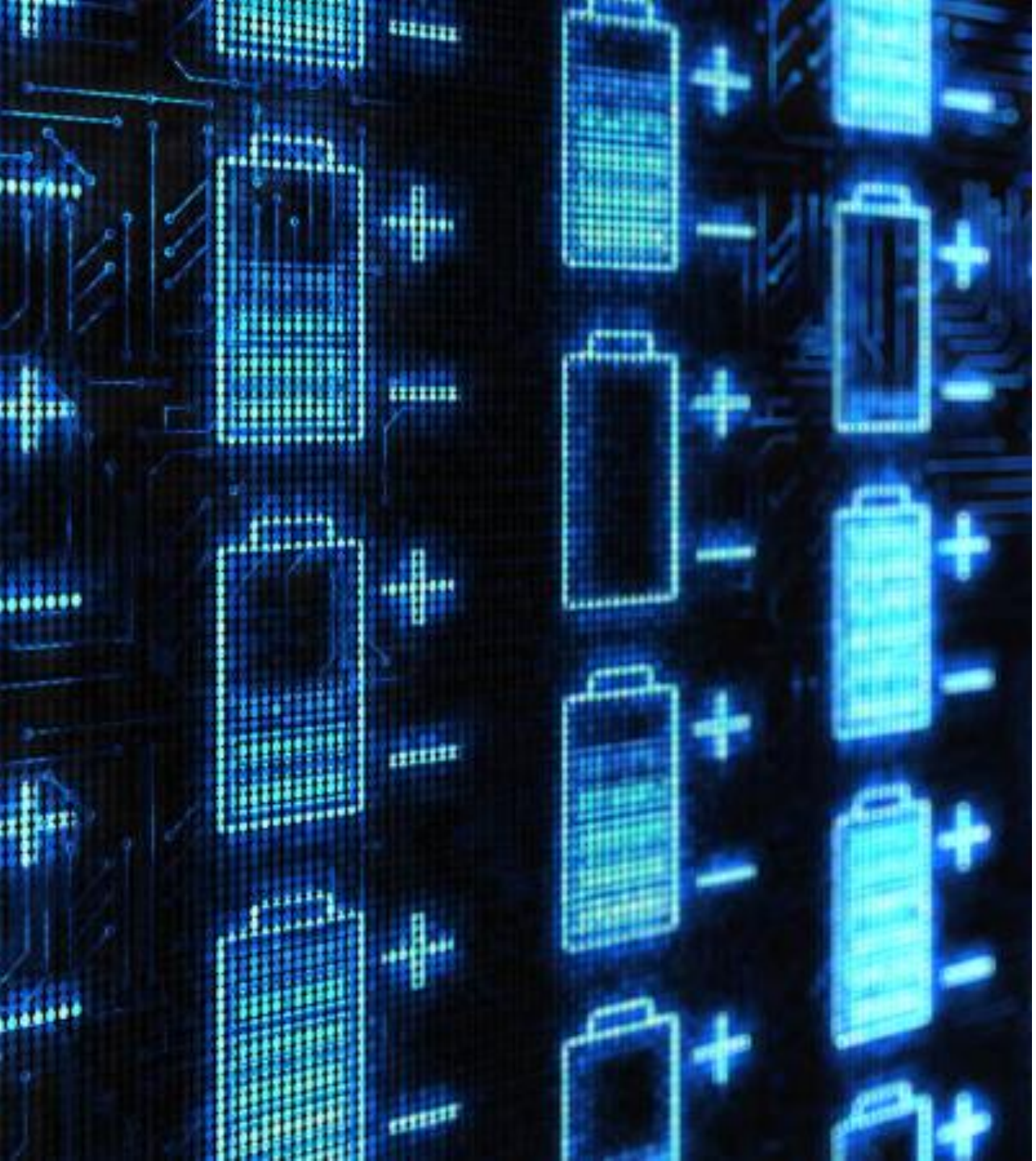


Recyclage des batteries Li-ion – 1ère partie

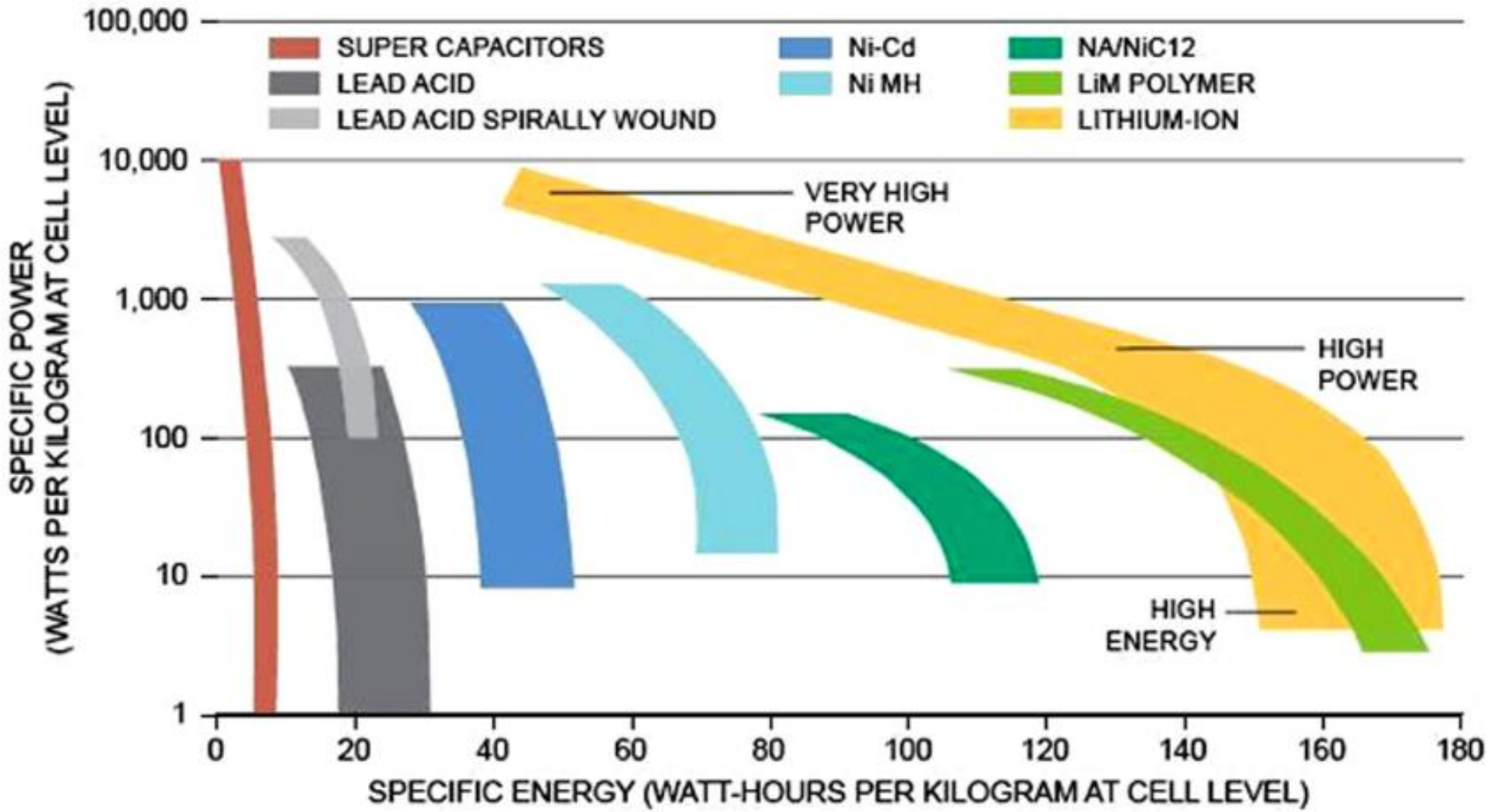
Généralités sur les batteries Li-ion et grands principes de recyclage

Clémence SIRET– Responsable Eco-conception Corporate - Saft

01.

Généralités sur les batteries Li-ion

Marché global des batteries rechargeables

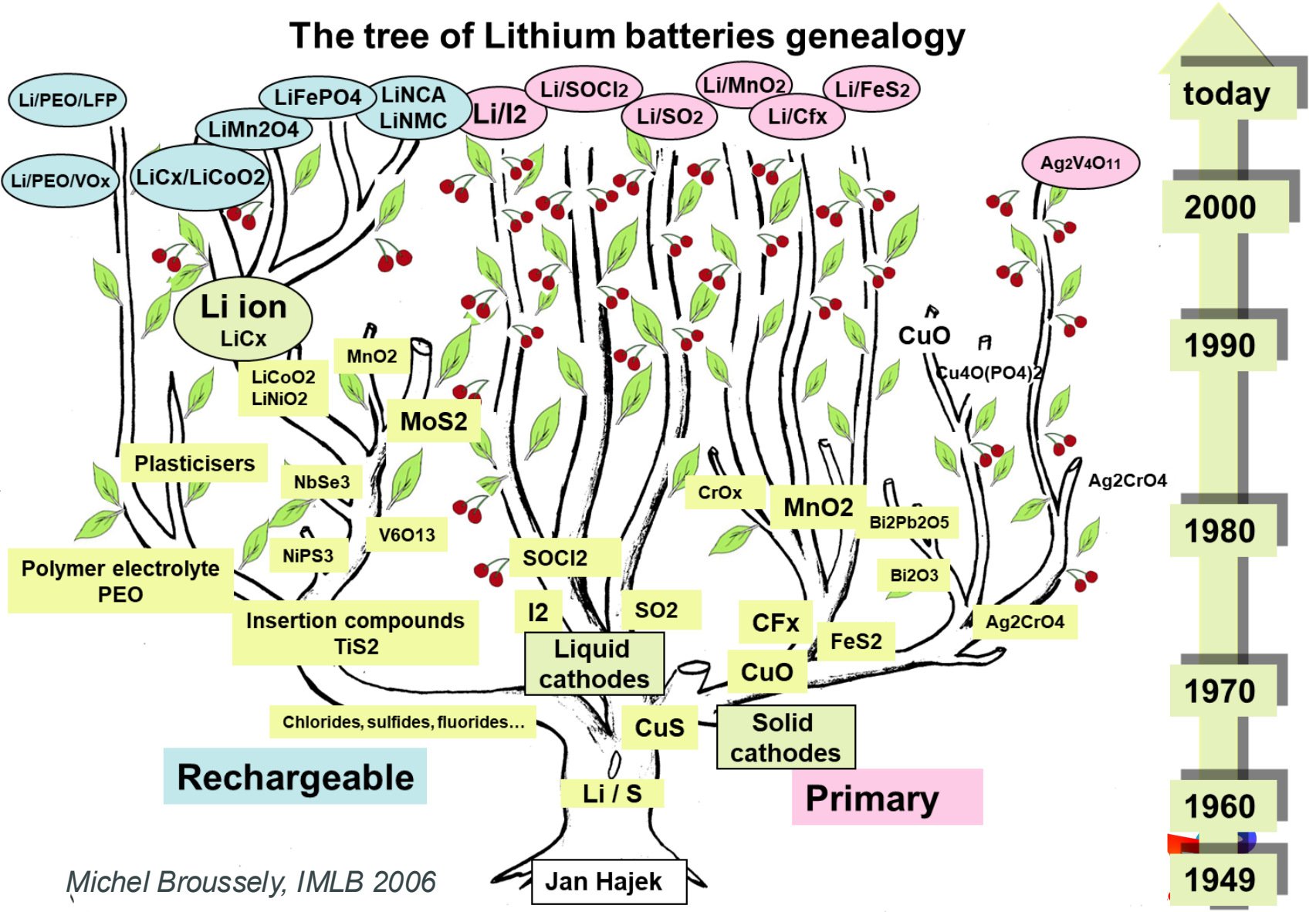


Un peu d'histoire: batteries au lithium

- **1949**: Jan Hajek , first patent on "Electrolyte for Light Weight Electrode" with examples of lithium anode and sodium anode

- **1991** : Commercialization of the 1st Li-ion cell by SONY

- **2019** : Nobel prize in Chemistry for **J. Goodenough, S. Whittingham, A. Yoshino** *for "the development of lithium-ion batteries"*



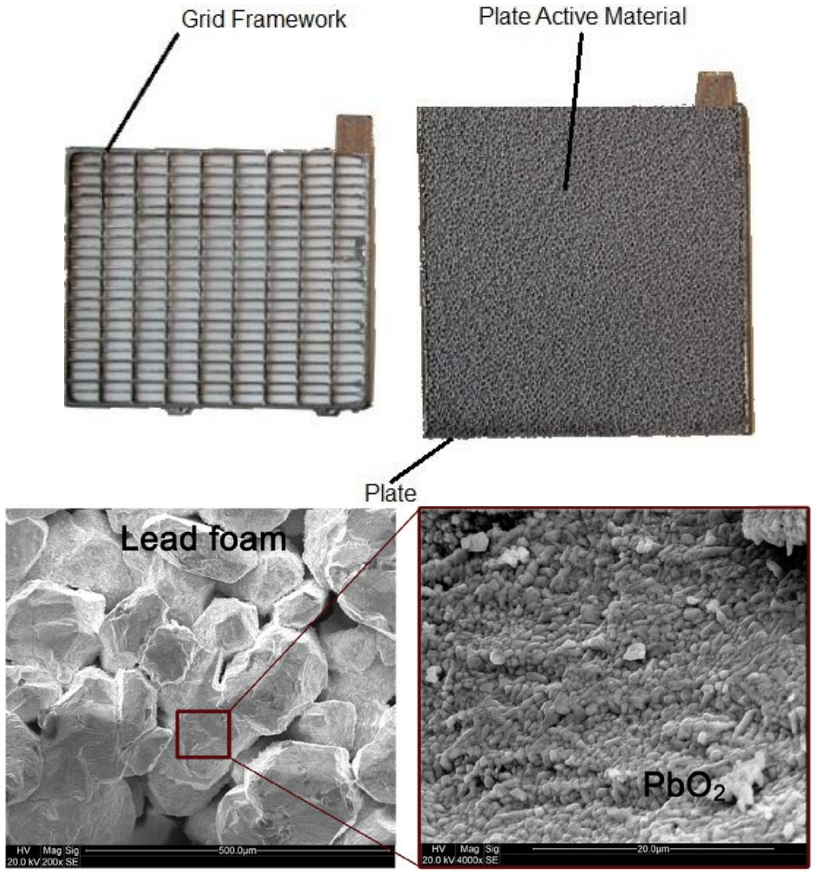
Michel Broussely, IMLB 2006

Fabrication des électrodes

“Paste” technology

Pb/acid , Ni-Cd

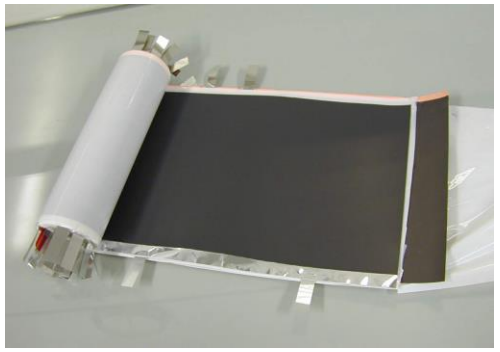
small amount of solvent (water)

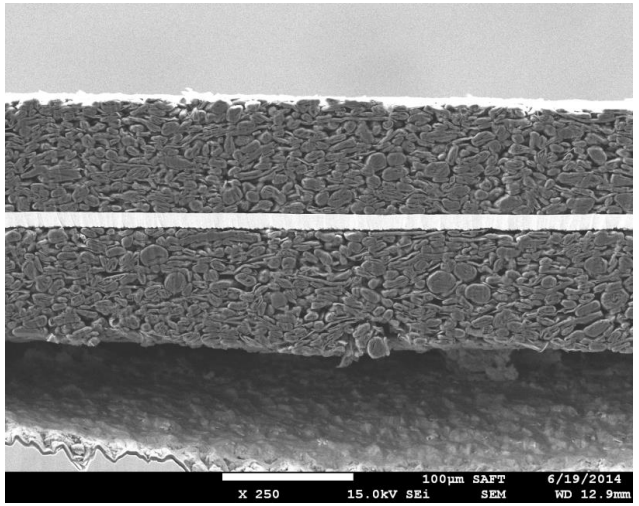


“Paint /Ink“ technology

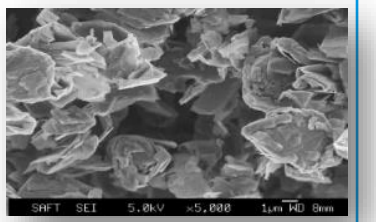
Li-ion

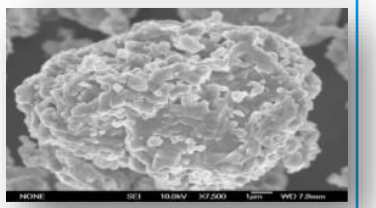
around 50% of solvent (organic)





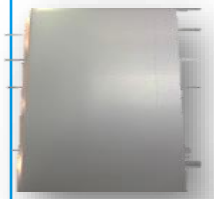
Des matières actives aux batteries

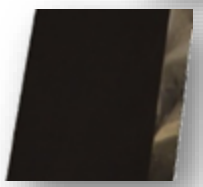




Matières actives

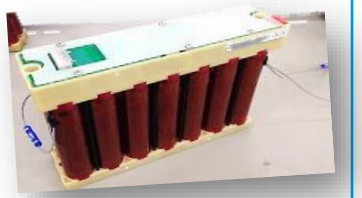
Electrodes

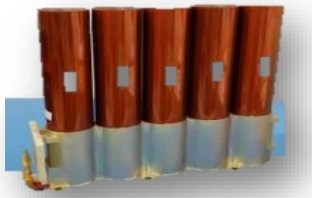




Cellules

Modules





Batteries

Lithium-ion : Principe de fonctionnement

- **Formation :**
  - Première charge électrique
  - Création de la couche de passivation sur l'électrode négative

- **Principe de fonctionnement : 3.6-3.8V**
  - Électrode négative :

$C_6 + xLi^+ + xe^- = Li_xC_6$ 0,150 Volts

Capacité théorique : 372 Ah/kg

  - Électrode positive : exemple simplifié : $LiCoO_2$

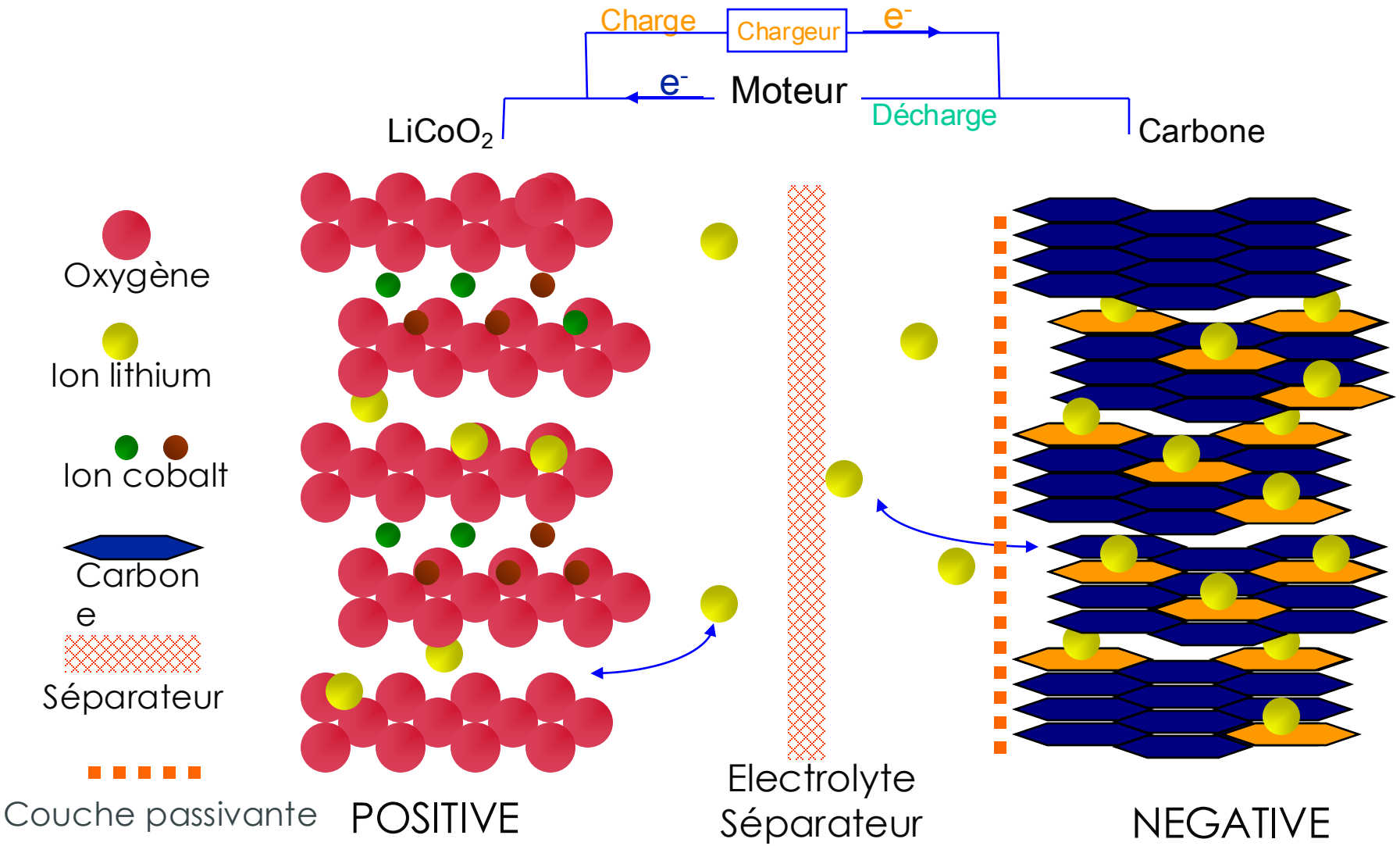
$LiCoO_2 = CoO_2 + Li^+ + e^-$ 3,85 Volts

Capacité théorique : 274 Ah/kg

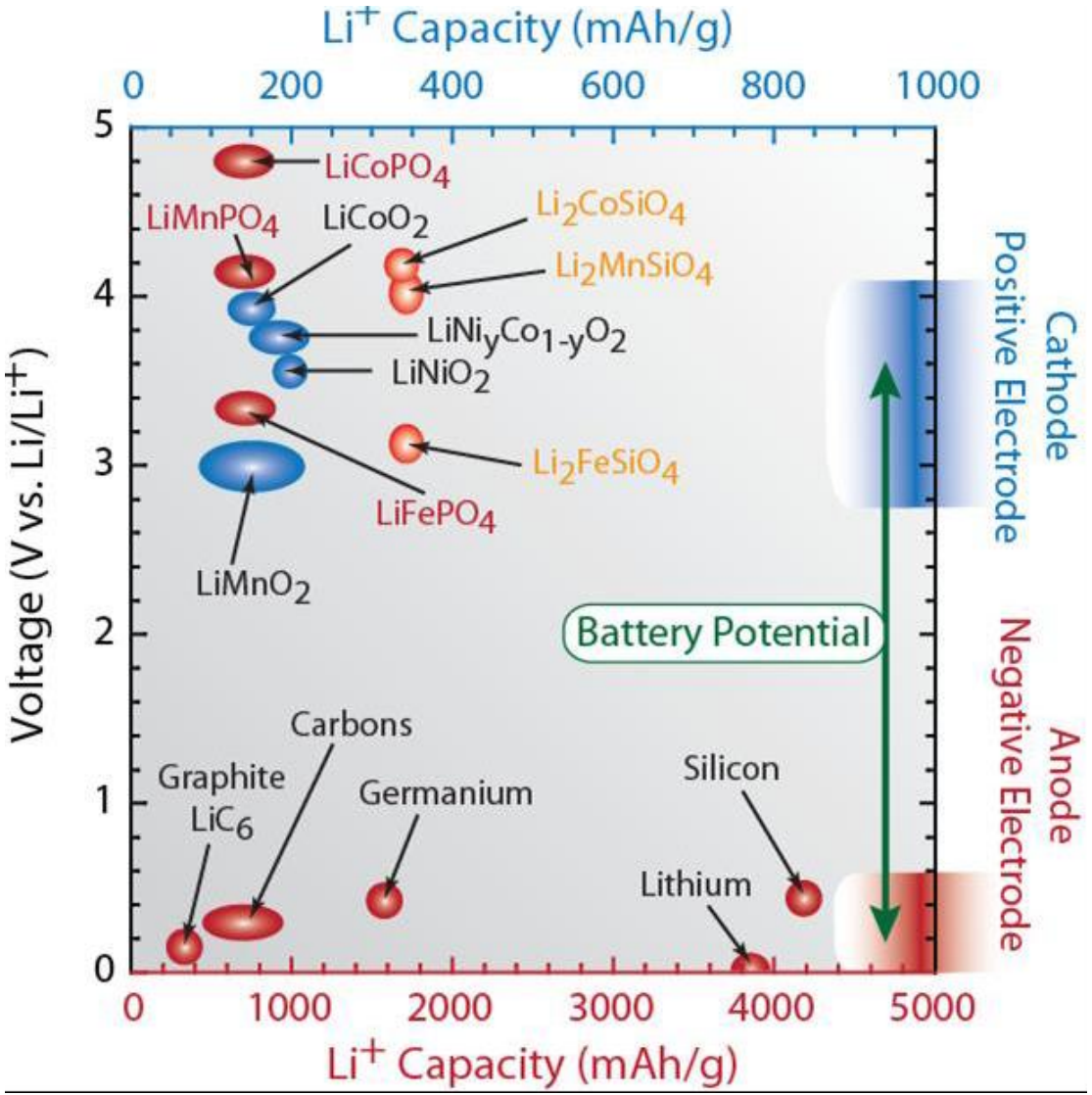
  - Bilan théorique :

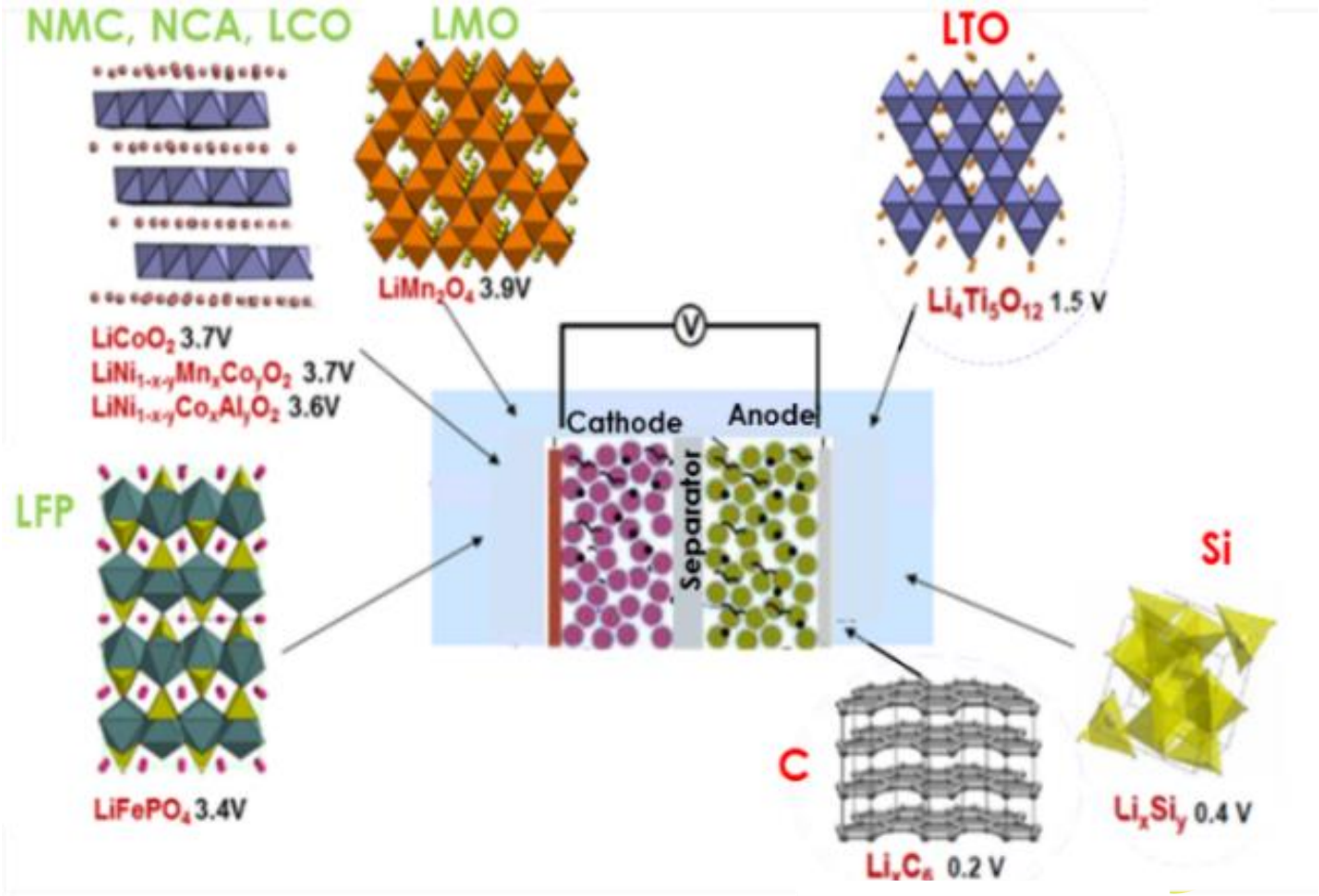
$$C_6 + LiCoO_2 = Li_{(1-x)}CoO_2 + Li_xC_6\ 3,7\ Volts$$

Lithium-ion : Cyclage



Nombreux matériaux d'électrodes évalués depuis plus de 30 ans, en constante évolution





Lithium-ion : des batteries portables dans les années 1990 & 2000 à une multitude d'applications industrielles aujourd'hui

Batteries portables

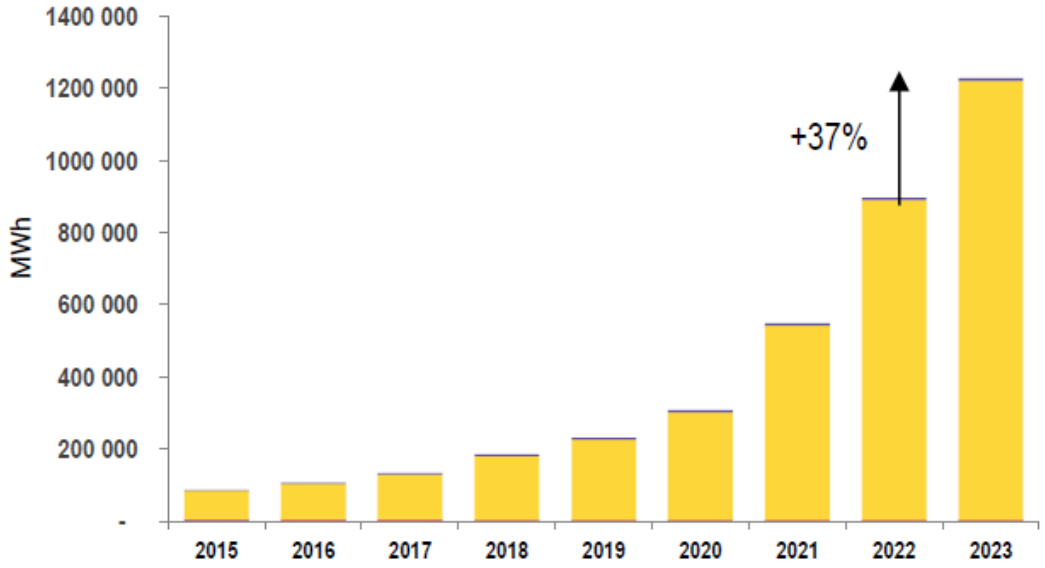
…

Batteries industrielles

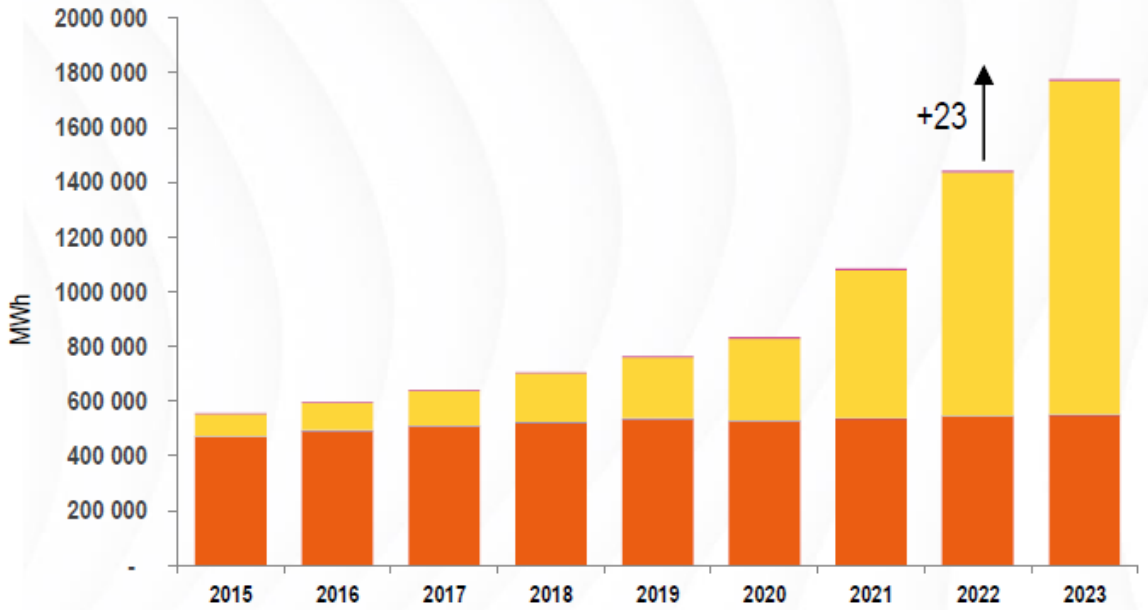
Marché mondial des batteries (en MWh)

Within the global battery market, the Lithium-Ion battery segment represents the highest growth & the major investment part, while Lead Acid batteries still represents >30% of the market

Worldwide battery market by Chemistry, 2015-2023, MWh



Worldwide battery market by Chemistry, 2015-2023, MWh



Others (Flow battery, NAS, ...) Li-ion NiMH NiCD

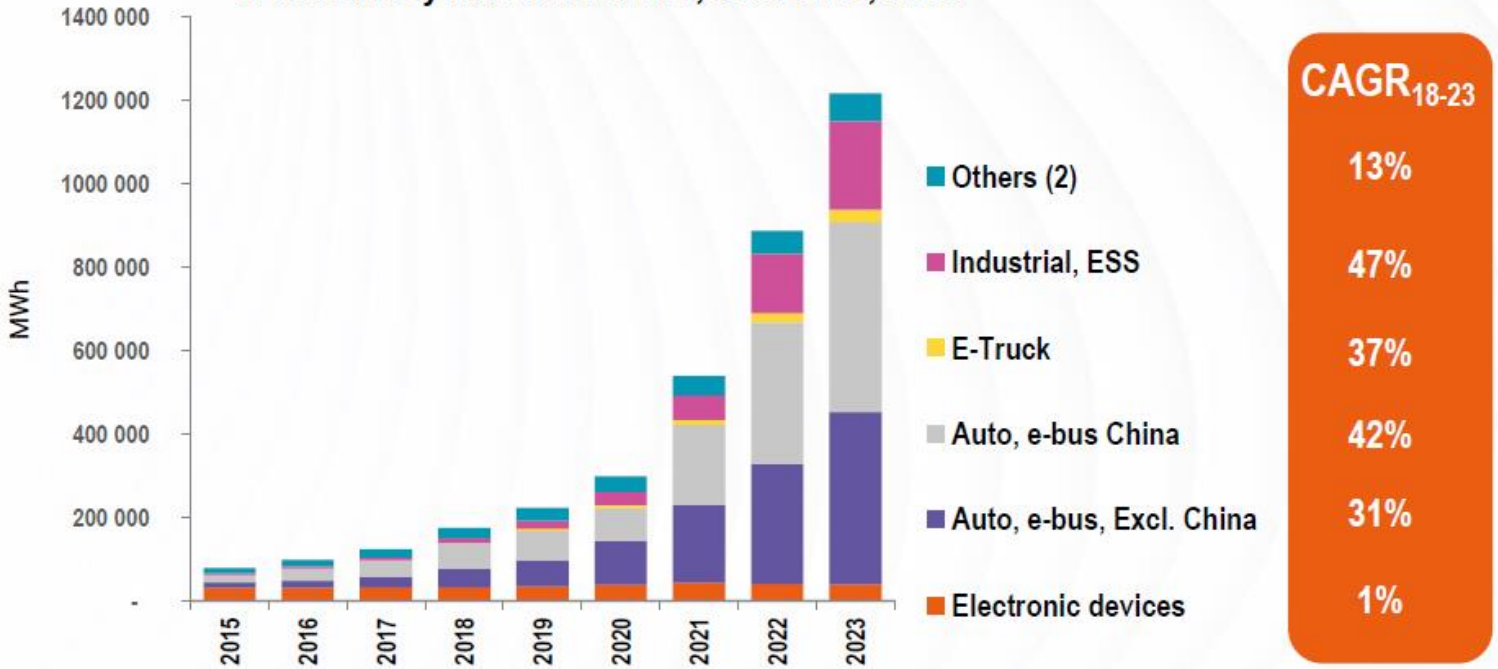
Others (Flow battery, NAS, ...) Li-ion NiMH NiCD Lead Acid

Source: Avicenne Energy 2024

Marché mondial des batteries Li-ion par applications

In 2023, EV, e-buses & e-trucks account for 75% of the li-ion battery market with a total LIB market of 1 200 000+ MWh

Li-ion Battery sales worldwide, 2000-2023, MWh



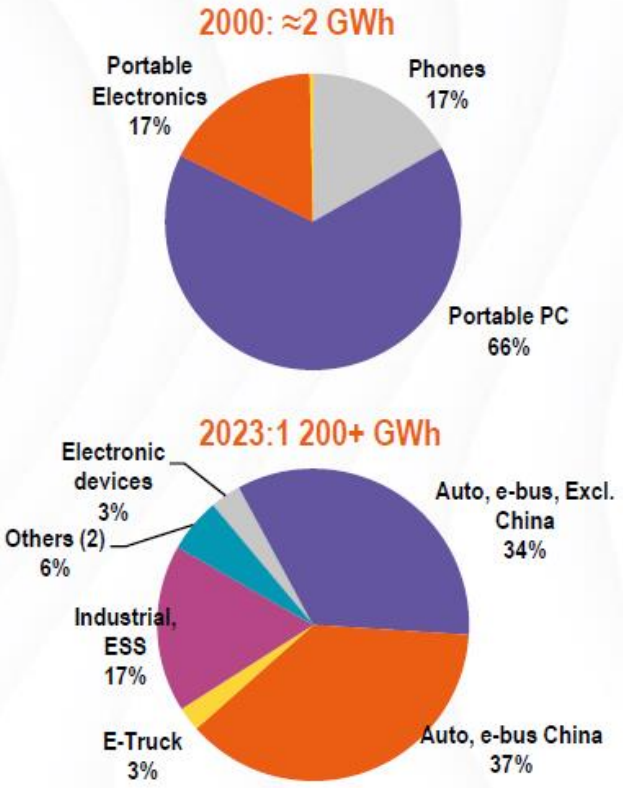
(1) Pack level

(2) Others: medical devices, power tools, gardening tools, e-bikes…

November 24

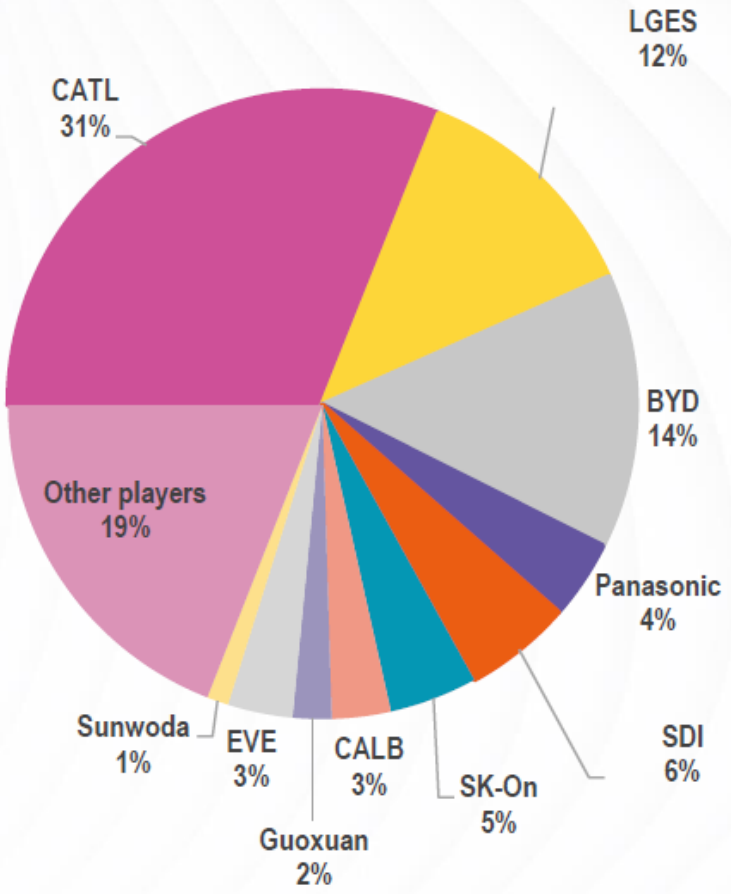
Source: Avicenne Energy 2024

CAGR $_{15-23}$: 37% per year in volume



Marché des batteries Li-ion dominé par l'Asie

Cell producer worldwide market share (all applications[1]), in 2023 % of GWh



(1) xEV including trucks, buses, ESS, industrial, portable, power tools, E-bikes, LSEV, Medical, Space, aviation, train, marine, and many more

Source: Avicenne Energy 2024

Major cell producers in 2023

TOP 5: CATL, LG, BYD, Panasonic, Samsung represent 70% of the global Litium-ion Market

CATL

LG Energy Solution

BYD

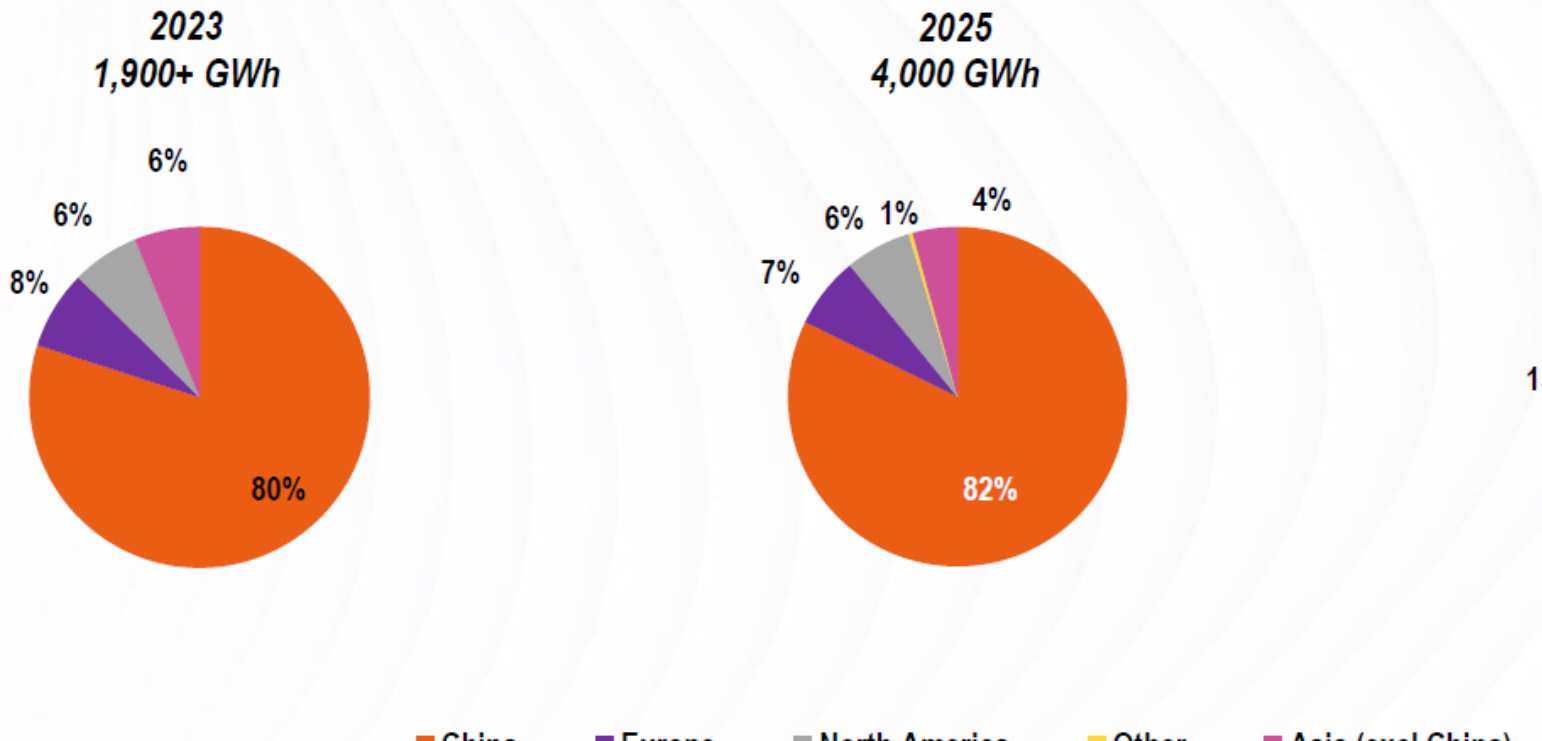
Panasonic

SAMSUNG SAMSUNG SDI

SK on

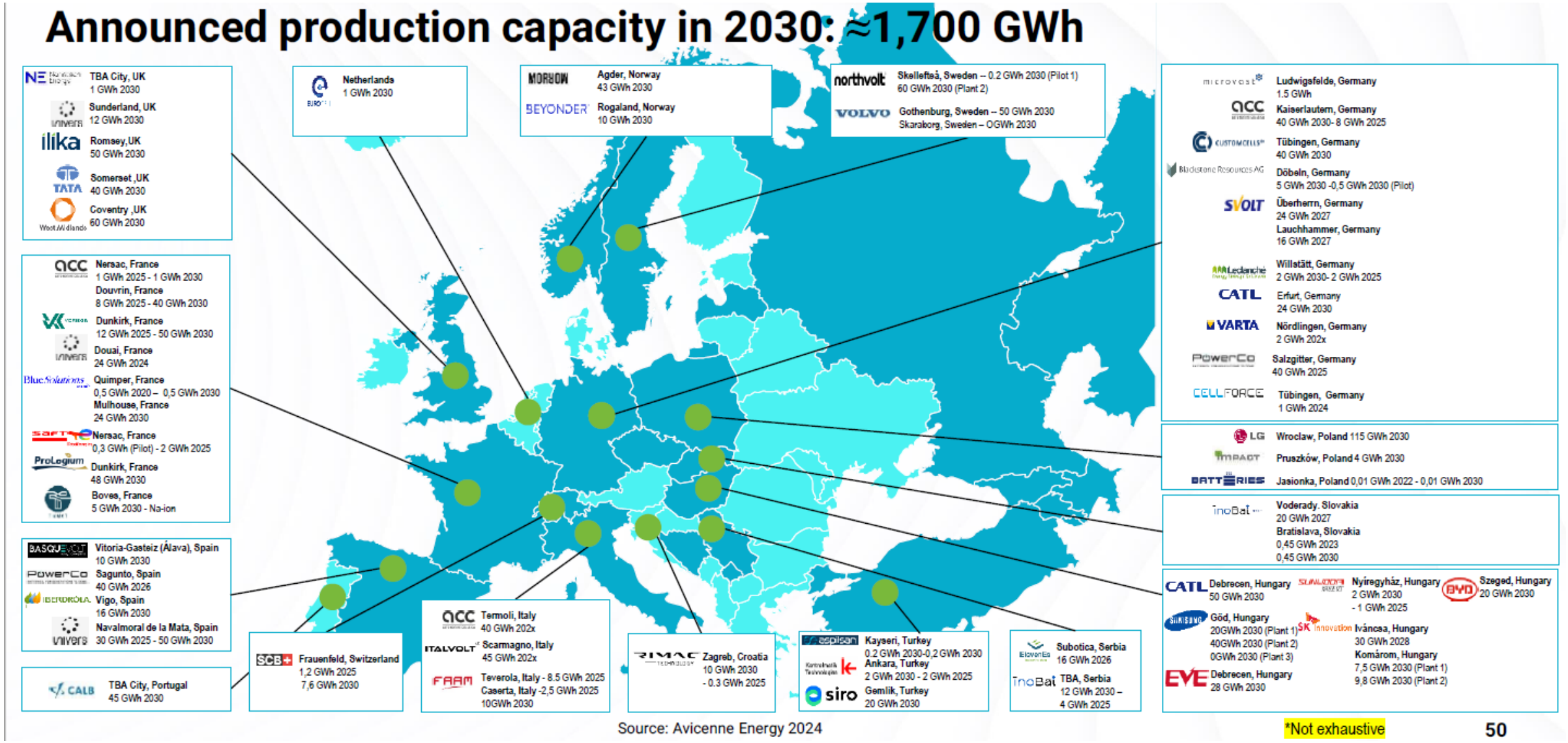
Augmentation des capacités de production mondiales

The Production capacity is estimated to grown from 1,9TWh in 2023 to 6,3 TWh in 2030, with the production capacity outside Asia reaching 2 TWH by 2030, representing +30%



Source: Avicenne Energy 2023

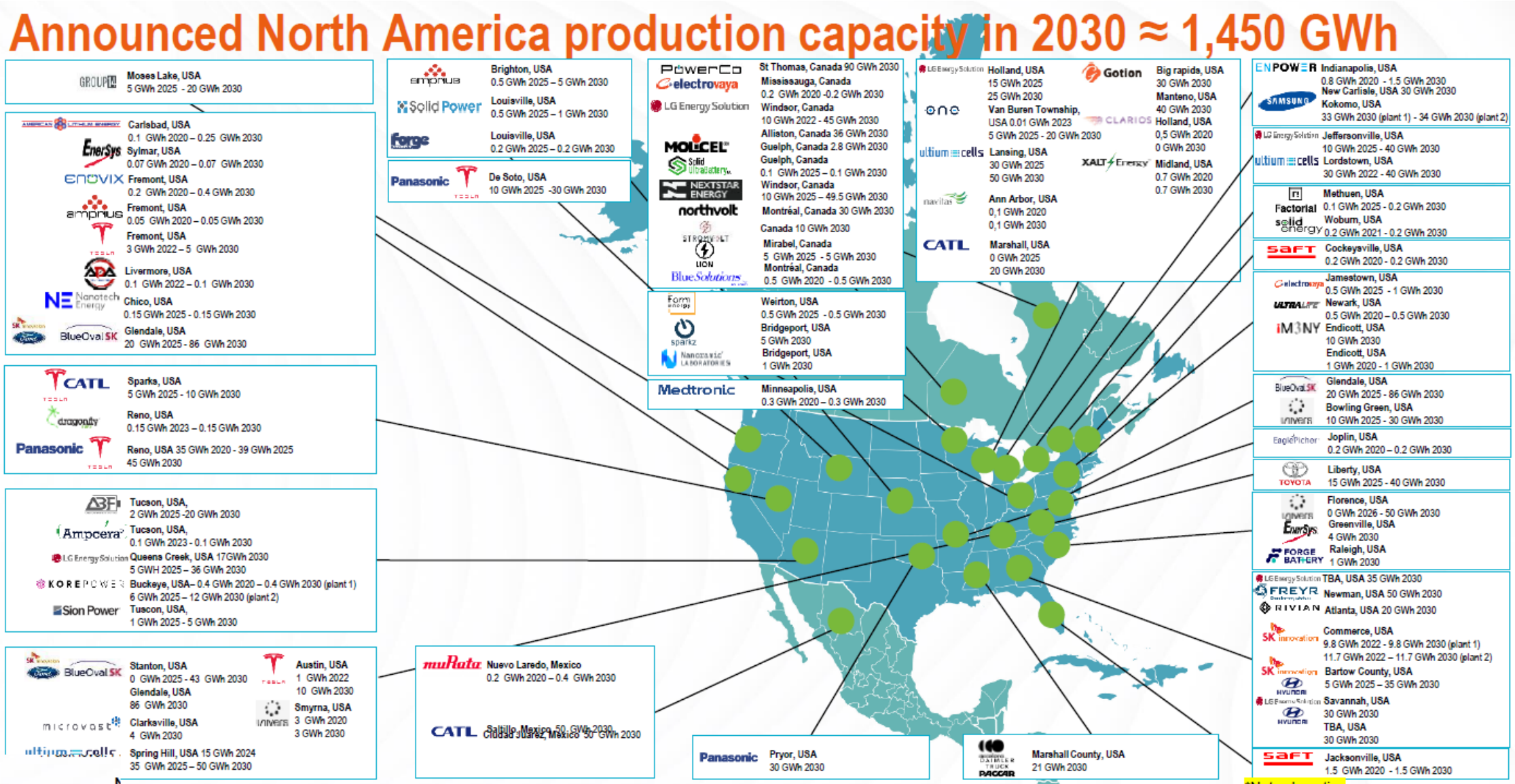
Futures productions de batteries Li-ion en Europe



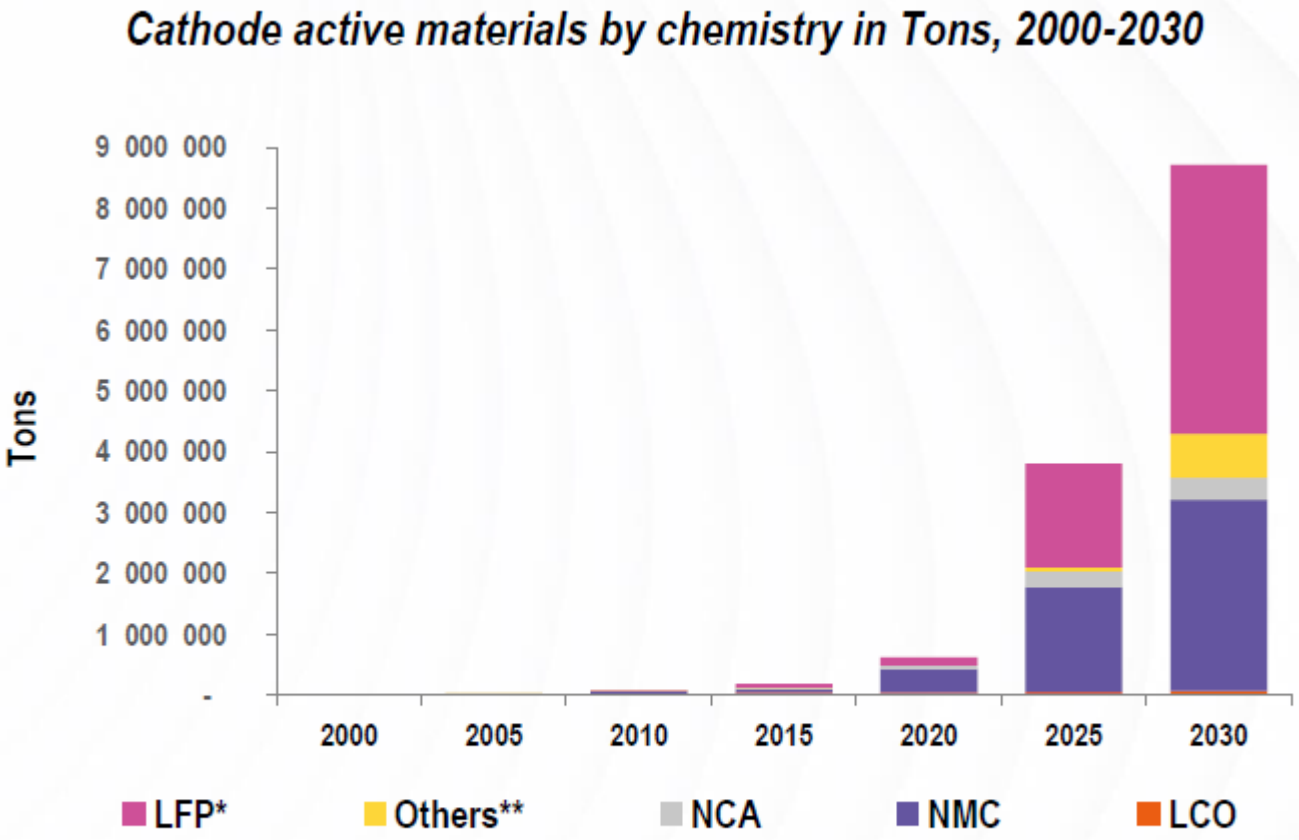
Source: Avicenne Energy 2024

*Not exhaustive

Futures productions de batteries Li-ion en Amérique du Nord



Principales matières actives positives

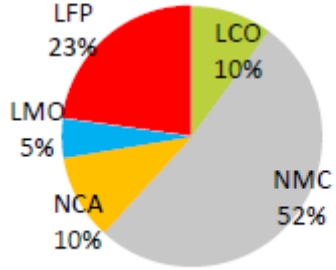


*: LFP: LFP+LFMP, NMC: Low-mid and High NMC, Lithium Rich High Mn

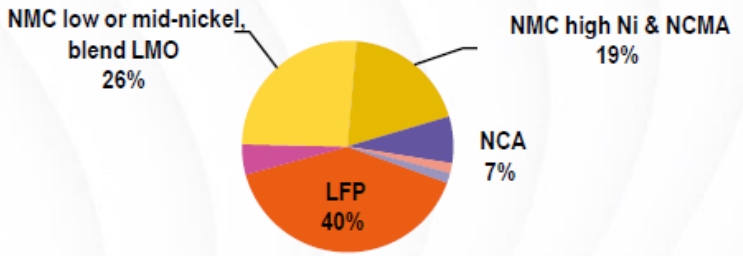
**: Others: Na-ion, Zinc…

Source: Avicenne Energy 2024

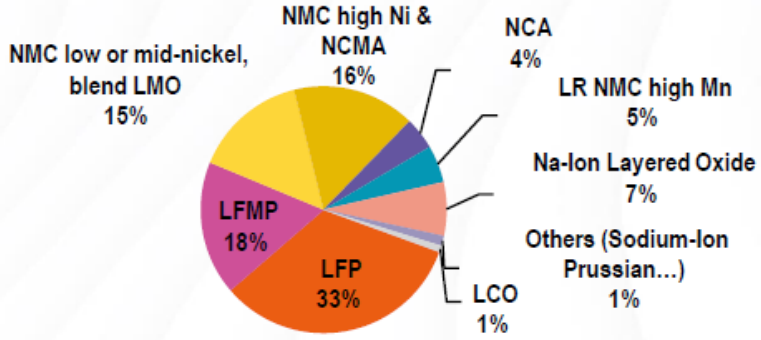
Cathode active materials in 2020
450 000 Tons



Cathode Active Materials in 2025: 3,800+ kTons



Cathode Active Materials in 2030: 8,700+ kTons



02.

Grands principes de recyclage

Pourquoi recycler les batteries ?

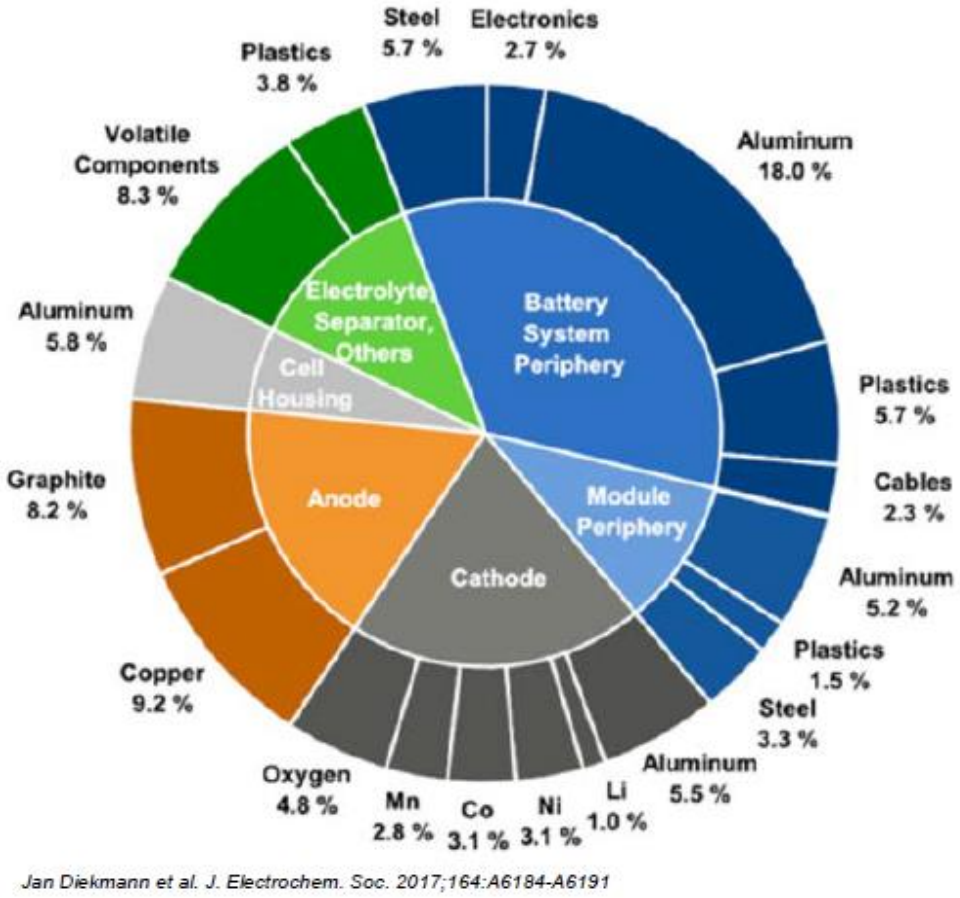
- À cause de leur contenu :
  - **“Mines urbaines” : Teneurs en métaux des batteries supérieures aux teneurs dans les mines**
  - **Pollution potentielle par des substances “dangereuses”**

- À cause des avantages environnementaux et de la valeur de certains métaux critiques qu’elles contiennent :
  - **Empreinte carbone des matériaux recyclés inférieure à celle des matériaux vierges**
  - **Fortes fluctuations des prix de certains métaux critiques**

- À cause de la législation :
  - **Mise en décharge interdite en Europe**
  - **Législation environnementale en constante évolution**

Composition moyenne d'une batterie Li-ion

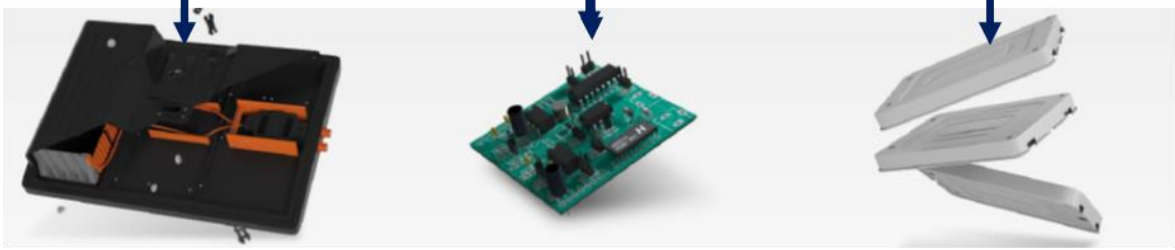
Plusieurs filières sont concernées par la fin de vie des batteries Li-ion : les métaux, l'électronique, la chimie, les plastiques



Jan Diekmann et al. J. Electrochem. Soc. 2017;164:A6184-A6191

Li-ion Battery dismantling

Potentiels problèmes de sécurité !



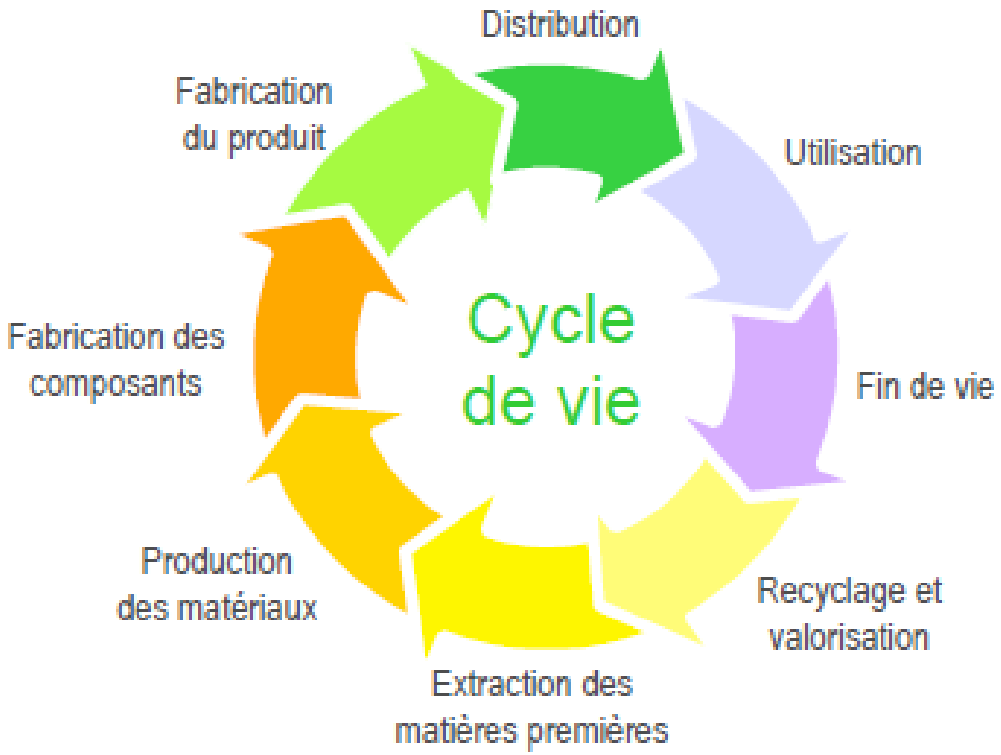
Pack material

(Cu cables, plastics, steel)

Electronical components

Li-ion modules & cells

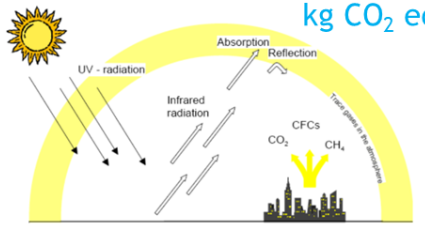
Analyse du Cycle de Vie (ACV) : Approche



Principaux indicateurs d'impact en ACV

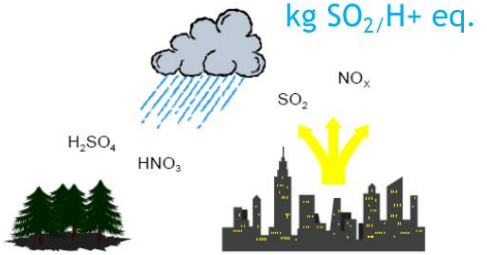
Emissions de gaz à effet de serre

kg CO_2 eq.



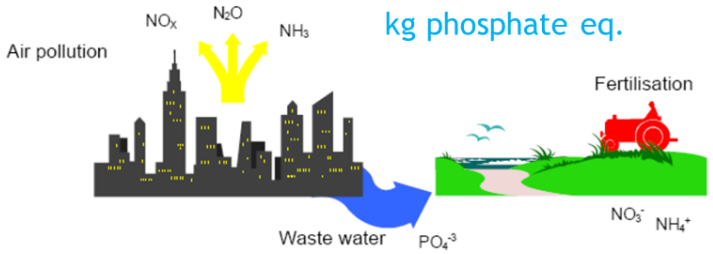
Potentiel d'acidification

kg SO_2/H+ eq.

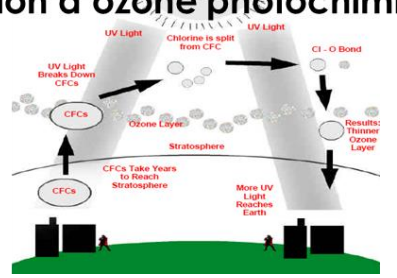


Potentiel d'euthrophication

kg phosphate eq.



Formation d'ozone photochimique

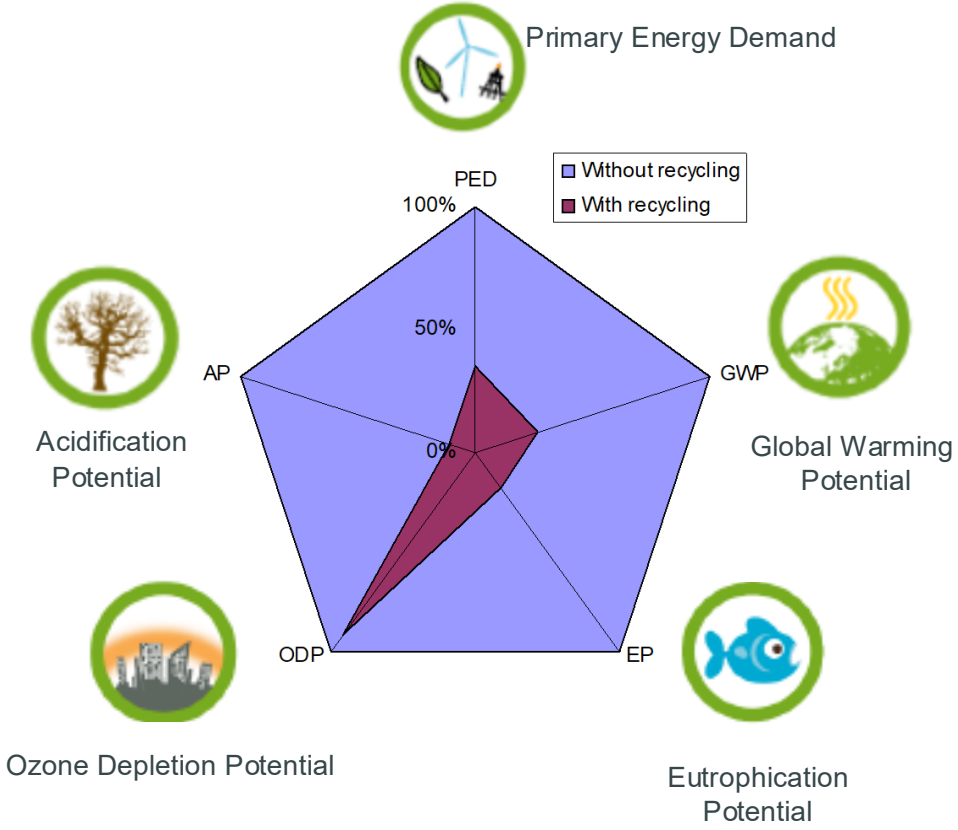


La méthode repose sur l'inventaire de cycle de vie, bilan quantifié **des flux matières et d'énergie** aux frontières d'un système représentatif d'un produit, d'une filière ou d'un procédé.

Exemple d'ACV montrant l'importance du recyclage

ACV d'un container de 560 kWh (1ère génération) pour « fermes solaires » avec recyclage:

- **Unité Fonctionnelle: fabrication, utilisation et fin de vie** *d'un système batterie (une batterie Li-ion avec électronique associée dans un container en acier de 20 pieds) servant au lissage de la production d'énergie d'**une ferme solaire de plusieurs MW** sur une période de 20 ans*

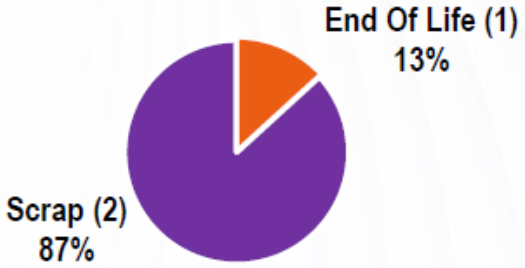


Forte baisse des impacts environnementaux comparés à l'utilisation de matériaux primaires **(- 65 % de demande en énergie primaire et -73% d'émissions GES)**

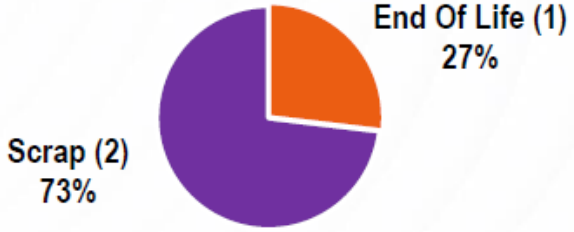
Prédominance des déchets de fabrication des gigafactories en construction dans les flux actuels

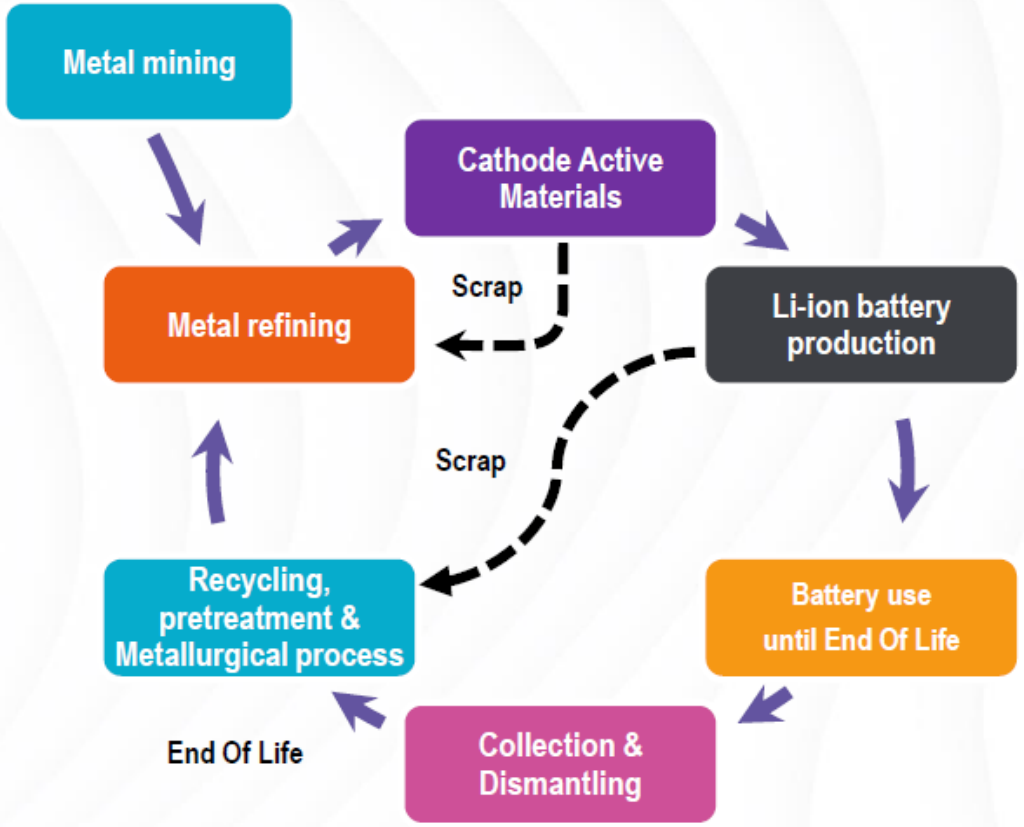
In the first few years, the recycling units are fed mainly with cells manufacturing Scrap (2), rather than by the flow coming from used battery packs (1)

Incoming GWh Eq. in 2023



Incoming kTons in 2023





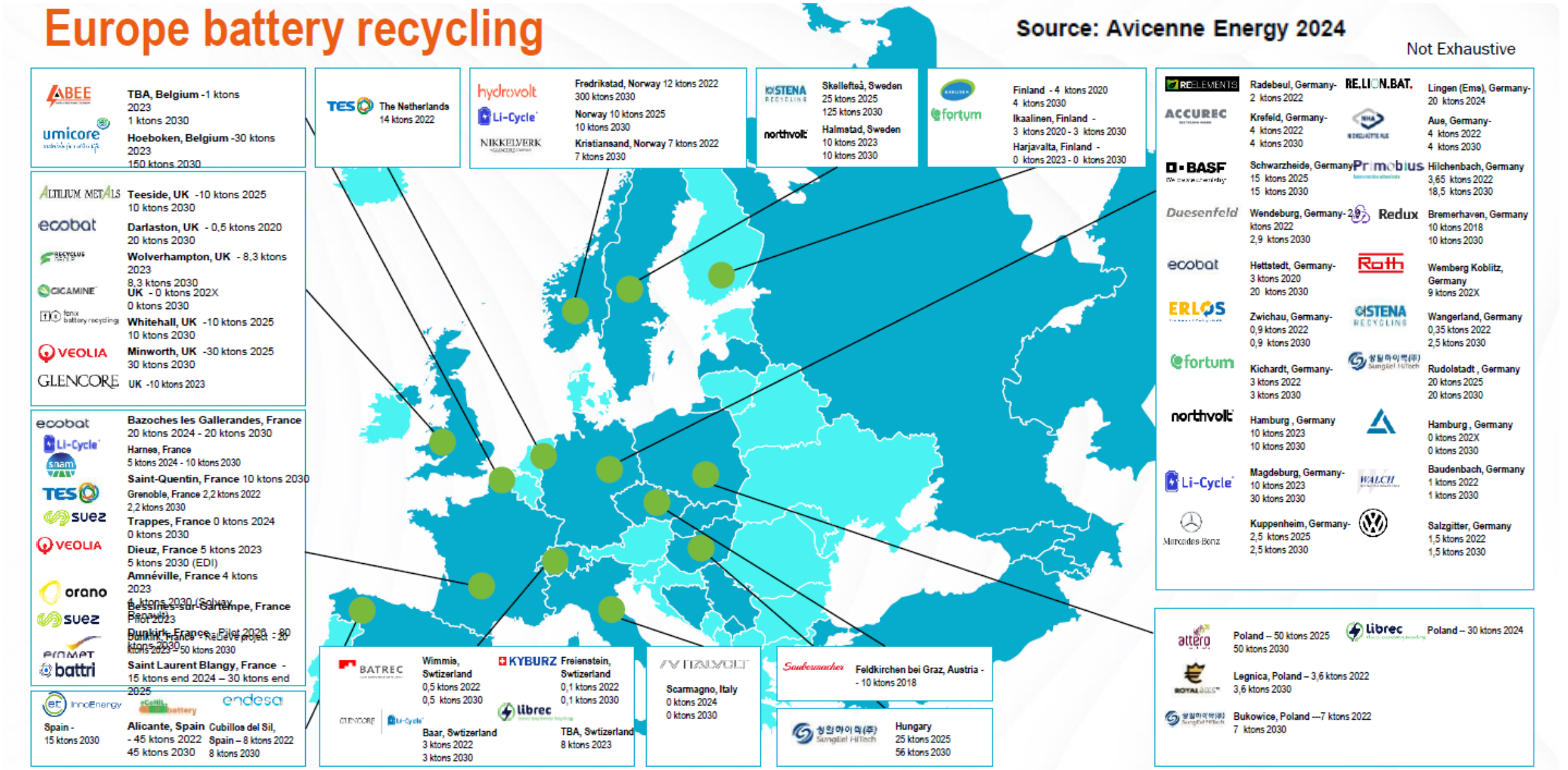
Source: Avicenne Energy 2024

Recyclage des batteries/modules : plusieurs procédés co-existent au niveau industriel

Procédé pyrométallurgique	Procédé hydrométallurgique	Combinaison pyro / hydro
		
traitement thermique permettant de récupérer les métaux purs ou dans un alliage Une partie de l'énergie nécessaire est amenée par la batterie elle-même (matières plastiques)	**traitement chimique** (T<130°C) qui permet de passer les métaux en solution Broyage mécanique ⚠ **BLACK MASS** Attaque chimique	**traitement thermique suivi d'un raffinage chimique** Les principaux métaux sont concentrés dans un alliage métallique, permettant un traitement hydrométallurgique plus efficace

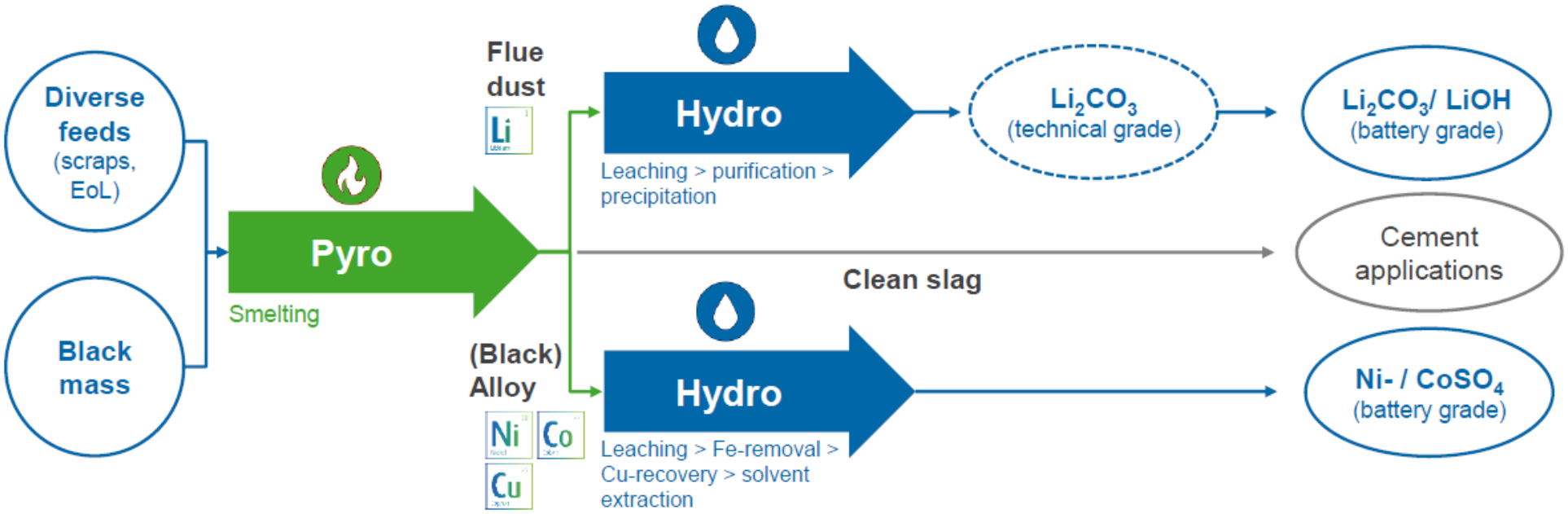
Beaucoup de R&D sur les procédés de « recyclage direct » (voir 2ème partie de la présentation)

Des capacités de recyclage existent en France et en Europe, avec des niveaux de maturité variables



UMICORE: pyrométallurgie + hydrométallurgie

Technology | Umicore's technology combines proprietary pyro and simple hydro processes



ORANO: traitement mécanique + hydrométallurgie

An innovative recycling process developed by Orano and adapted to different inputs

EoL modules

Pre-treatment

Activated components

Electrical discharged components

Deactivation

- Components secured trough a disruptive deactivation process
- Release of energy avoiding thermal runaway, gas generation, inflammability and/or explosion

Stack extraction

Casing (Al)

Electrode separation

Liquid (Electrolyte)

Graphite Separation

Graphite

Sorting and sieving

Al

Cu

Plastics

Cathode Mix purity > 90 %

Manufacturing scraps

Hydrometallurgy

Leaching

Impurities precipitation

Cu, Al, Fe...

2 Resolution to PCAM

Purification

1 Resolution to SALTS

SX Mn

SX Co

SX Ni

Li_2SO_4 Na_2SO_4

Mn sulfate crystallization

Co sulfate crystallization

Ni Sulfate crystallization

Li crystallization

$MnSO_4.H_2O$

$CoSO_4.7H_2O$

$NiSO_4.6H_2O$

$LiOH.H_2O$

Purification of graphite

Regeneration to battery grade

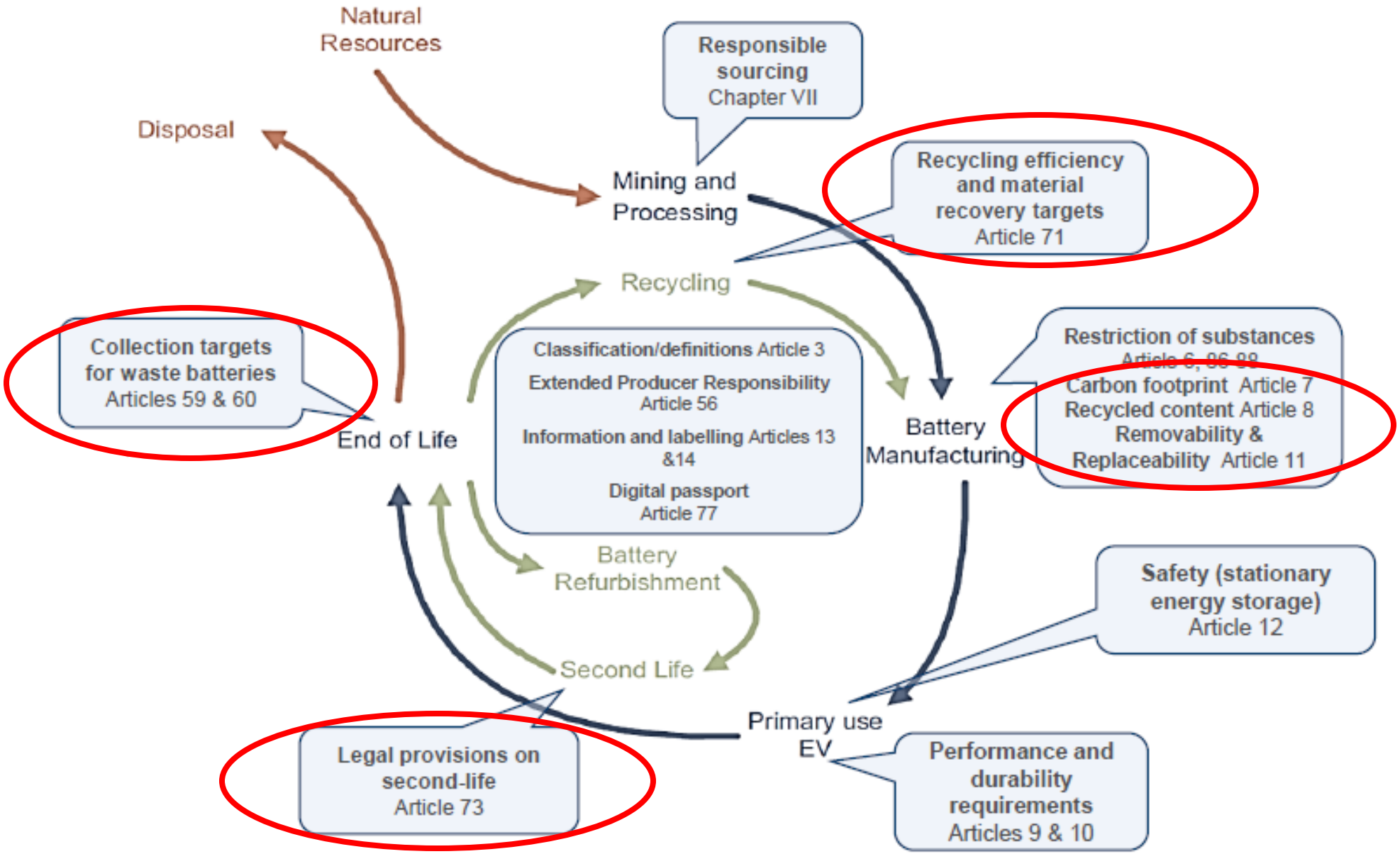
PCAM/CAM

Stoechiometric adjusment

PCAM synthesis via coprecipitation

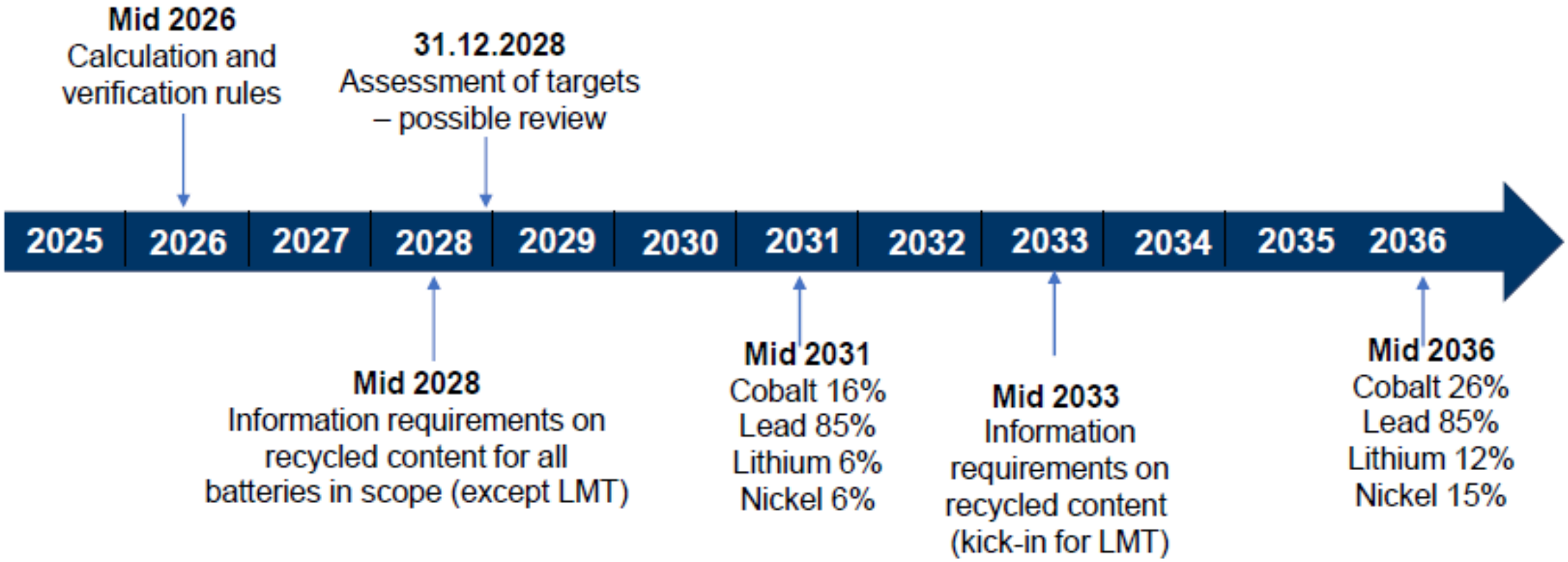
CAM plant

Nouvelle législation européenne « batteries » (2023/1542/EC)



Nouvelles exigences lors de la conception des batteries

- Article 8 : Contenu recyclé : applicable pour les batteries industrielles, automobiles, EV et 5 ans plus tard pour LMT



Nouvelles exigences lors du recyclage des batteries (article 71)

RECYCLING EFFICIENCIES BY 2025 AND 2030 (by average weight)

- 75 % for lead-acid batteries; & 80% in 2030
- 65% for lithium-based batteries; & 70% in 2030
- 80% for nickel-cadmium batteries
- 50% for other waste batteries

MATERIAL RECOVERY TARGETS BY 2027 AND 2031

- 90 % for cobalt; & 95% in 2031
- 90 % for copper; & 95% in 2031
- 90 % for lead; & 95% in 2031
- 50 % for lithium; & 80% in 2031
- 90 % for nickel, & 95% in 2031

By 18 February 2025
Rules on calculation and verification

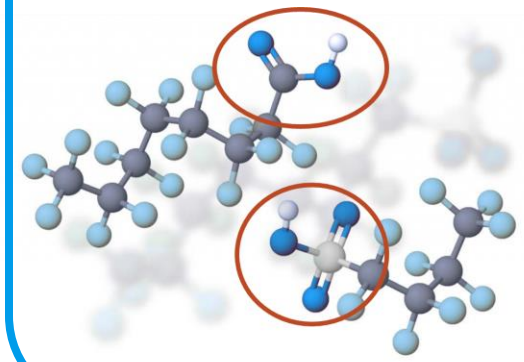
By 18 August 2026
Commission to review all targets for recycling efficiencies and material recovery

No fixed deadine:
The Commission can add other batteries chemistries and materials to the targets

Proposition de restriction européenne sur les PFAS (Per- and poly-fluoroalkyl substances)

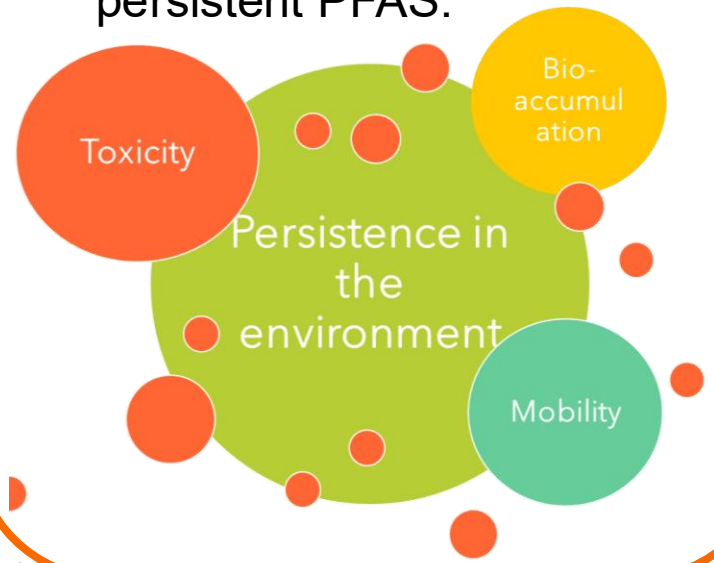
Definition:

at least one –CF_2– or one –CF_3 group, without any H/Cl/Br/I attached to it.



Forever chemicals:

- Persistence due to the strength of the carbon-fluorine bond.
- PFAS are either persistent themselves or degrade to other persistent PFAS.



PFAS restriction proposal in EU :

- Proposed in Feb 2023
- 5600 comments received during ECHA Public Consultation
- Comments assessed by ECHA expert committees
- Potential time-limited derogations

ECHA
EUROPEAN CHEMICALS AGENCY

Ban on manufacture, use and placing on the market

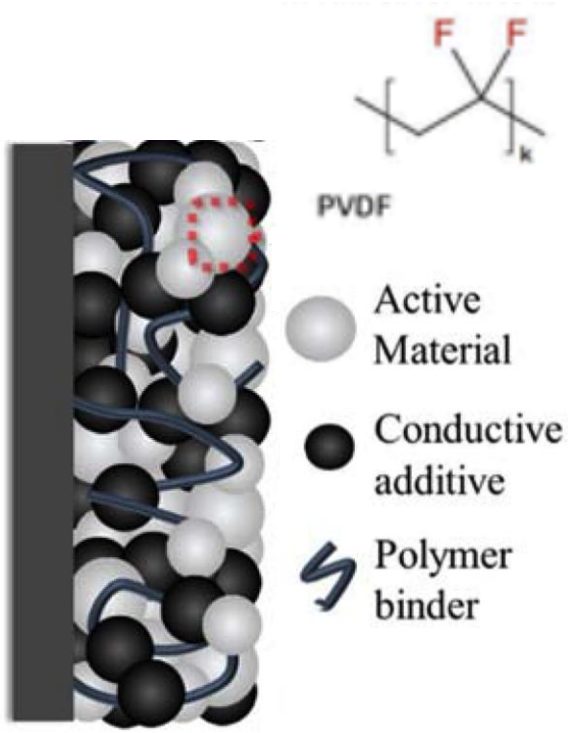
- As substances on their own
- As a constituent
- A mixture
- An article

≥ 25 ppb for any PFASs
≥ 250 ppb for sum of PFASs
≥ 50 ppm * for PFASs

* If total fluorine exceeds 50 mg F/kg the manufacturer, importer or downstream user shall upon request provide to the enforcement authorities a proof for the fluorine measured as content of either PFASs or non-PFASs.

Devenir du PVDF pendant le recyclage des batteries Li-ion ???

- PVDF : Liant de l'électrode positive des batteries Li-ion



Lithium-ion battery recycling: a source of per- and polyfluoroalkyl substances (PFAS) to the environment?

Environ. Sci.: Processes Impacts, 2023, **25**, 1015-1030

Conclusion : Currently the most common LIB recycling process involves **pyrometallurgy**,which operates at **high temperatures (up to 1600 °C), sufficient for PFAS mineralization.** However, **hydrometallurgy,** an increasingly popular alternative recycling approach, operates under milder temperatures (<600 °C), **which could favor incomplete degradation and/or formation and release of persistent fluorinated substances.**