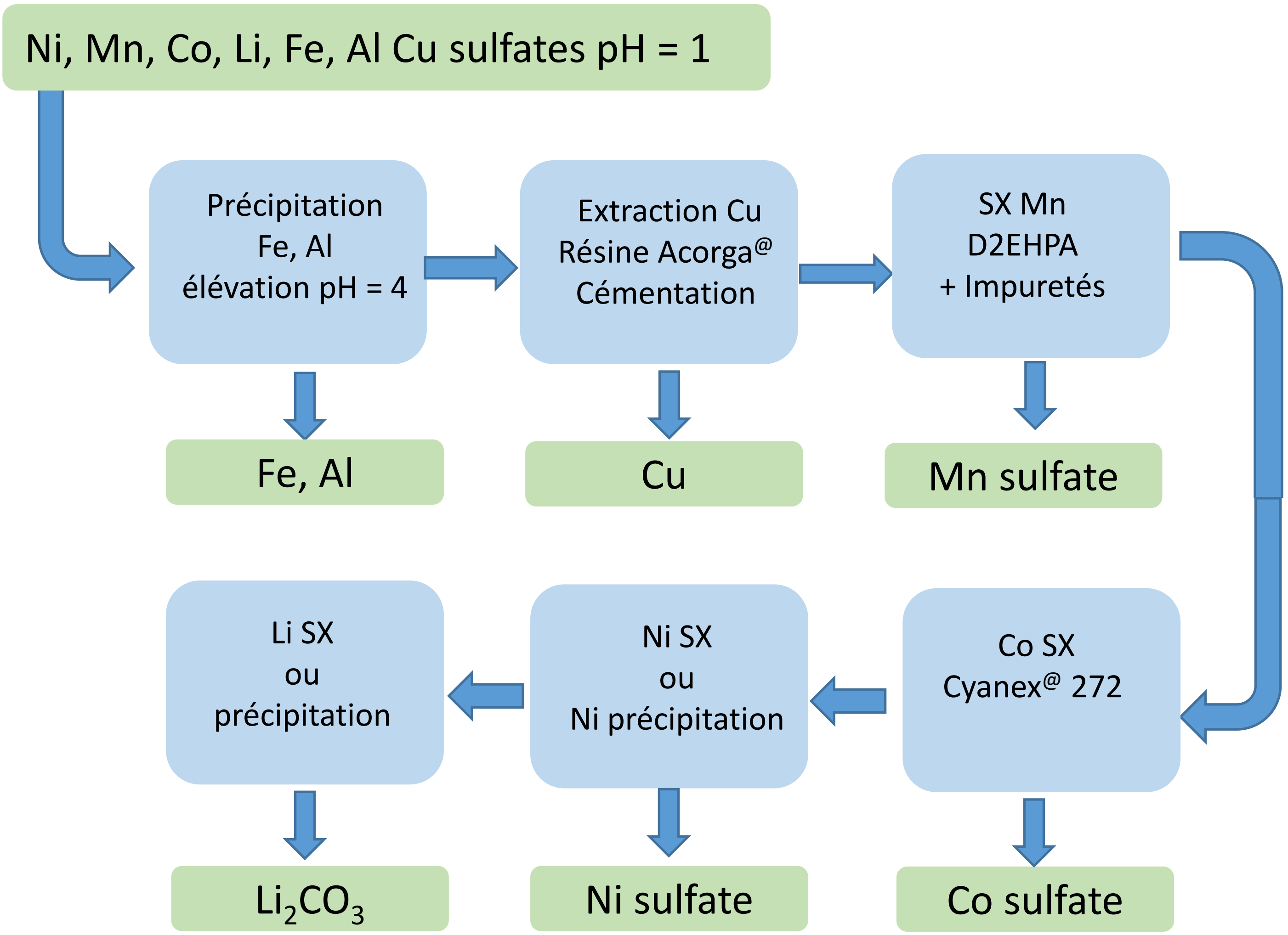


$Co^{2+} + 2(RH)_{2org} \leftrightarrow Co(R_2H)_{2org} + 2H^+$

$Ni^{2+} + 3(RH)_{2org} \leftrightarrow Ni(R_2H_2)_2(RH)_2 + 2H^+$

Moats, M.S., Davenport, W.G., 2014. Chapter 2.2 - Nickel and Cobalt Production, in: Seetharaman, S. (Ed.) Treatise on Process Metallurgy. Elsevier, Boston, pp. 625-669.

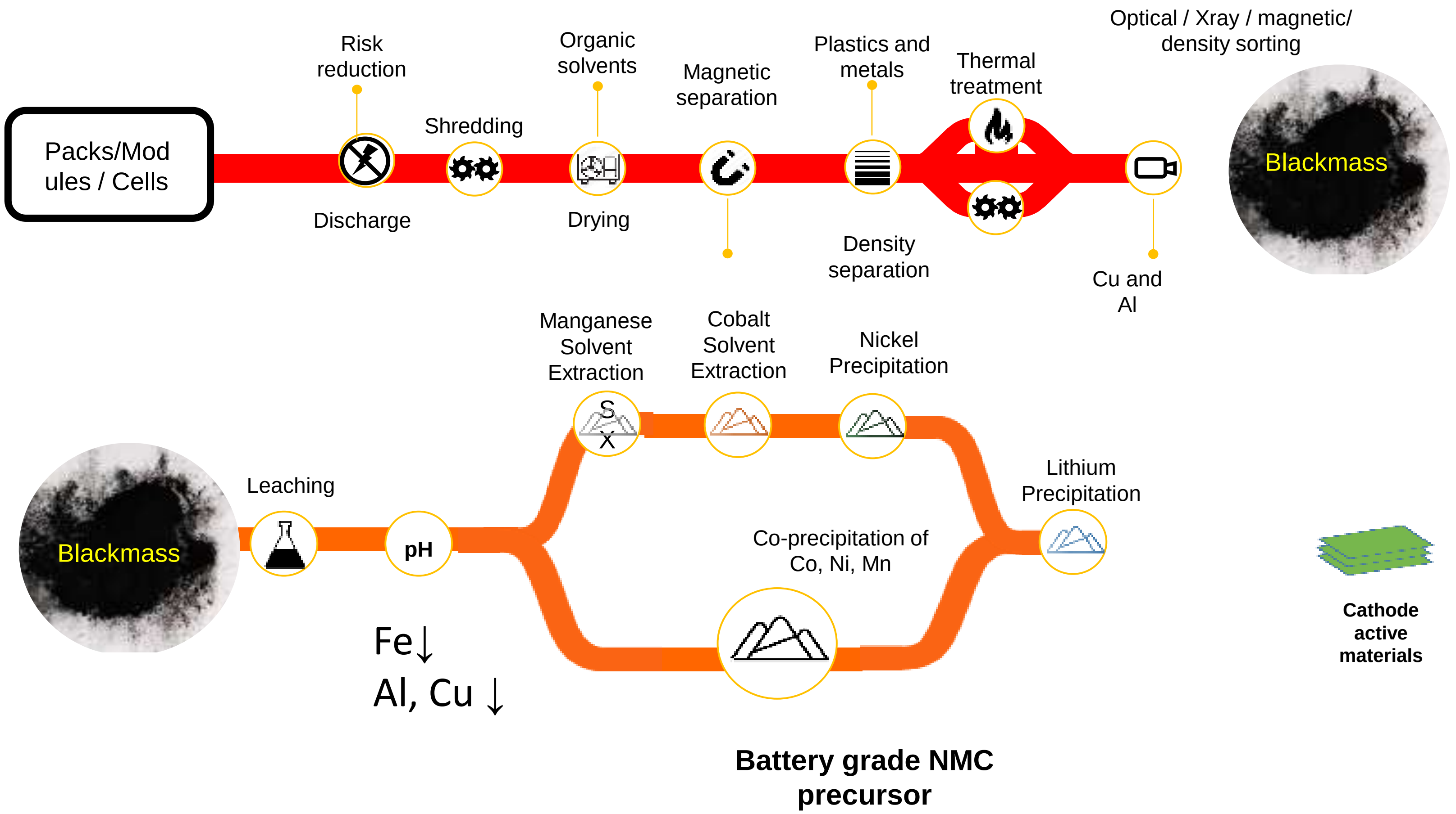
Hydrométallurgie



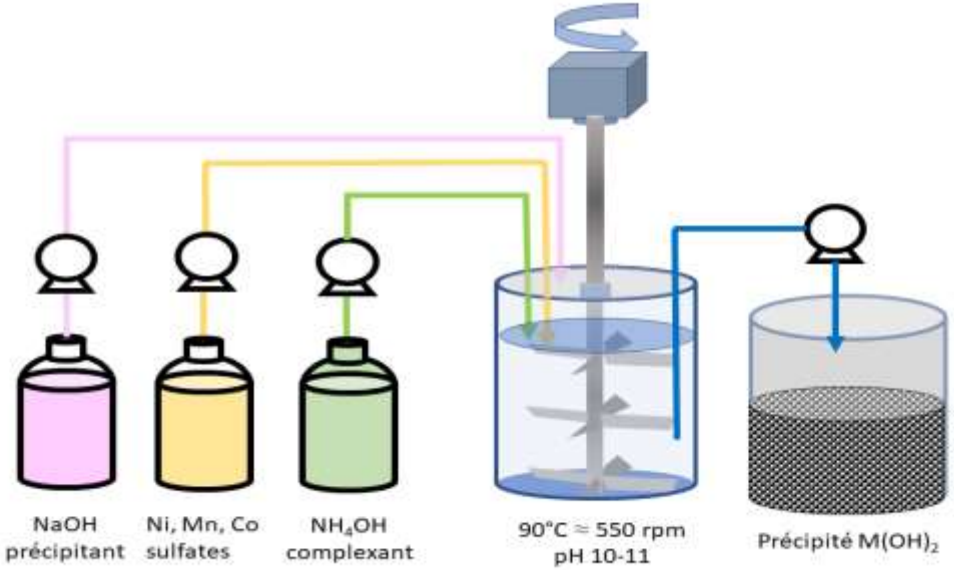
Procédé

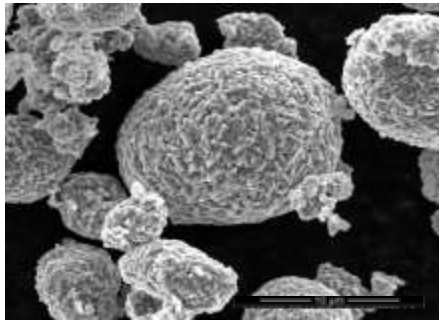
Solvay

Procédé Eramet



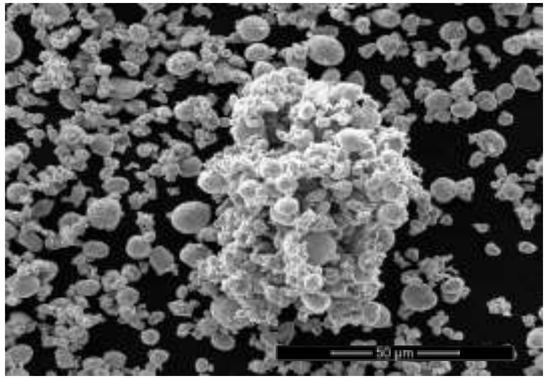
Synthèse boucle courte





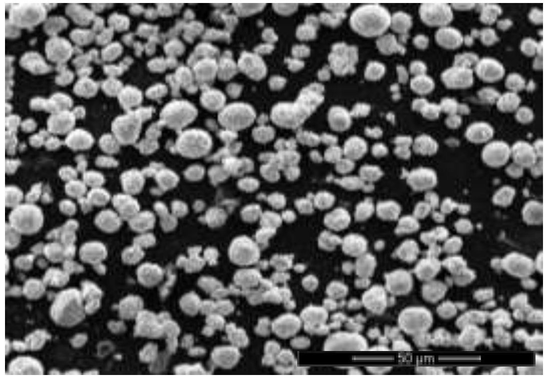
Conventional NMC synthesis

Cas NMC 622
Broyage avec LiOH
650-950°C 12 h



Rôle des impuretes

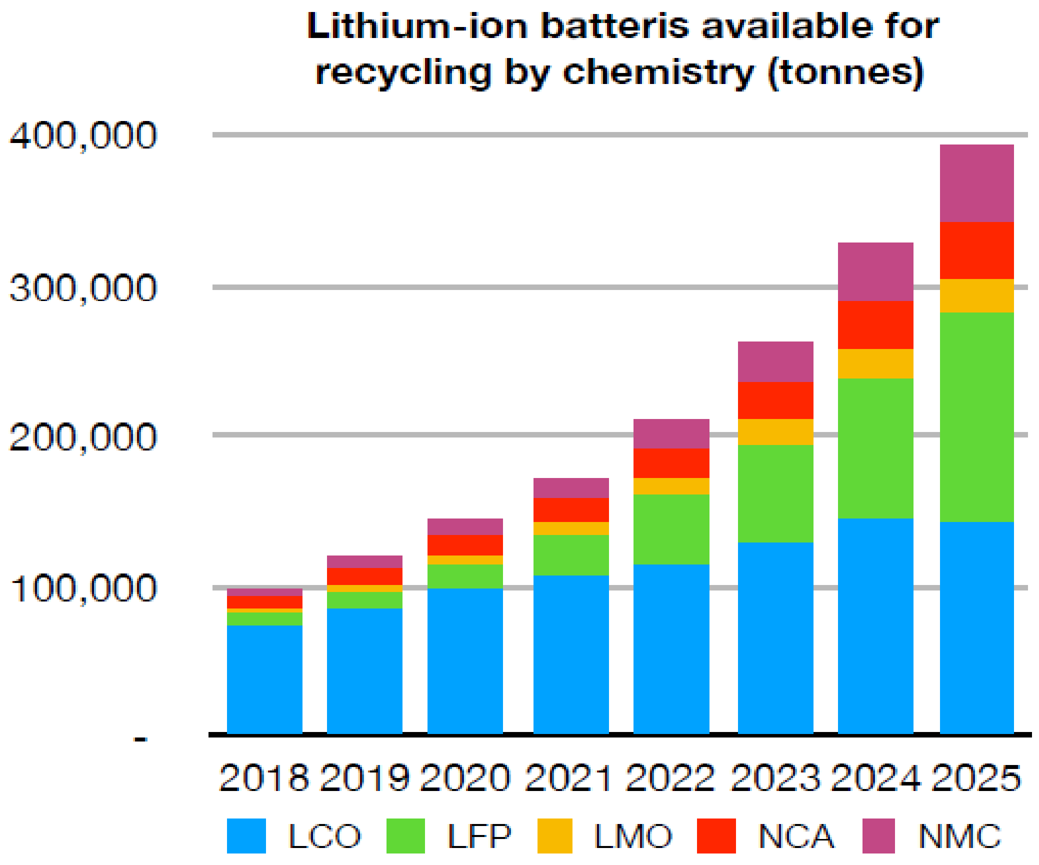
Lavage
desagglomération



Direct precipitation of NMC from recycling loop using the conventional process is possible

Recyclage direct
Délamination

Évolution du contenu



Marché dominé par la Chine

Limiter le coût des procédés
Limiter les émissions

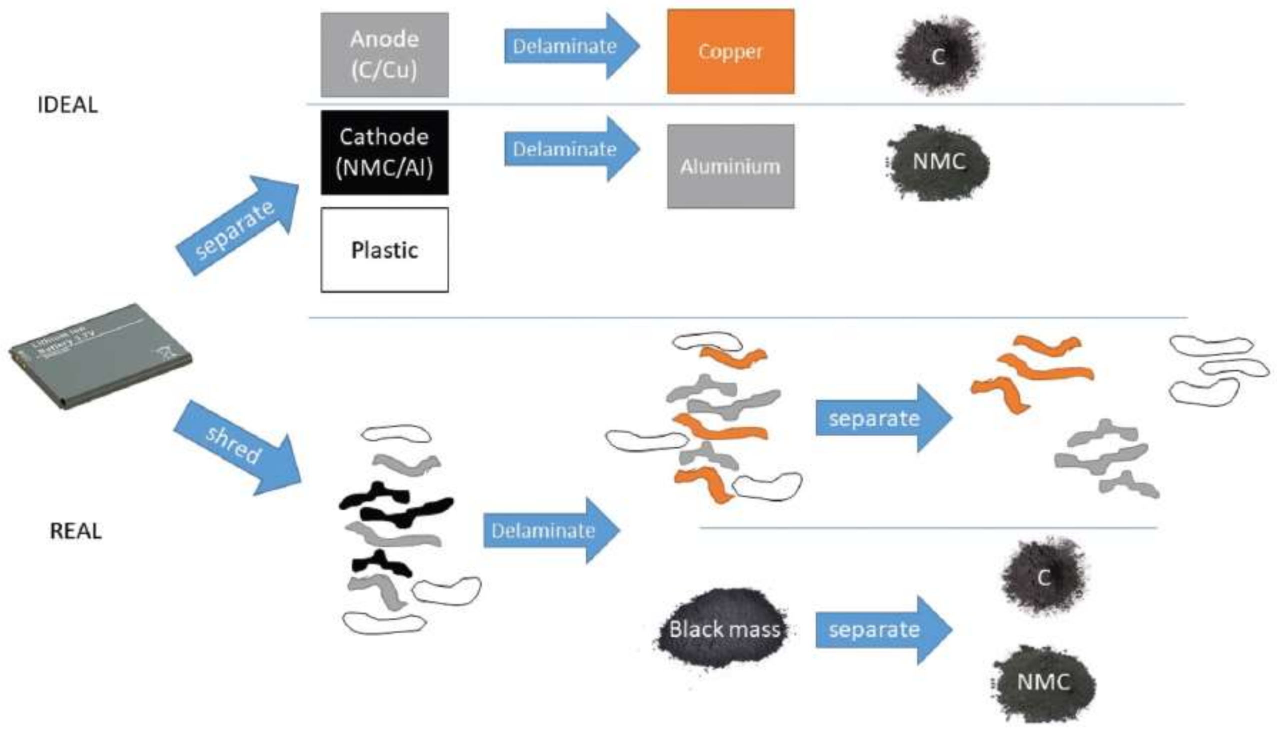
➔ Faire du recyclage direct (NMC, LFP)

Hans Eric Melin, Circular Energy Storage, global battery alliance, 2017

Module	NMC811	LFP	Cours $ /t	ratio %	NMC811	LFP
			$ 2022	%	$\ tonne	$\ tonne
Li	1,6	1,6	40000	70,00%	448	448
Co	1,3	0	51500	70,00%	469	0
Ni	10,5	0	22470	70,00%	1652	0
Mn	1,2	0	2200	70,00%	18	0
O	7,2	7,2	0	70,00%	0	0
LiPF6	1,8	1,8	0	70,00%	0	0
DMC	10,9	11	0	70,00%	0	0
Graphite	15,5	15,7	1300	70,00%	141	143
Al (métal)	30,2	30,3	2290	70,00%	484	486
Cu (métal)	7,3	7,4	7580	70,00%	387	393
Fe chassis(métal)	4,4	4,4	550	70,00%	17	17
Plastique	7,5	7,5	0	70,00%	0	0
Autres (ou FePO4)	0,7	22,4	0	70,00%	0	0
RECYCLE	70,8%w	59,4%w		$	3616	1486
Diagnostic					343	343
Logistique					400	400
Broyage					157	157
Hydrométallurgie					643	643
Bénéfice $ / ton					2073	-57

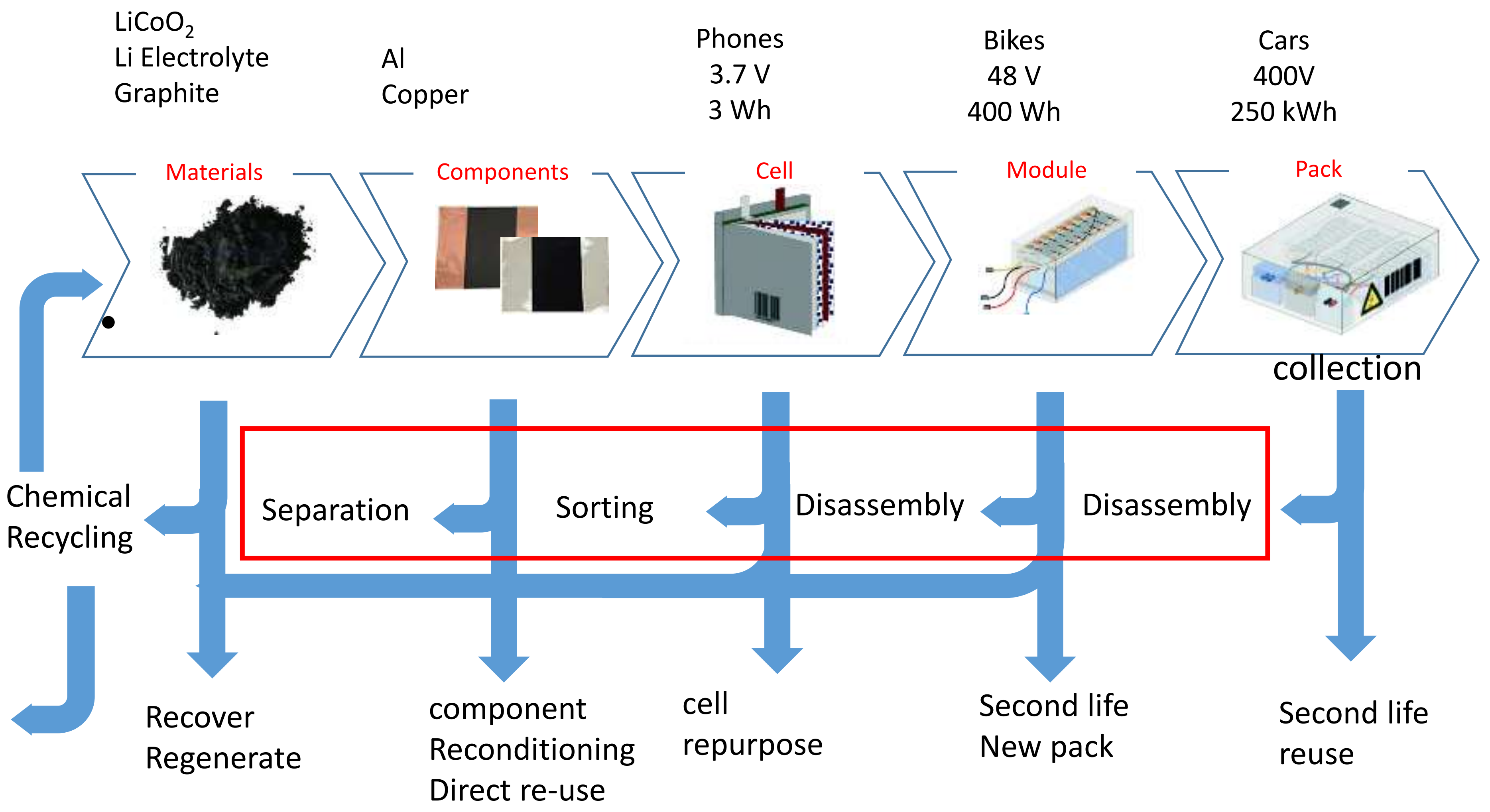
Estimations coûts du recyclage:
Roland Berger estimates accessed oct 2021 https://www.rolandberger.com/en/Insights/Publications

To shred or not to shred ?



Thompson, D.; Hyde, C.; Hartley, J. M.; Abbott, A. P.; Anderson, P. A.; Harper, G. D. J. To Shred or Not to Shred: A Comparative Techno-Economic Assessment of Lithium Ion Battery Hydrometallurgical Recycling Retaining Value and Improving Circularity in LIB Supply Chains. *Resour. Conserv. Recycl.* **2021**, *175*, 105741

Désassemblage multi- étapes



Cost delamination Space time yield

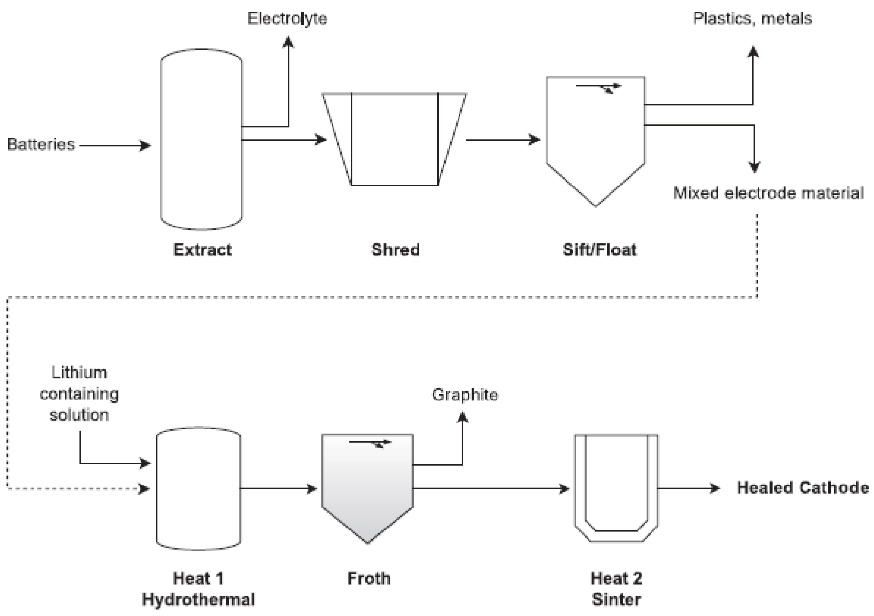
Table 4 Comparison of space time yield, cost and efficiency of different delamination methods and lixiviants

	STY[a]/kg m^{-3} min^{-1}	Cost[b]/kg^{-1}	Efficiency[c]/%
Cathode			
1.0 M H_2SO_4	0.045	1.29	67.2
1.0 M HCl	0.20	1	61.1
0.5 M NaOH	0.66	0.56	99.0
High power solvomechanical	2.84	0.14	99.5
NMP	0.033	70.2	96.9
Anode			
Low power solvomechanical	0.071	0.2	99.0
High power solvomechanical	2.84	0.12	99.4

[a] Electrode material delaminated. [b] Energy and solvent cost relative to HCl. [c] Percentage of material recovered in non-contaminated bins.

Thompson, D. L.; Hartley, J. M.; Lambert, S. M.; Shiref, M.; Harper, G. D. J.; Kendrick, E.; Anderson, P.; Ryder, K. S.; Gaines, L.; Abbott, A. P. The Importance of Design in Lithium Ion Battery Recycling – a Critical Review. Green Chem. ***2020****, 22 (22), 7585–7603. https://doi.org/10.1039/D0GC02745F.*

Fluides superpercritiques inertage



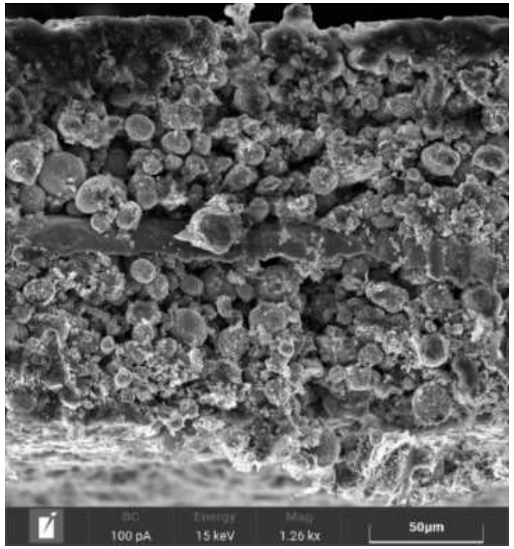
Electrolyte 89%
Ouverture de la batterie par pression CO_2
(Broyage recommandé)
Hydrothermal healing

Sloop, S.; Crandon, L.; Allen, M.; Koetje, K.; Reed, L.; Gaines, L.; Sirisaksoontorn, W.; Lerner, M. A Direct Recycling Case Study from a Lithium-Ion Battery Recall. Sustain. Mater. Technol. ***2020****, 25, e00152. https://doi.org/10.1016/j.susmat.2020.e00152*

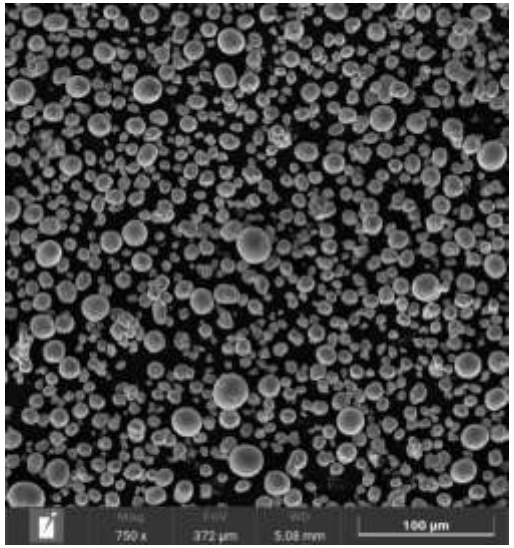
Direct recycling of Li-ion batteries assisted by supercritical fluids

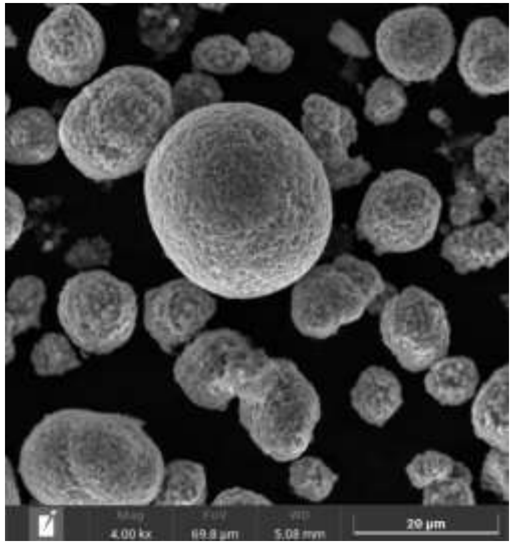
Delamination of the positive electrode - SEM image analysis

Before treatment



After treatment

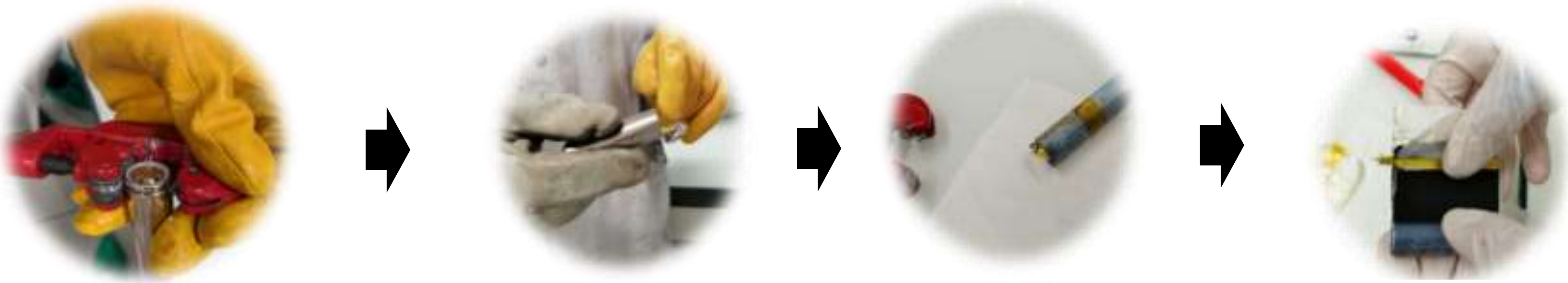




Preservation of spherical morphology with minimal residual PVDF

Pending patent & publication

Recyclage direct du LFP:

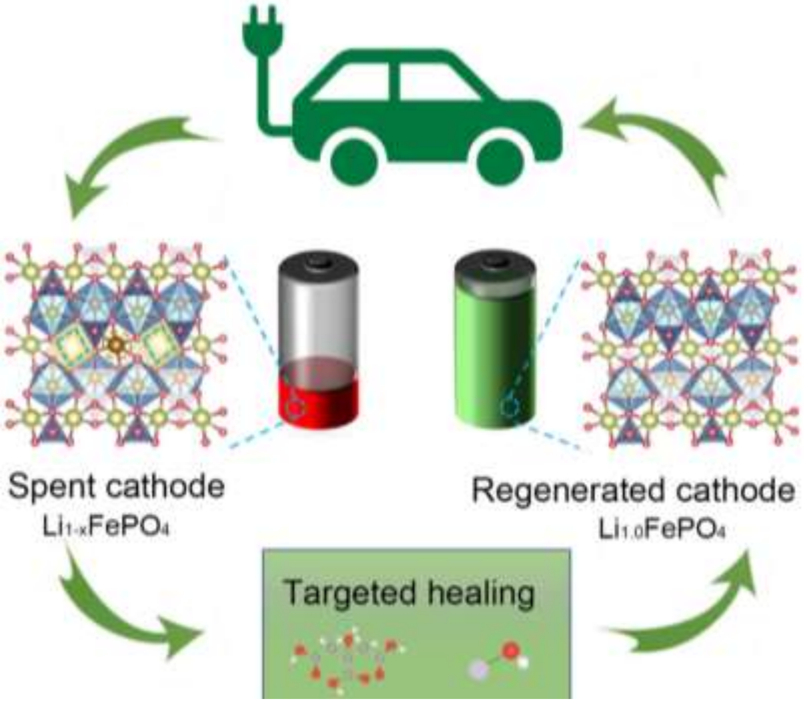


Cellules vieillies A123 LFP

Dés-assemblage
Séparation mécanique
Séparation chimique

Nettoyage chimique

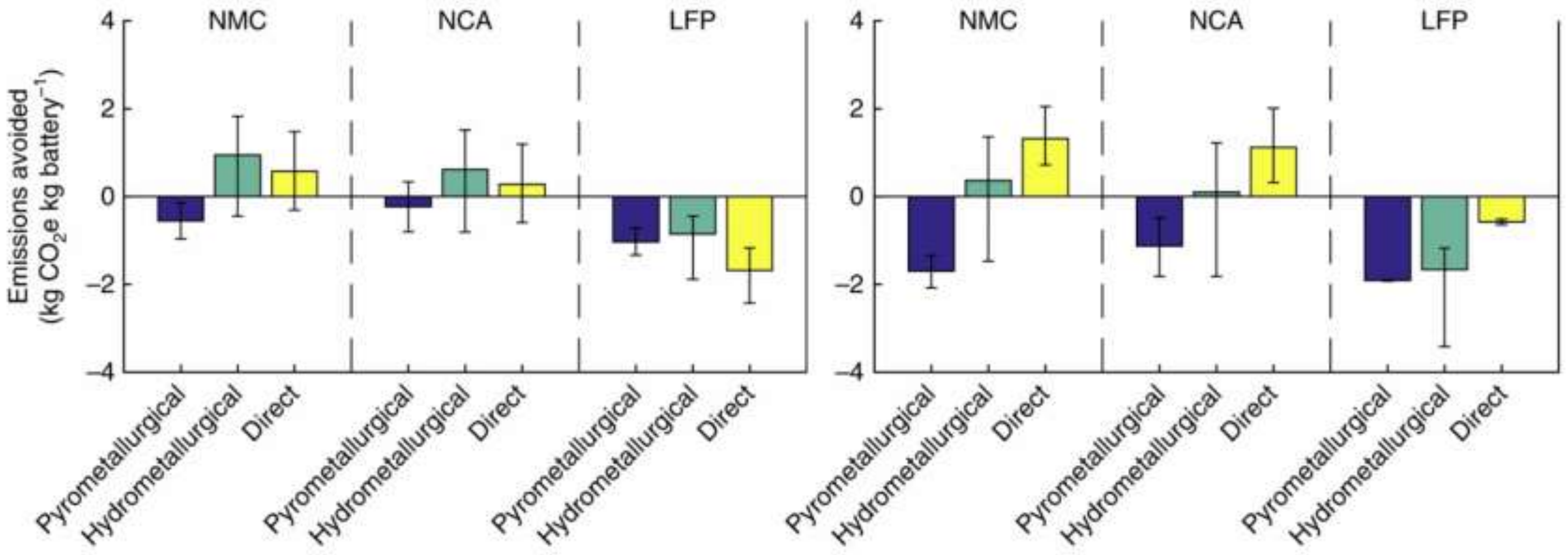
Régénération thermique et chimique:
Li/ cristallinité/carbone coating



62750 Loos-En-Gohelle

Bilan environnemental

cylindrical pouch



R. E. Ciez and J. F. Whitacre, "Examining different recycling processes for lithium-ion batteries," Nature Sustainability, vol. 2, no. 2, pp. 148–156, Feb. 2019

Récupération sélective du lithium ?

Separate recovery of Lithium

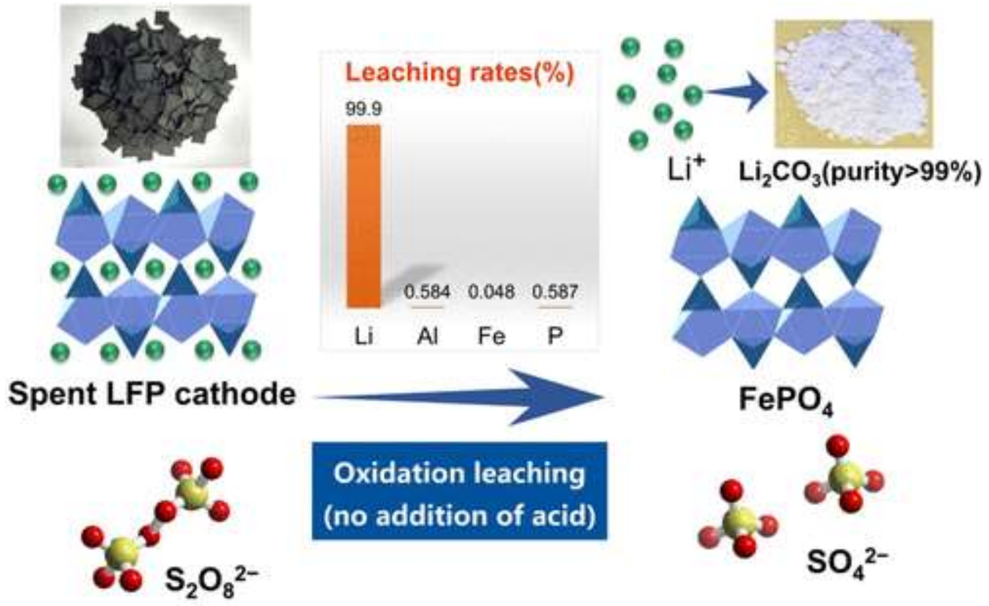


Table 5 The chemical reagent prices to treat 1 ton of spent $LiFePO_4$ batteries by the present green process in China

Substance	Price ($\$ \ kg^{-1}$)	Ref.	Process (kg)	Economic benefits (\$)
CH_3COOH	0.56	60	132	−73.92
35 wt% H_2O_2	0.976	61	184.8	−180.36
Na_2CO_3	0.265	62	72.6	−19.24
NaOH	0.76	63	0.924	−0.70
Waste Al foil	2.06	64	56.1	115.36
$FePO_4$	1	65	260.7	260.70
Li_2CO_3	21.6	66	49.5	1069.20

$2LiFePO_4 + Na_2S_2O_8 \rightarrow 2FePO_4 \downarrow + Li_2SO_4 + Na_2SO_4$

$2LiFePO_4 + H_2O_2 + H^+ \rightarrow 2FePO_4 + 2\ H_20 + 2\ Li^+$

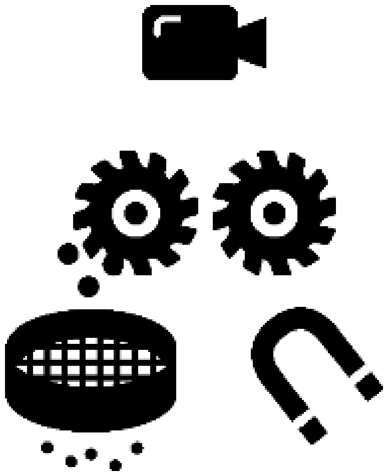
J. Zhang, J. Hu, Y. Liu, Q. Jing, C. Yang, Y. Chen, C. Wang, Sustainable and facile method for the selective recovery of lithium from cathode scrap of spent LiFePO4 batteries, ACS Sustain. Chem. Eng. 7 (2019) 5626–5631.

Yang, Y.; Meng, X.; Cao, H.; Lin, X.; Liu, C.; Sun, Y.; Zhang, Y.; Sun, Z. Selective Recovery of Lithium from Spent Lithium Iron Phosphate Batteries: A Sustainable Process. *Green Chem.* **2018**, *20* (13), 3121–3133

Conclusion 1/3

Age I Pyrométallurgie

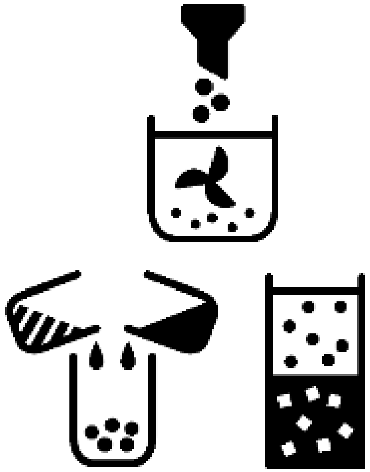
Récupération Co-Cu- Ni
Simple, sécurisé
Versatile pêle- mêle
Pas si énergétique
Émissions CO_2
Perte Li, Al
Boucle ouverte



Age IIa Broyage- séparation

Récupération Co- Ni
Récupération Al , Cu polymères

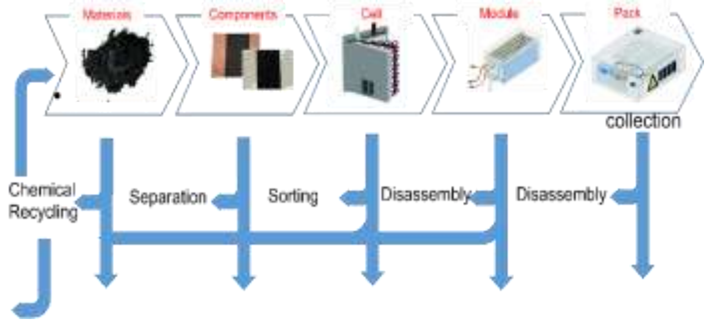
Complexe dangereux
Démantèlement manuel
Bilan énergétique ?



Age IIb Hydrométallurgie

Boucle fermée
Récupération précurseurs NMC
Récupération Li (?)

Beaucoup d’étapes
Beaucoup de réactifs

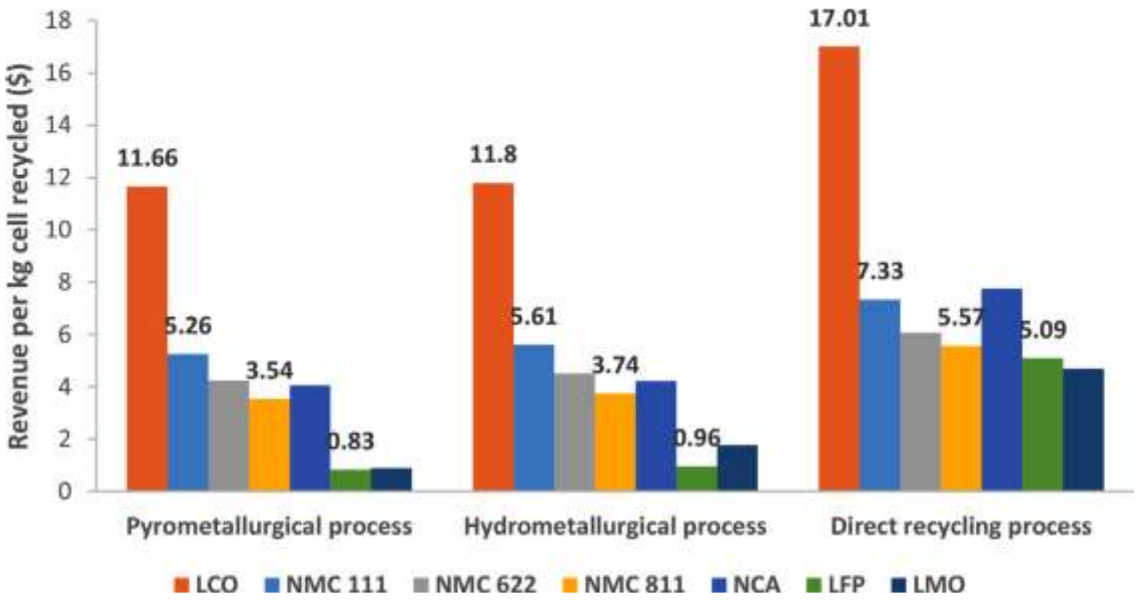


Age III Recyclage 4.0

Récupération 100%
Matériaux

Tri complexe
Robotisation
Standardisation

Conclusion 2/3



Aspects techno- économiques

- Standardisation des batteries (forme, robotisation)
- Ecoconçues (Cell toPack ? vs Debonding)
- Consortiums de recyclage

- Evolution des prix du Lithium, du Nickel
- Arrivée de produits sans Cobalt
- Facteurs Gigafactories et scraps

On the sustainability of lithium ion battery industry –A review and perspective
Yue Yang Energy Storage Materials 36 (2021) 186–212

Conclusion 3/3

Quelle est la place des académiques ?

2025

- Méthodes séparatives économes (Ni, Co, Li)
- Fermeture de la boucle synthèse de NMC
- Définition du battery grade / Rôle des impuretés sur la 99.99%

2030

- Ingénierie procédés 4.0
- Méthodes de de- assemblage (CO_2; liants verts)
- Méthodes de recyclage direct
- Matériaux sans cobalt LMO + LFP

Merci pour votre attention