
NANTES | 29 AOÛT - 2 SEPT. 2022

Congrès Français de Mécanique

Enjeux et défis du déploiement massif du stockage électrochimique de l'énergie : matériaux organiques et éco-conception

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***Chem. Rev.*, 2020**

PILE ≠ ACCUMULATEUR (… batterie d'accumulateurs)

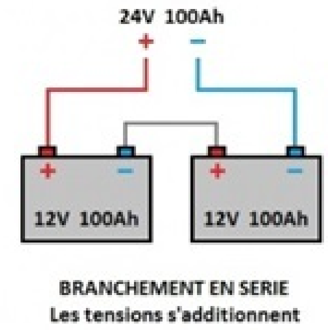
Pile : difficulté à ramener l'état initial par simple recharge

- → Système électrochimique non RECHARGEABLE
- → Existe différents systèmes électrochimiques ; un exemple, les piles à combustible (O_2/H_2)
- → Une pile rechargeable, ça n'existe pas !

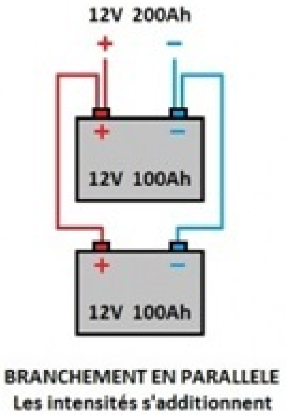
PILE ≠ ACCUMULATEUR (… batterie d'accumulateurs)

Accumulateur : les systèmes électrochimiques utilisés permettent le retour à l'état initial du système par **recharge** (en inversant le sens des réactions par inversion de la polarisation)

→ Batterie d'accumulateurs



BRANCHEMENT EN SERIE
Les tensions s'additionnent



BRANCHEMENT EN PARALLELE
Les intensités s'additionnent

→ Existe différents systèmes électrochimiques pour accumulateur (Plomb-acide, Ni-Cd, Ni-MH, Li-ion)

Li-ion >2000 cycles de charge/décharge

Plan de l'exposé

I/ Situation mondiale en quelques chiffres

⇒ Données/sources robustes

II/ Vers une électrification massive de nos sociétés

⇒ Problématique du stockage de l'électricité, des batteries, des ressources…

III/ Batteries organiques

⇒ Une chimie complémentaire aux composés inorganiques

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The key indicators of world: *a constant increase!*

Primary energy supply

Motorized transportation (ICEs)

Ore demand

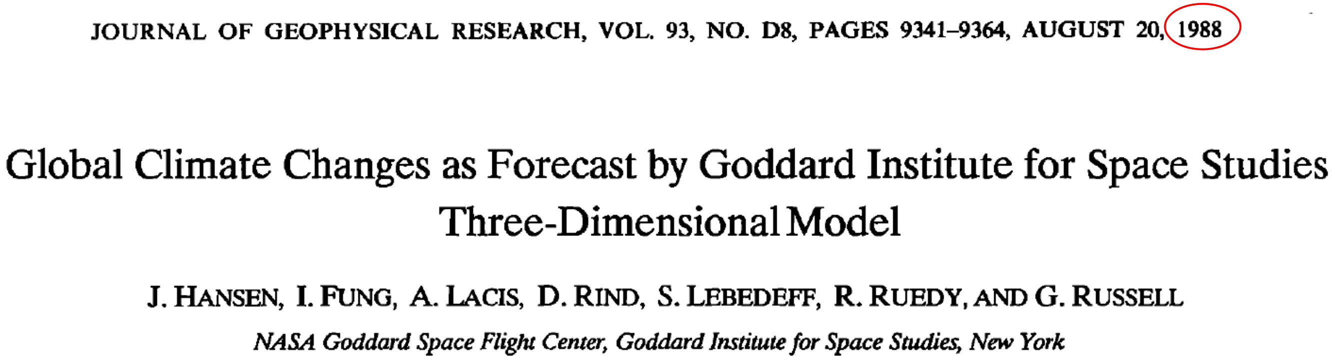
Metal exhaust

GHG emissions

⇒ Booming from the industrial revolutions of the 19th century

⇒ Not sustainable

The key indicators of world: GHG & Global Warming



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 93, NO. D8, PAGES 9341–9364, AUGUST 20, 1988

Global Climate Changes as Forecast by Goddard Institute for Space Studies
Three-Dimensional Model

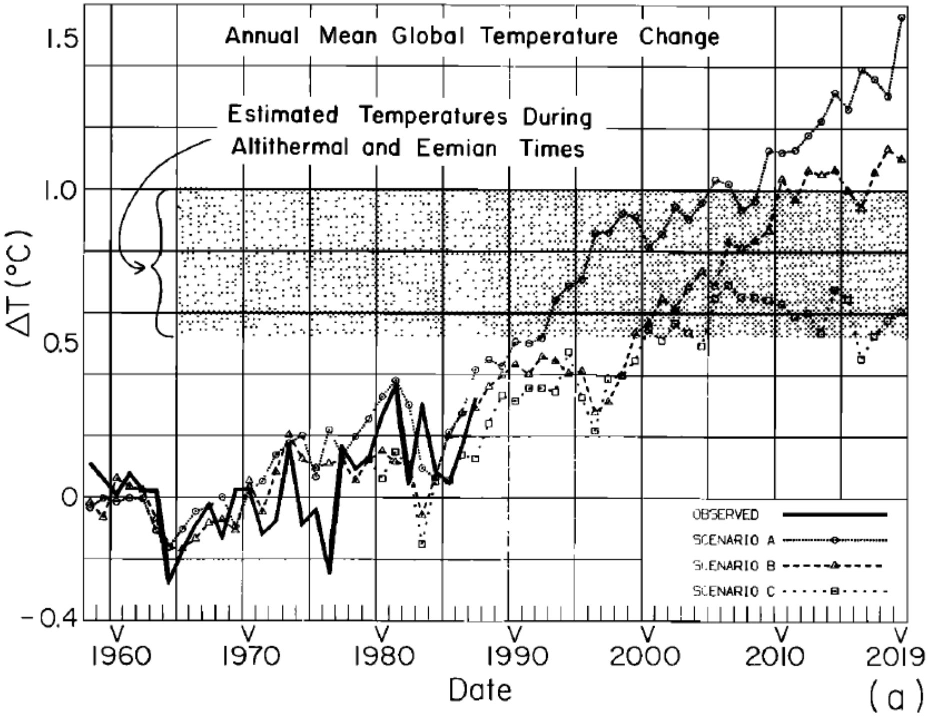
J. HANSEN, I. FUNG, A. LACIS, D. RIND, S. LEBEDEFF, R. RUEDY, AND G. RUSSELL
NASA Goddard Space Flight Center, Goddard Institute for Space Studies, New York

P. STONE
Massachusetts Institute of Technology, Cambridg

1988 : création du Groupe d'experts intergouvernemental sur l'évolution du climat (GIEC ou IPCC en anglais)

1987: Sustainable development: concept of the public interest was proposed by the Brundtland Commission

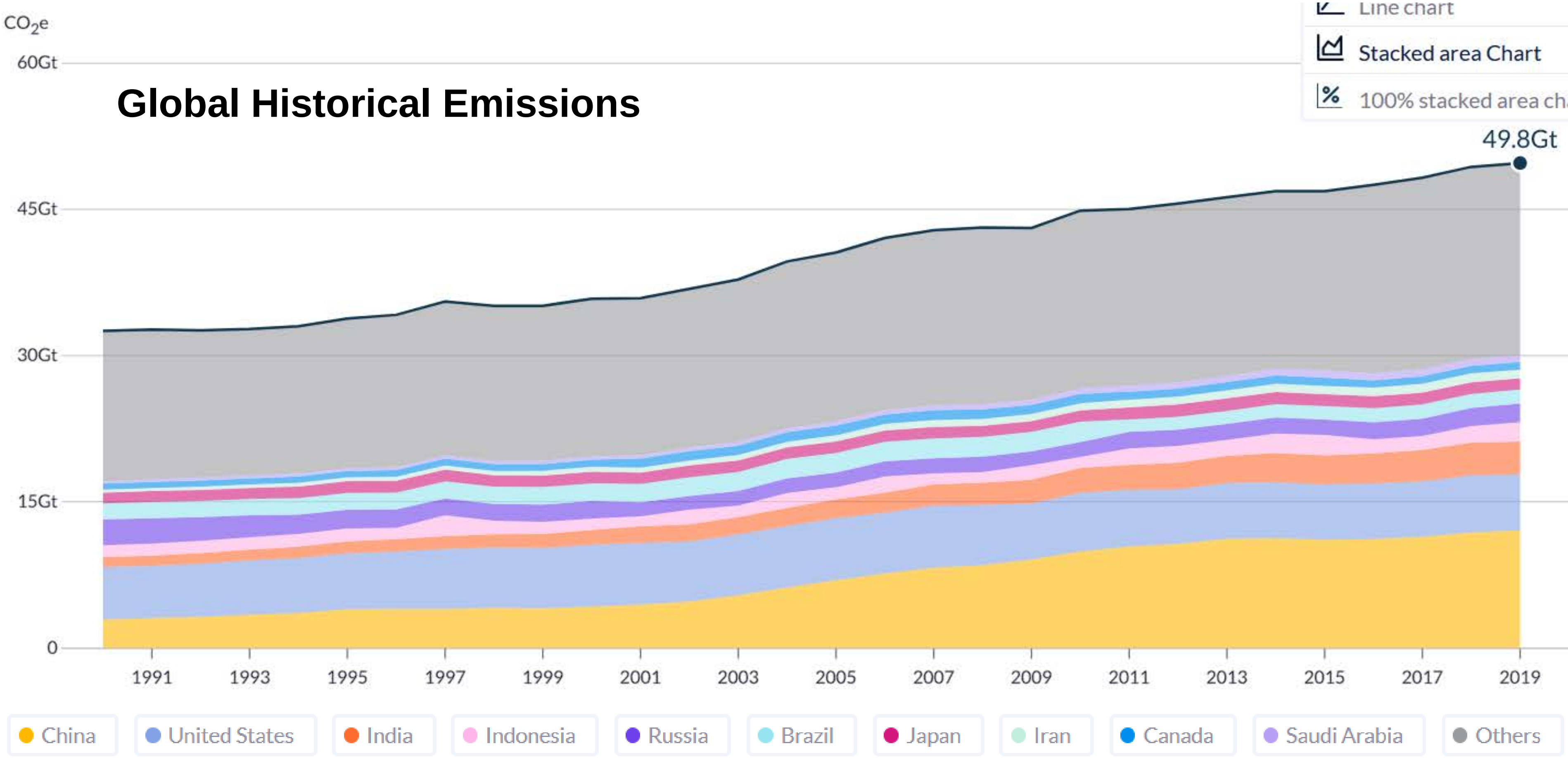
⇒ G. Brundtland, **Our Common Future**: The World Commission on Environment and Development, Oxford University Press, Oxford.



The key indicators of world: GHG & Global Warming

CLIMATEWATCH World Resources Institute (WRI) - https://www.climatewatchdata.org/ghg-emissions

Global Historical Emissions



The key indicators of world: GHG & Global Warming

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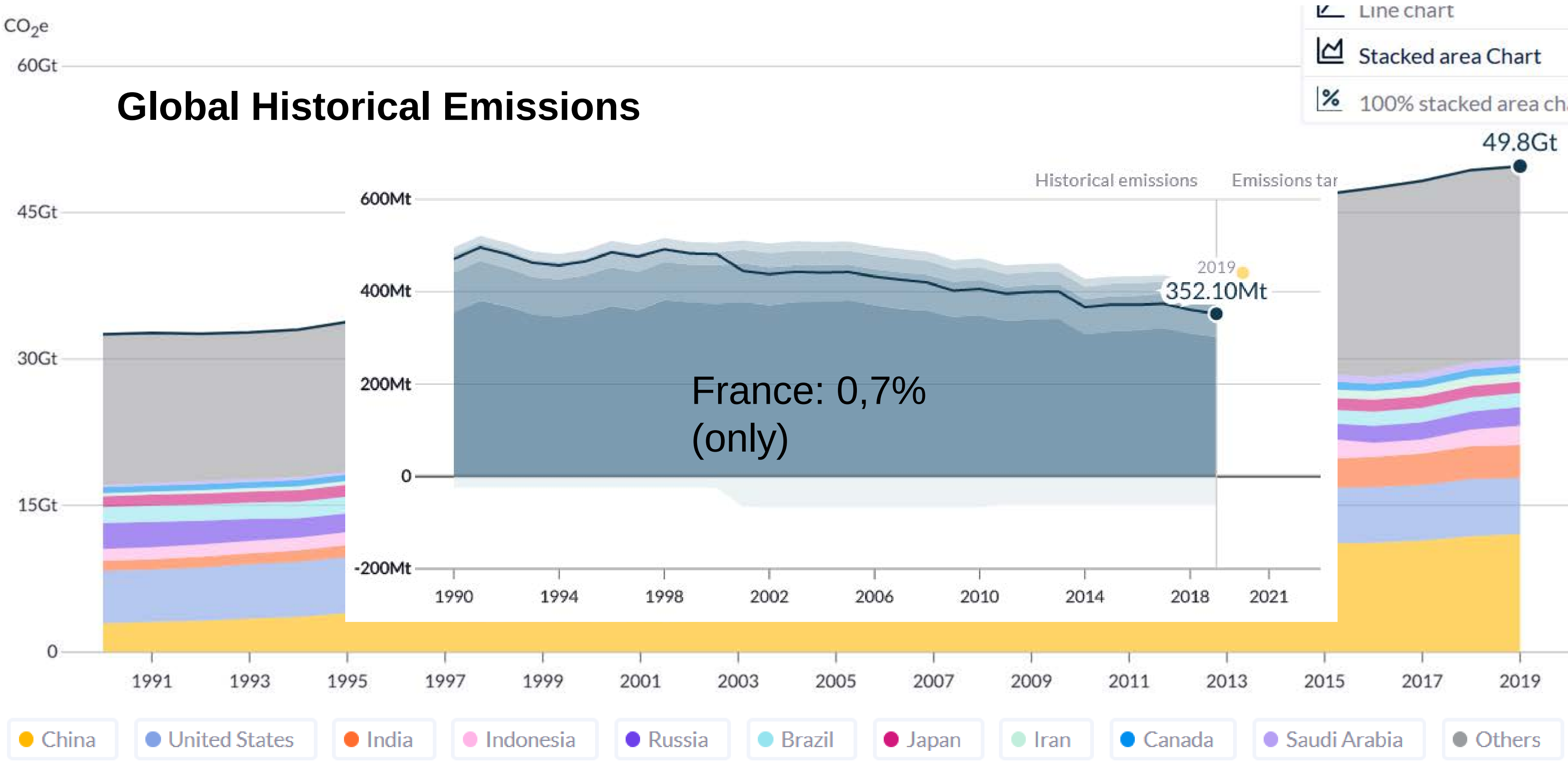
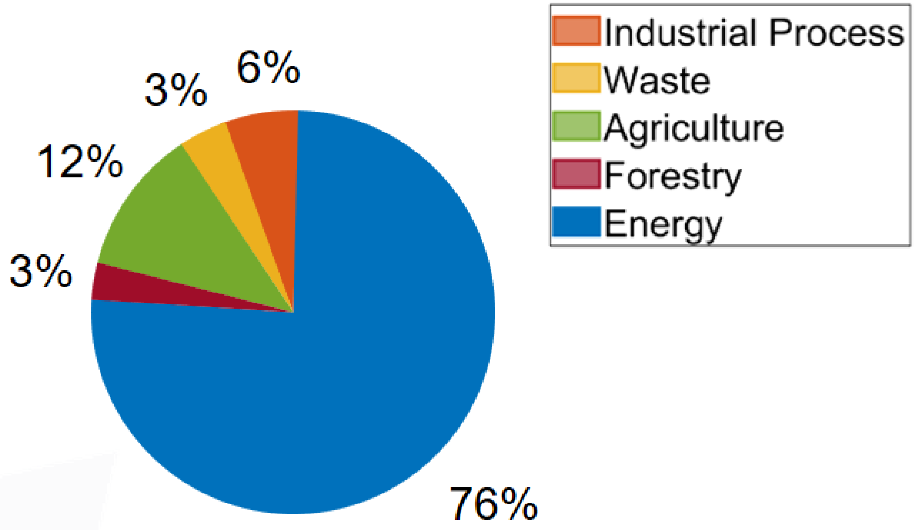


Global Historical Emissions

France: 0,7% (only)

The key indicators of world: GHG & Global Warming

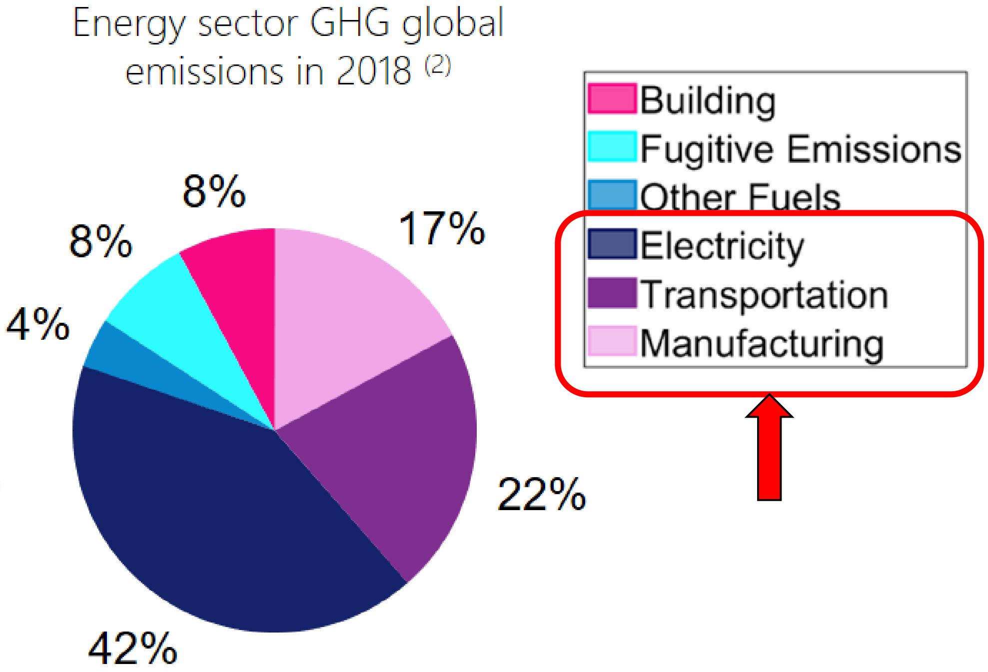
GHG global emissions in 2018 (2)



76 % of CO_2 emissions comes from the energy sector

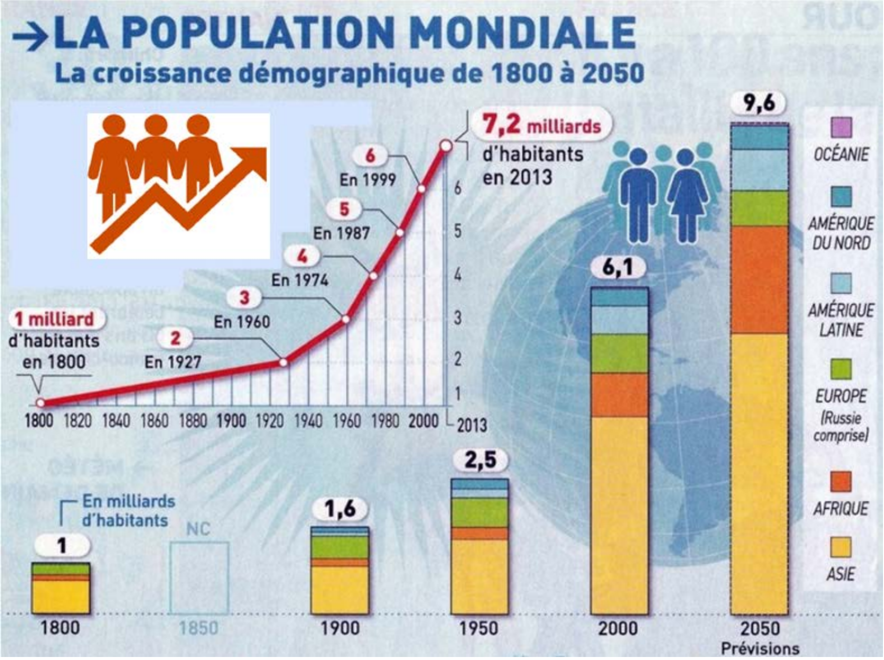
(2) World Resources Institute (WRI) - https://www.climatewatchdata.org/ghg-emissions

The key indicators of world: GHG & Global Warming



(2) World Resources Institute (WRI) - https://www.climatewatchdata.org/ghg-emissions

The key indicators of world: *World population*



From UN data, https://www.un.org/development/desa/pd/

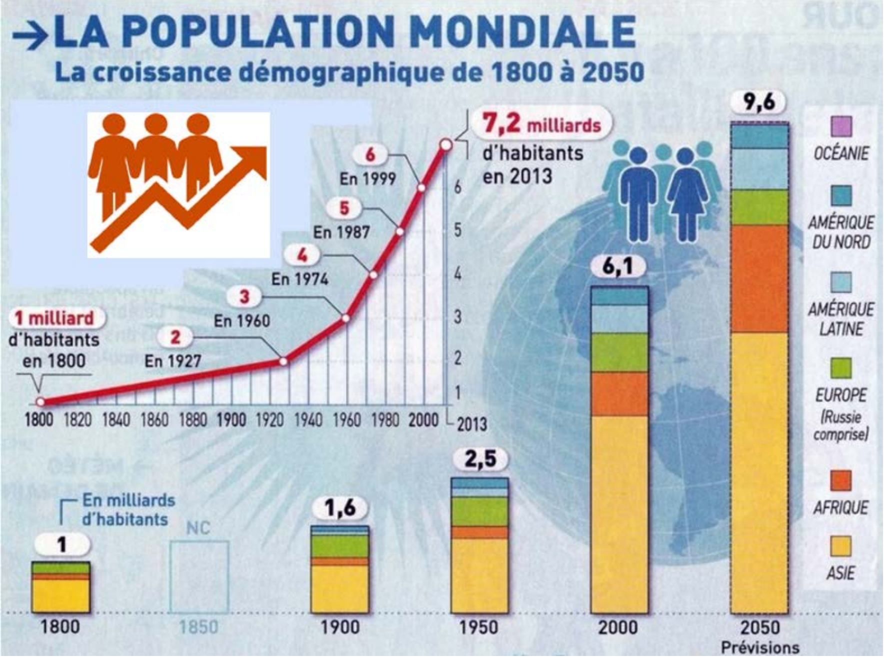
https://www.futuribles.com/fr/revue/434/la-population-mondiale-a-lhorizon-2100-critique-de/

⇒ 79% of the Human load localized in « emerging » countries

⇒ Human being = consumer especially in developed countries (GHGs makers)

The key indicators of world: *World population*

World population



→LA POPULATION MONDIALE

La croissance démographique de 1800 à 2050

"Human demand may well have exceeded the biosphere's regenerative capacity since the 80's"

(Wackernagel et al., PNAS, 2002, **99**, 9266)

⇒ Changes in our daily life are needed

⇒ New population policies???

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III/ Batteries organiques

⇒ Une chimie complémentaire aux composés inorganiques

Reconsider our energy engineering…

1 - Decarbonize the Power supply

Electricity = Functionality /everyday life necessity

LIFE EXPECTANCY
Rapid depletion when the electricity consumption per inhabitant is lower than 1600 kWh per year

☐ *Energy*, **23**, 791−801 (1998)

Reconsider our energy engineering…

1 – Decarbonize the Power supply

Electricity = Functionality /everyday life necessity

2 – Decarbonize the Transportation sector currently based on ICEs

A necessary trend: Electrification of the Transportation Systems

❑ *Chem. Rev.*, **120**, 6490−6557 (2020)

…Entering a so-called 4th Industrial Revolution

3 – Digitalization, IoT, service robots,… the growing consumption of electronic devices

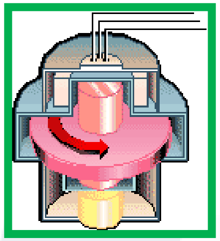
https://martechtoday.com/, Accessed June 2017

☐ *Chem. Rev.*, **120**, 6490−6557 (2020)

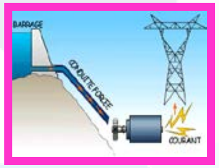
The critical electricity storage issue:

Only a few technological solutions

Capacitors
Super capacitors



Flywheels



Dam
pumping
station

Compressed Air
Technology
(CAT)

...

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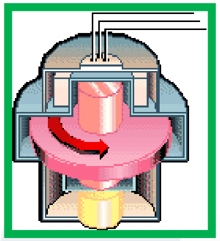
Super capacitors



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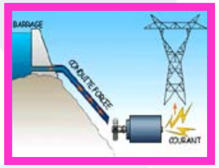
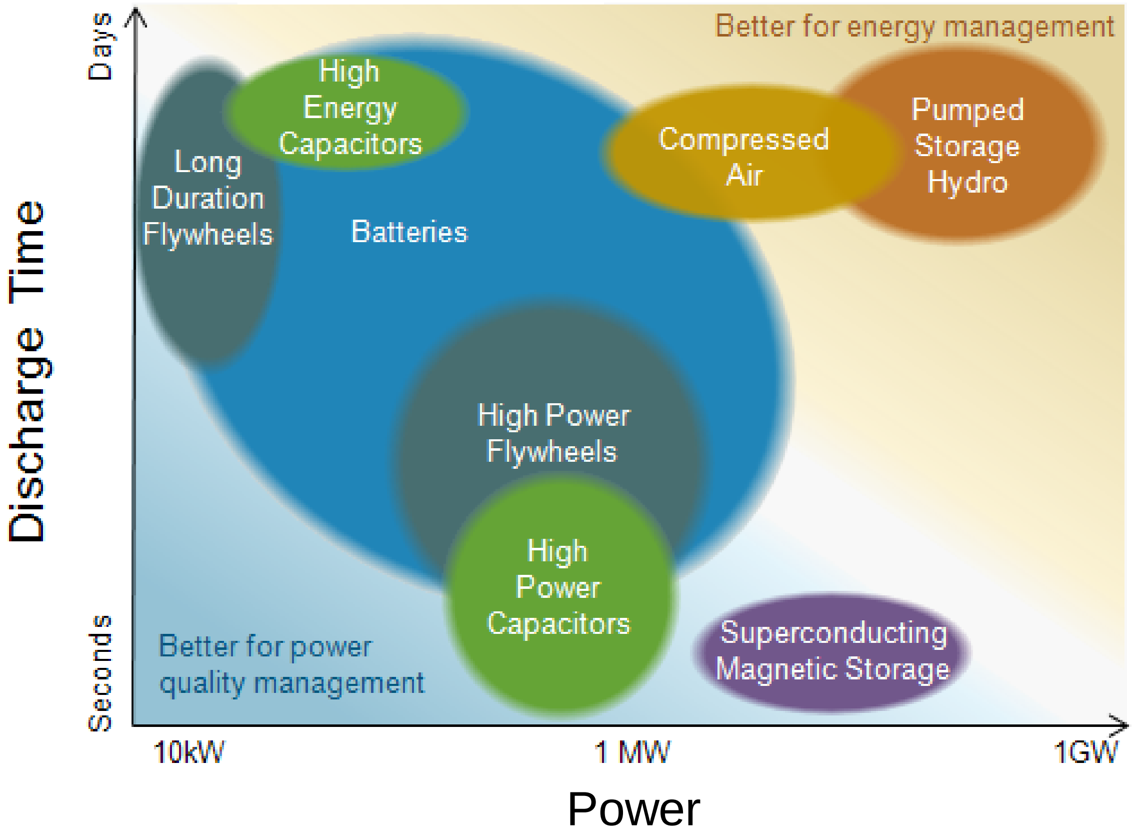


Dam pumping station

Compressed Air Technology (CAT)

…



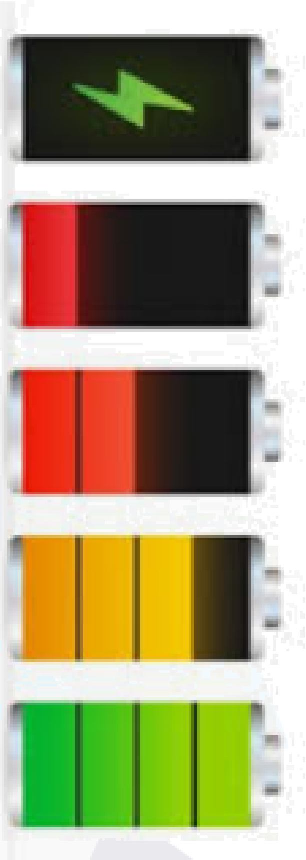
Electricity Storage Technologies

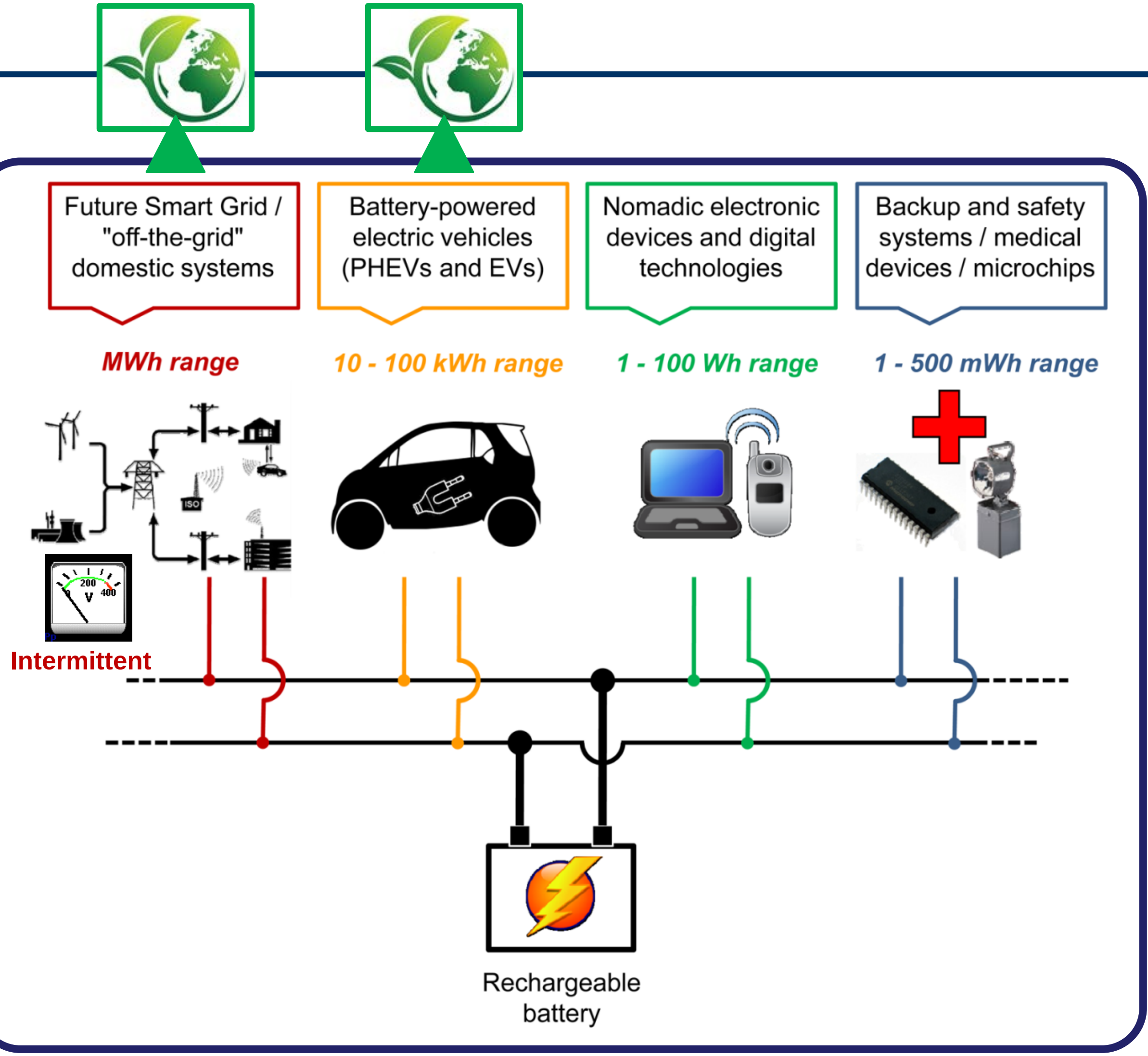
→ Efficiency, maintenance costs, …

❑ *Red Mountain Insights* (2014)
ISBN: 978-1-62484-002-9

The critical electricity storage issue:

Rechargeable BATTERIES



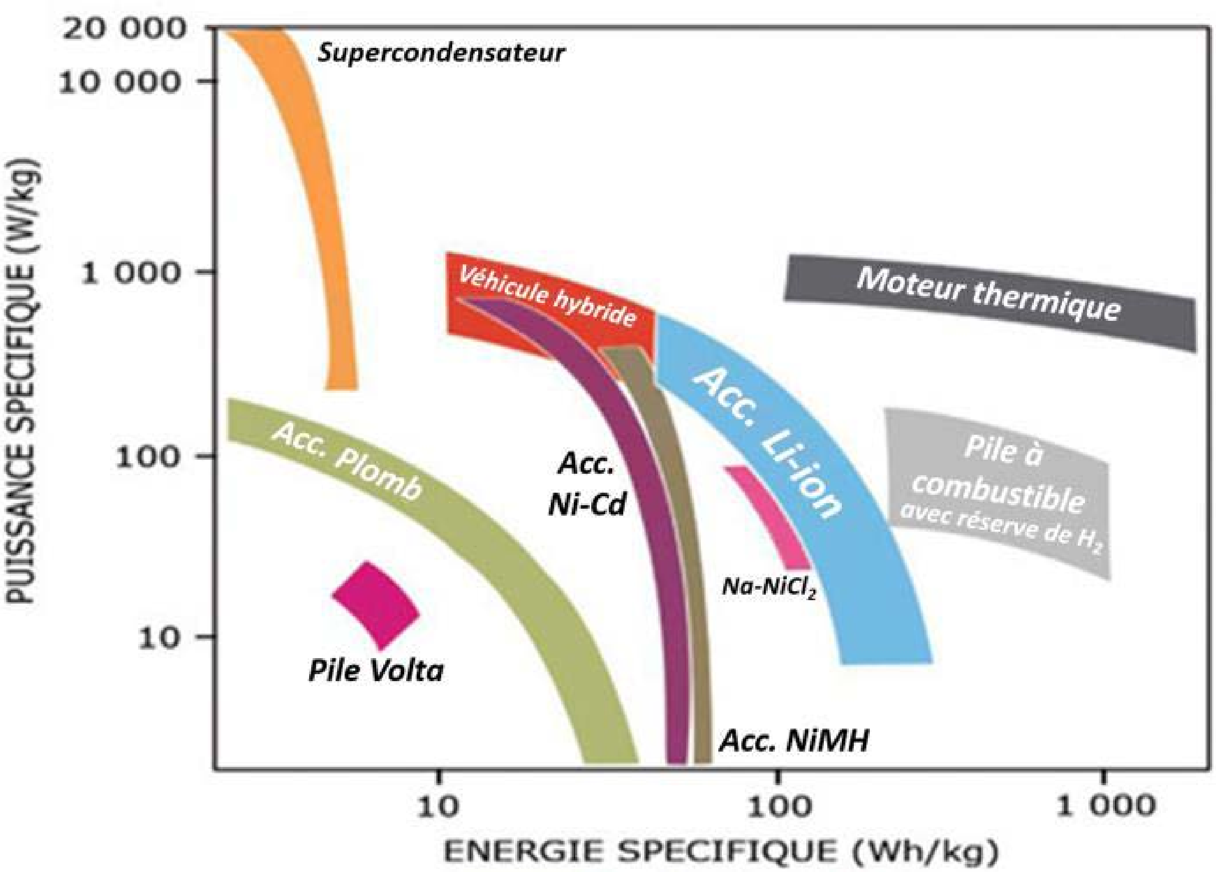


Future Smart Grid / "off-the-grid" domestic systems	Battery-powered electric vehicles (PHEVs and EVs)	Nomadic electronic devices and digital technologies	Backup and safety systems / medical devices / microchips
MWh range	*10 - 100 kWh range*	*1 - 100 Wh range*	*1 - 500 mWh range*

- *Energy Environ. Sci.*, **4**, 2003−2019 (2011)

The critical electricity storage issue:

Li-ion batteries, the flagship technology

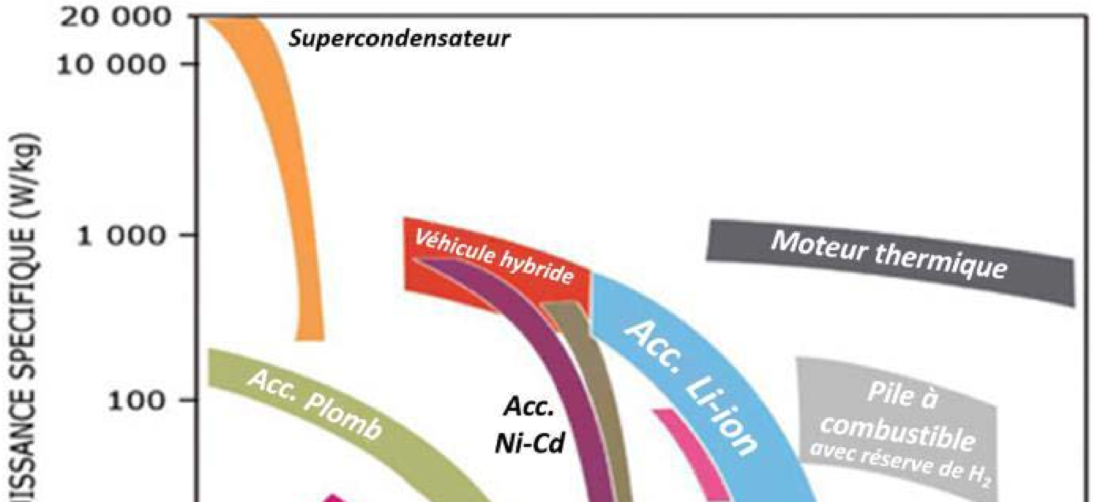


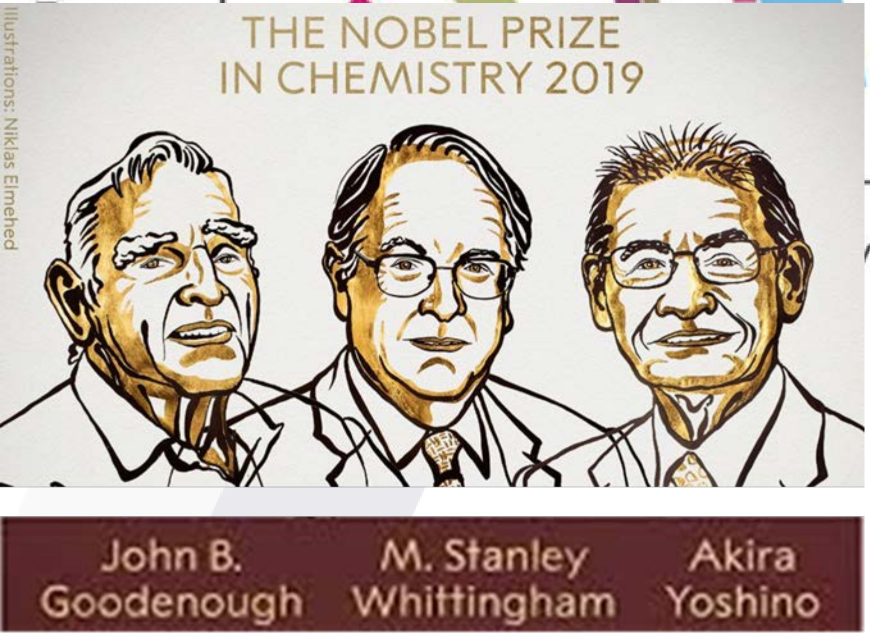
Le Li-ion est devenu la technologie universelle pour l'électronique et les véhicules électrifiés (mais pas encore pour le stationnaire = batteries Pb-acide)

Efficacité Energétique
Li-ion > 85% !!
2000 cycles 10 ans

The critical electricity storage issue:

Li-ion batteries, the flagship technology





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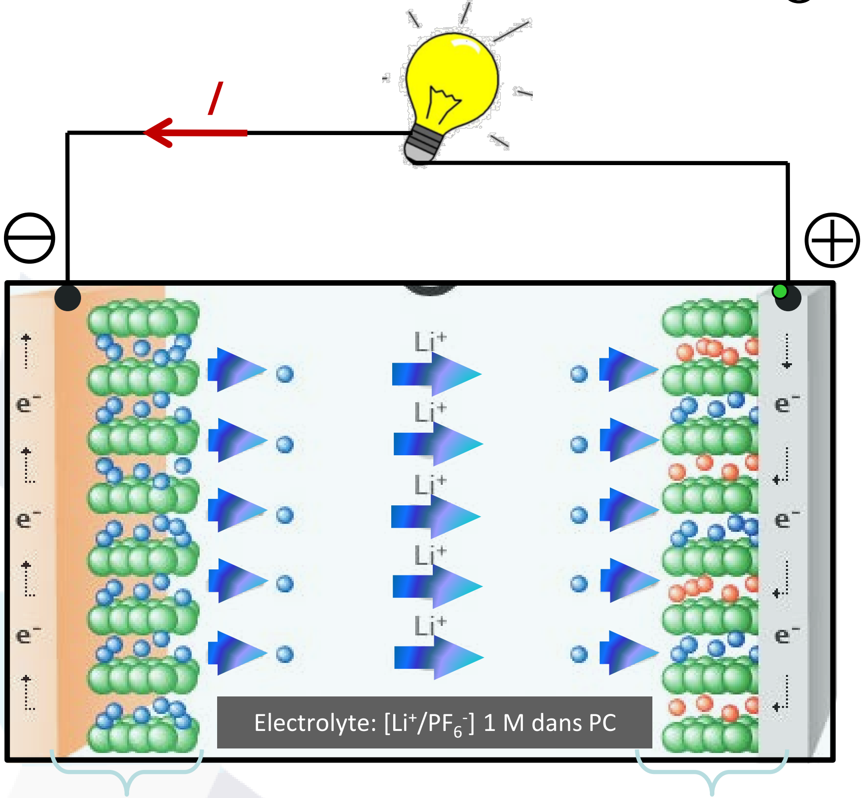
Efficacité Energétique Li-ion > 85% !! 2000 cycles 10 ans

Working principle of a Li-ion cell:

historical example (SONY, 1991)

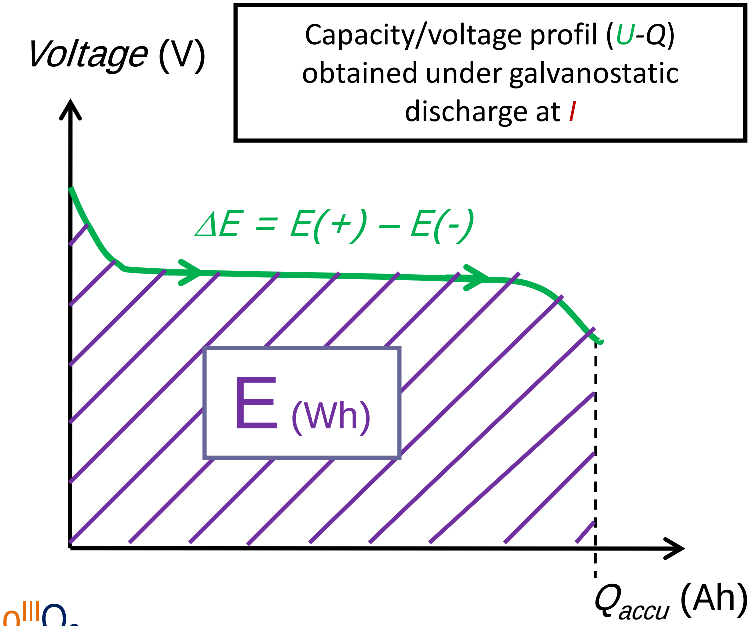
CHARGED STATE (Initial state): ⊖ LiC_6 | electrolyte | $Li_{0.5}Co^{III,IV}O_2$ ⊕

DISCHARGED STATE: ⊖ C_6 | electrolyte | $LiCo^{III}O_2$ ⊕



$LiC_6 \rightarrow C_6 + e^- + Li^+$

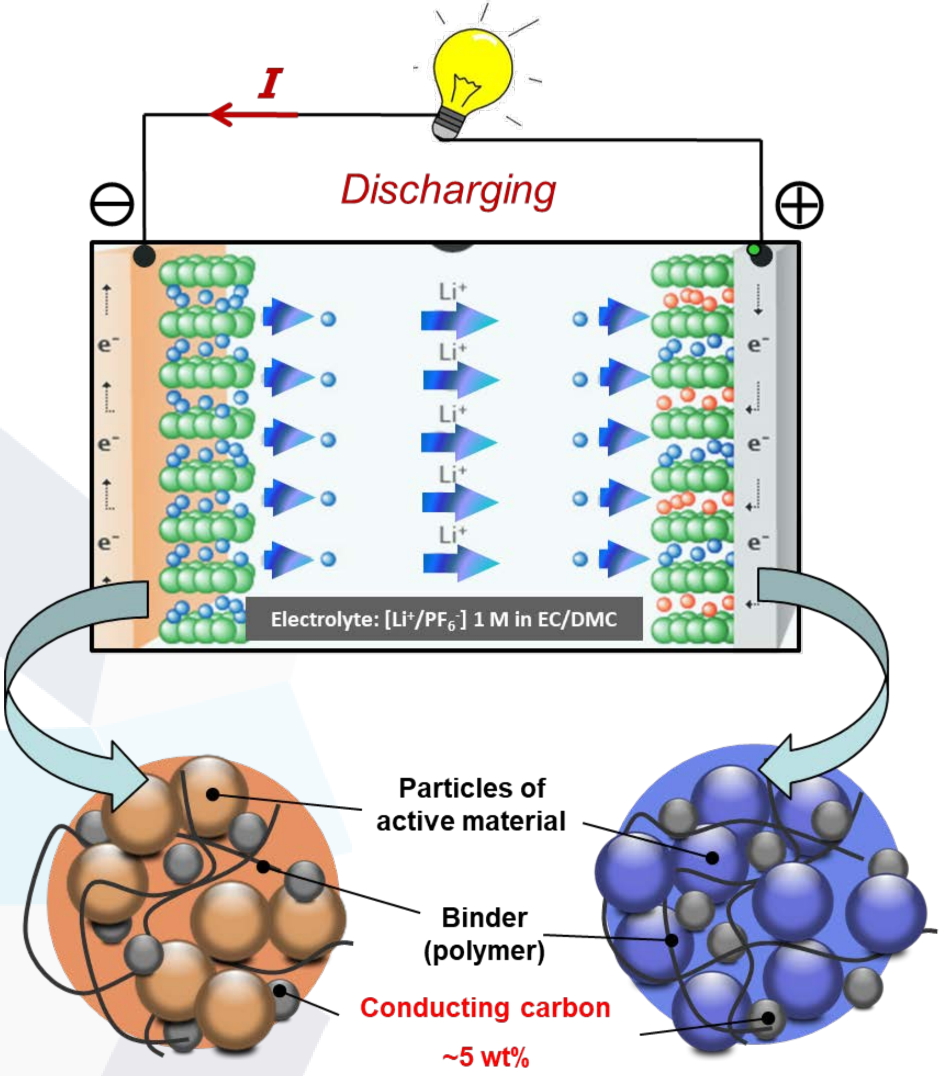
$(\times 2)\ Li_{0.5}Co^{III,IV}O_2 + 0.5\ e^- + 0.5\ Li^+ \rightarrow LiCo^{III}O_2$



⇒ **Insertion materials** as electroactive chemical compounds

Working principle of a Li-ion cell:

historical example (SONY, 1991)



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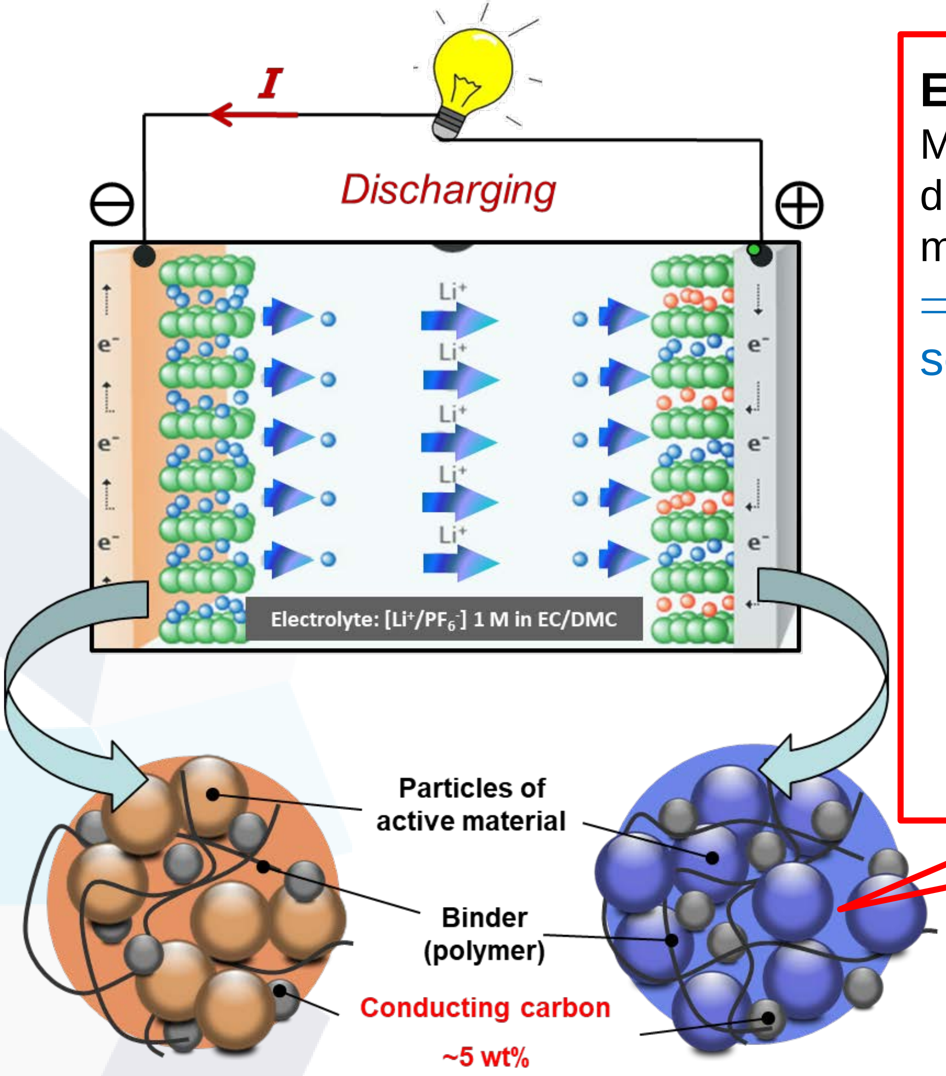
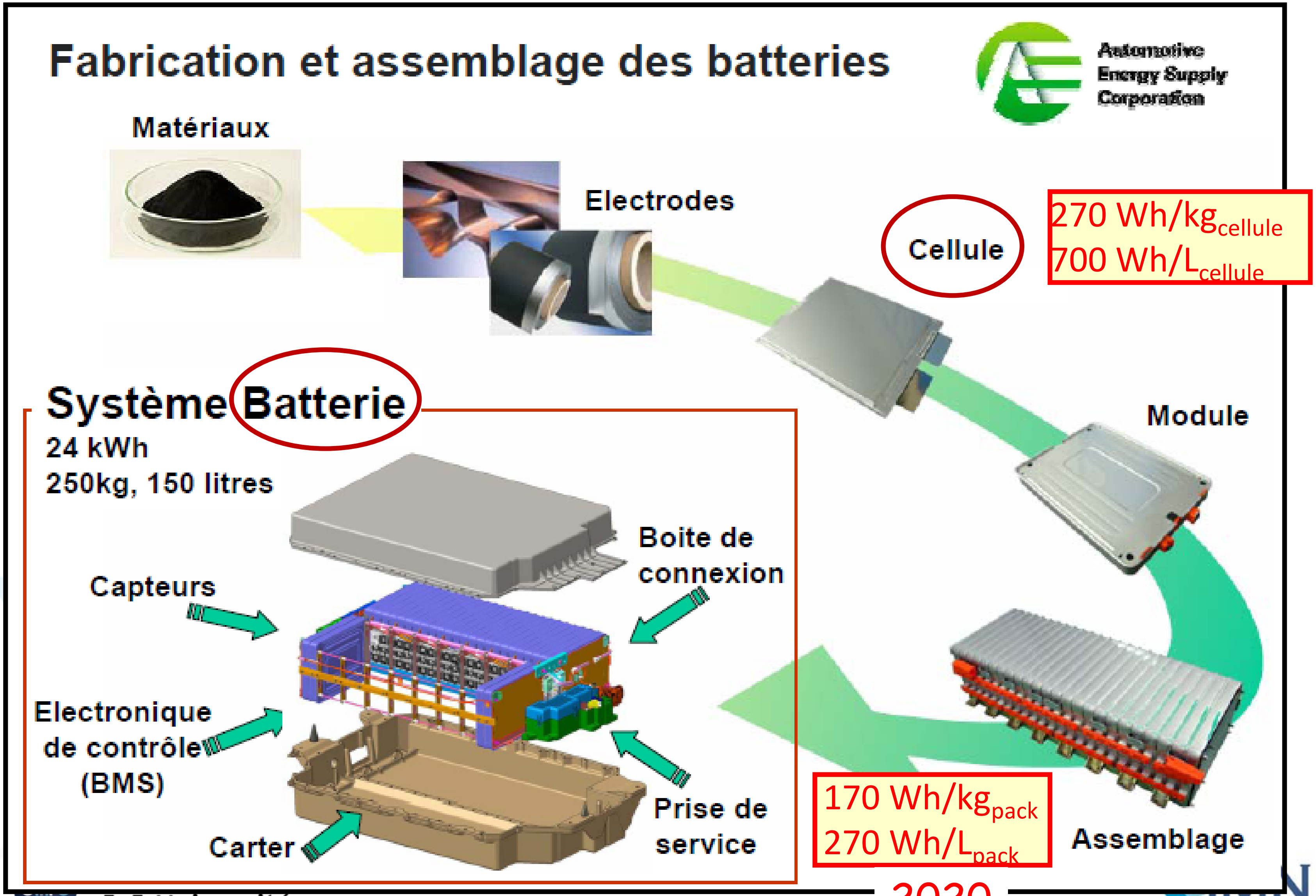


Encre d'électrode :
Matière (électro)active+liant+carbone+solvant du liant, déposé sur collecteur de courant métallique
⇒ Étape de séchage (évaporation du solvant)

Working principle of a Li-ion cell:

from the active materials to the battery pack



Fabrication et assemblage des batteries

270 Wh/$kg_{cellule}$
700 Wh/$L_{cellule}$

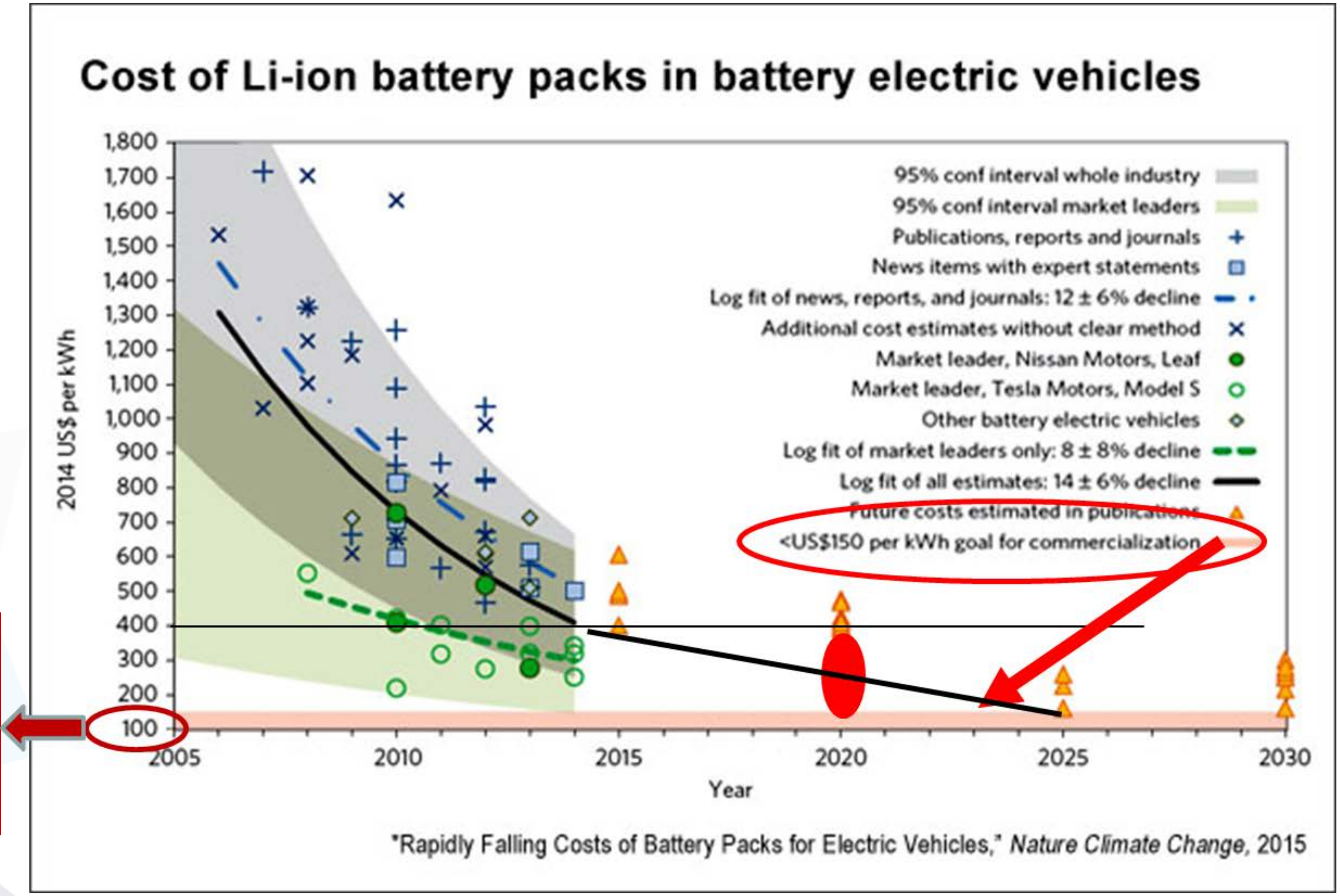
2020

170 Wh/kg_{pack}
270 Wh/L_{pack}

2020

Cost of Li-ion batteries

Coût divisé par 5 en 10 ans
2020 ⇔ 150 $/kWh



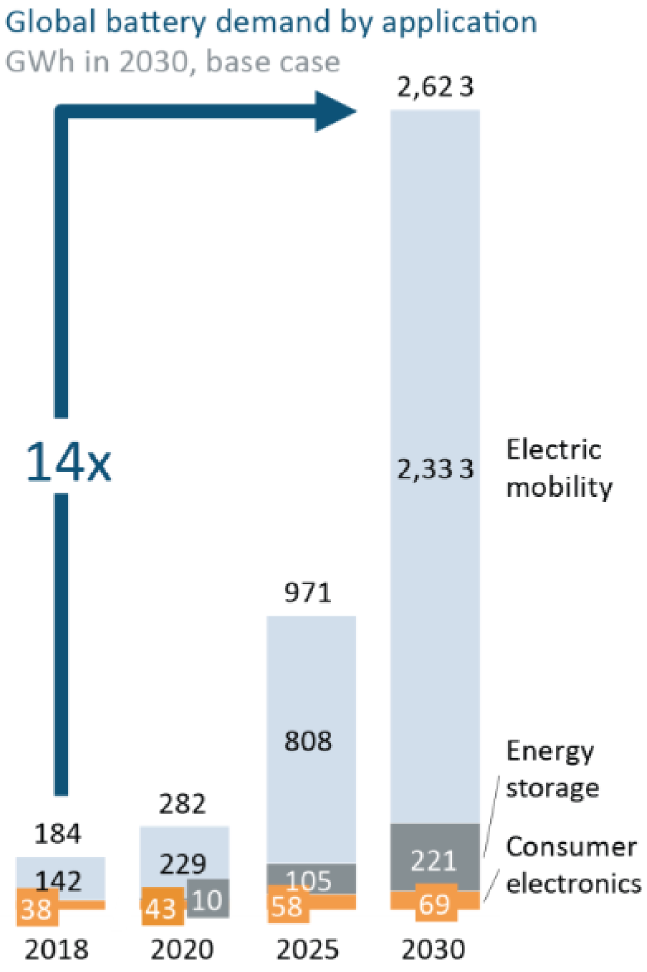
Cost of Li-ion battery packs in battery electric vehicles

"Rapidly Falling Costs of Battery Packs for Electric Vehicles," *Nature Climate Change*, 2015

Seuil d'« explosion » des marchés VE et stationnaire (ENR)

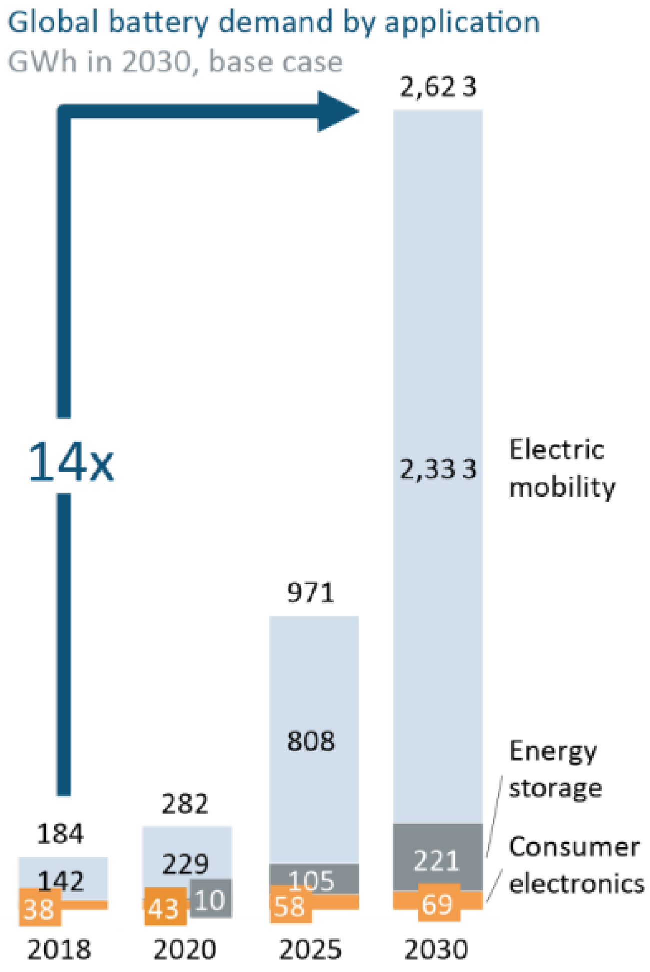
Big pressure on secondary batteries (**especially LIBs**)

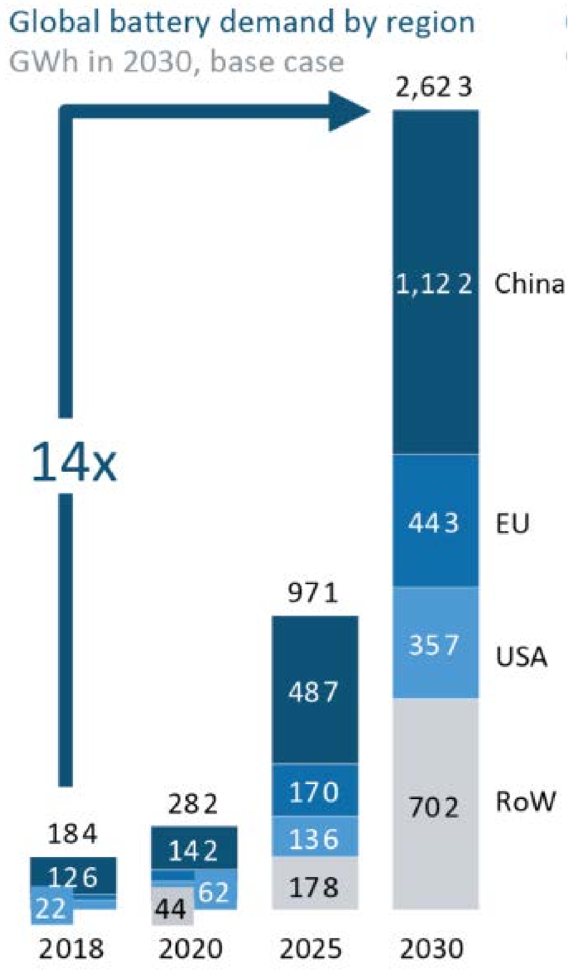
→ *Global demand & projections*



❑ BATTERY 2030+ Roadmap

Big pressure on secondary batteries **(<u>especially LIBs</u>)**
→ *Global demand & projections*


Global battery demand by application
GWh in 2030, base case


Global battery demand by region
GWh in 2030, base case

❑ BATTERY 2030+ Roadmap
https://battery2030.eu/news/activities/the-long-term-research-roadmap/

Big pressure on secondary batteries **(especially LIBs)**

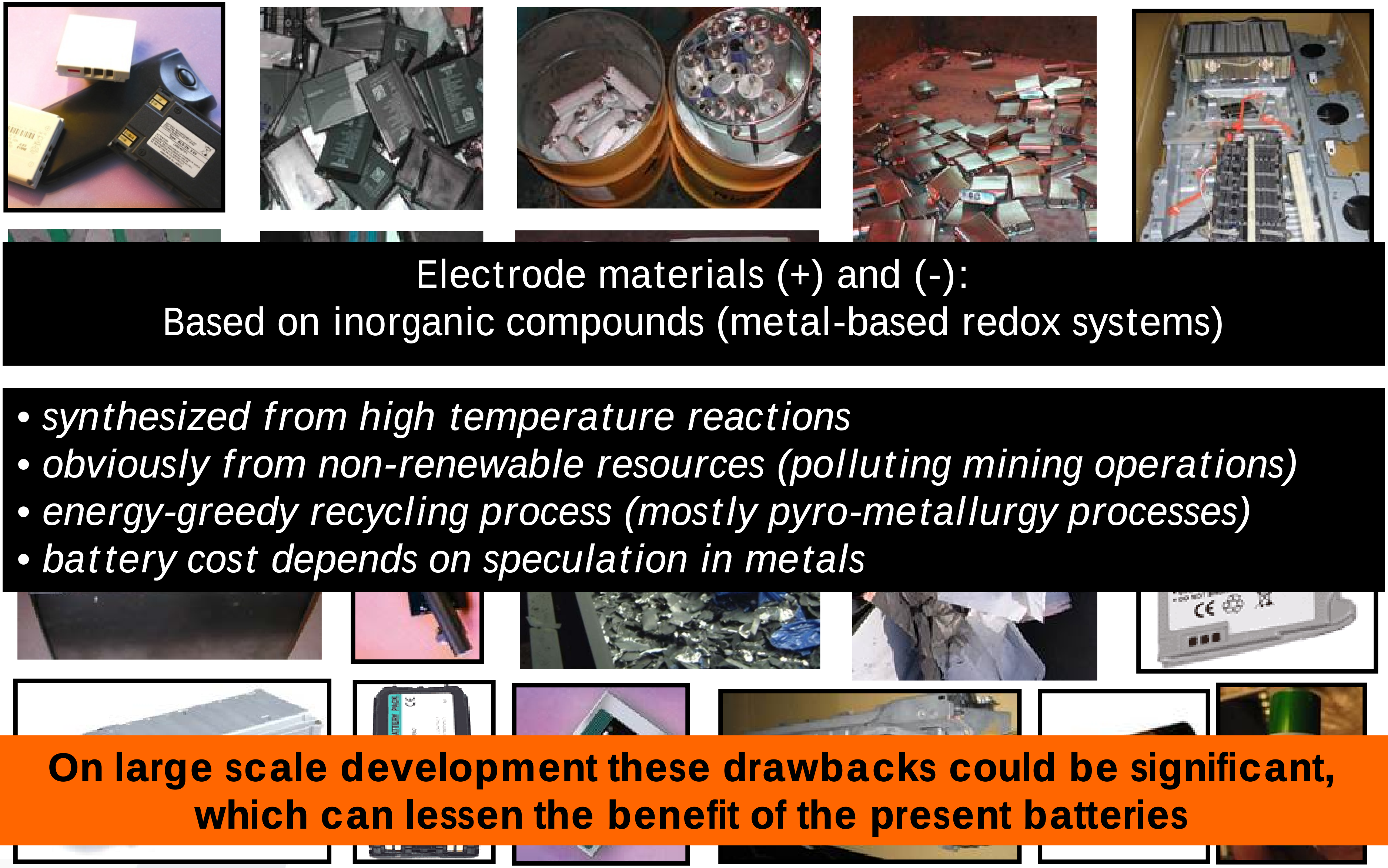
→ *Global demand & projections*

northvolt
SEAT
FREYR
Panasonic
BEYONDER
VERKOR
MORROW
ITALVOLT
BRITISHVOLT
Envision AESC
Leclanché
amte power
SAMSUNG
CATL
TESLA
acc
VARTA
microvast
SVOLT
FARASIS
LG Energy Solution
BASQUEVOLT - NABATT
ROSATOM
SK innovation
FAAM

Gigafactory:

- Factory producing batteries at a very large scale
- Europe: 600 GWh/y full regime production

Common batteries: chemistry of metals and ceramic chemistry



Electrode materials (+) and (-):
Based on inorganic compounds (metal-based redox systems)

- *synthesized from high temperature reactions*
- *obviously from non-renewable resources (polluting mining operations)*
- *energy-greedy recycling process (mostly pyro-metallurgy processes)*
- *battery cost depends on speculation in metals*

On large scale development these drawbacks could be significant, which can lessen the benefit of the present batteries

RECYCLABILITY: LCA studies for LIBs - A REVIEW

Renewable and Sustainable Energy Reviews 67 (2017) 491–506

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

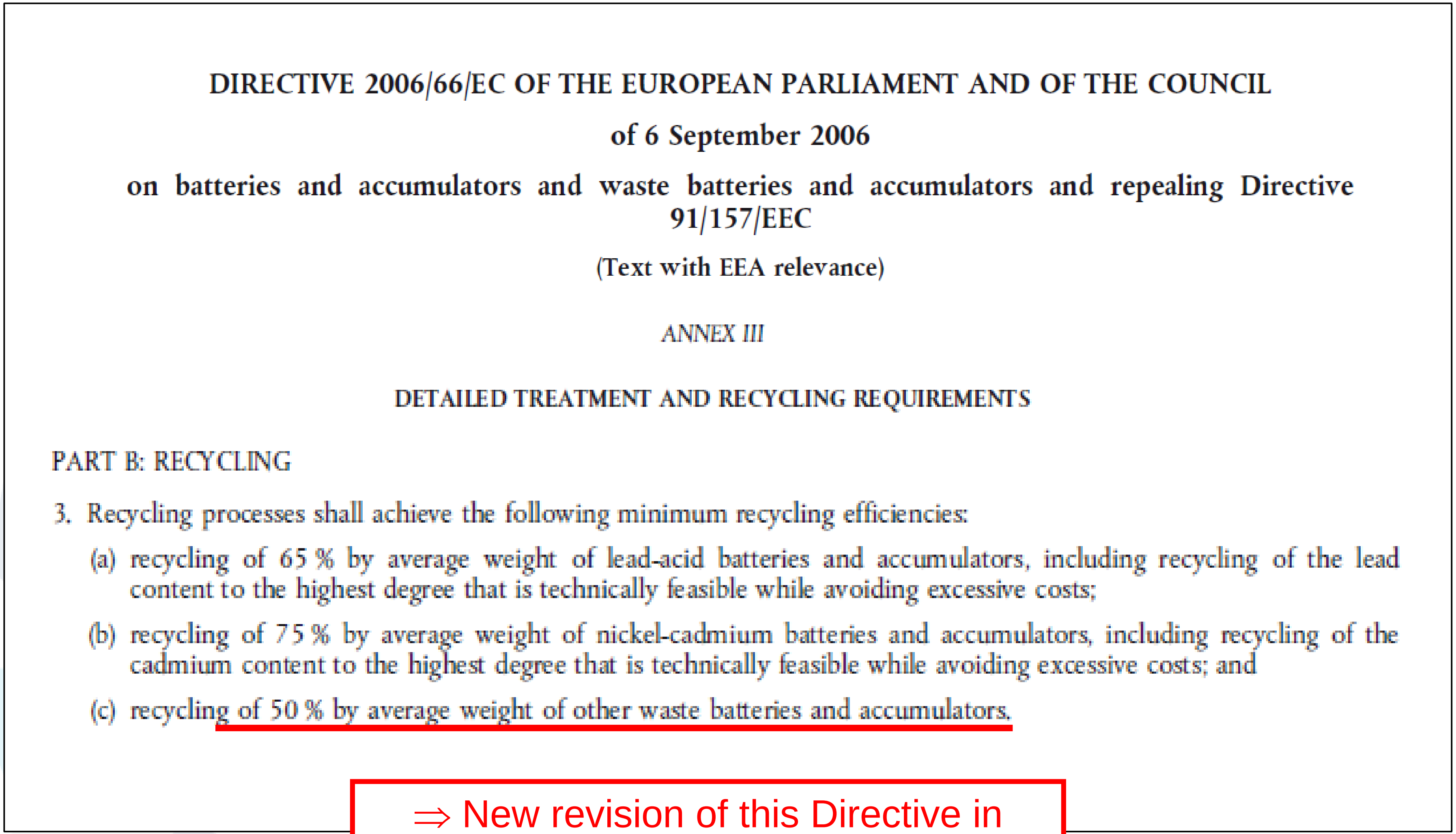
journal homepage: www.elsevier.com/locate/rser

The environmental impact of Li-Ion batteries and the role of key parameters – A review

Jens F. Peters [a,*], Manuel Baumann [b,c], Benedikt Zimmermann [b], Jessica Braun [b], Marcel Weil [a,b]

1/ review of 113 available publications on the topic.
2/ a total of 36 LCA studies were identified as very reliable.
3/ ≈320 kWh is needed across all chemistries to produce 1 kWh of stored electrochemical energy producing GHG emissions of 110 $kgCO_2eq$.
4/ “cradle-to-gate analyses” and not “cradle-to-grave analyses”, both collection and recycling steps are not included.
5/ other Eco indicators such as human toxicity (HTP) are not really studied and might be even more important (from mining excavation to the recycling step).

RECYCLABILITY & Eco-design: new regulations



DIRECTIVE 2006/66/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 6 September 2006

on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC

(Text with EEA relevance)

ANNEX III

DETAILED TREATMENT AND RECYCLING REQUIREMENTS

PART B: RECYCLING

3. Recycling processes shall achieve the following minimum recycling efficiencies:

   (a) recycling of 65 % by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;

   (b) recycling of 75 % by average weight of nickel-cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs; and

   (c) recycling of 50 % by average weight of other waste batteries and accumulators.

⇒ New revision of this Directive in progress with higher expectations

From: https://eur-lex.europa.eu/legal-content/FR/ALL/?uri=CELEX%3A32018R2066

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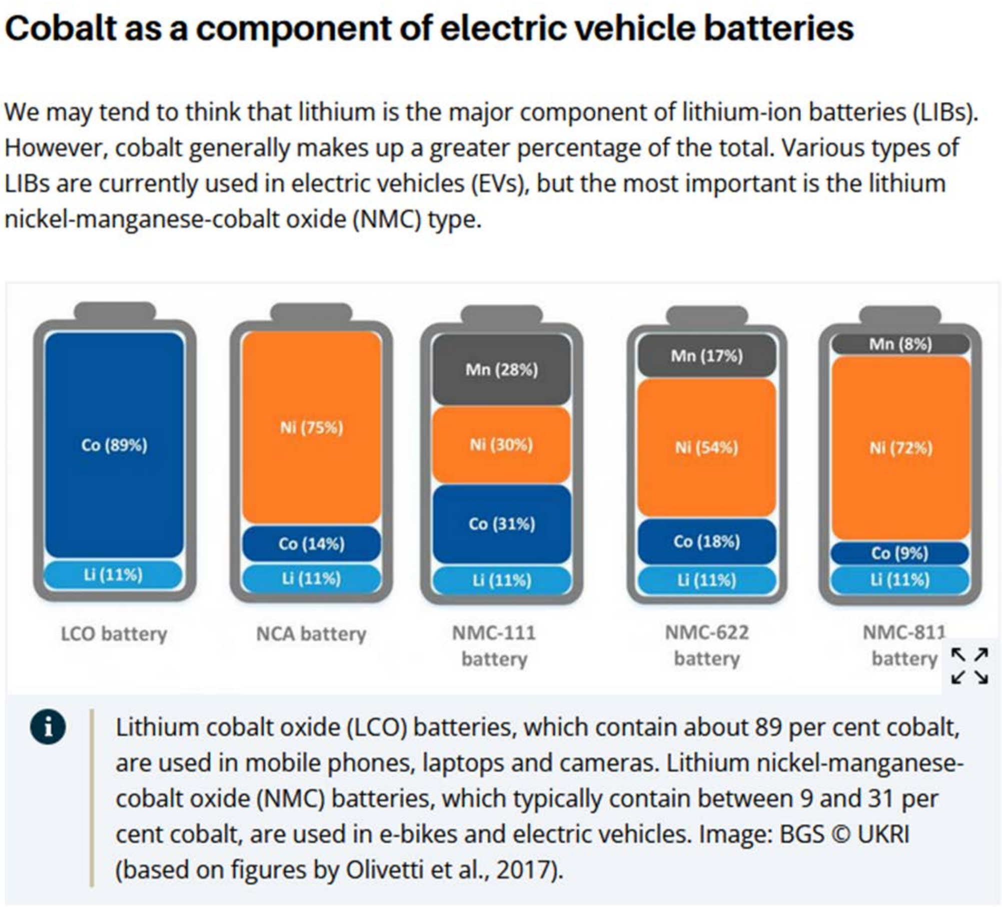
⇒ Une chimie alternative aux composés inorganiques

… *promoting organic batteries?*

Can be seen as a possible alternative to stabilize the pressure on redox-active metals vs. global demand



Cobalt as a component of electric vehicle batteries

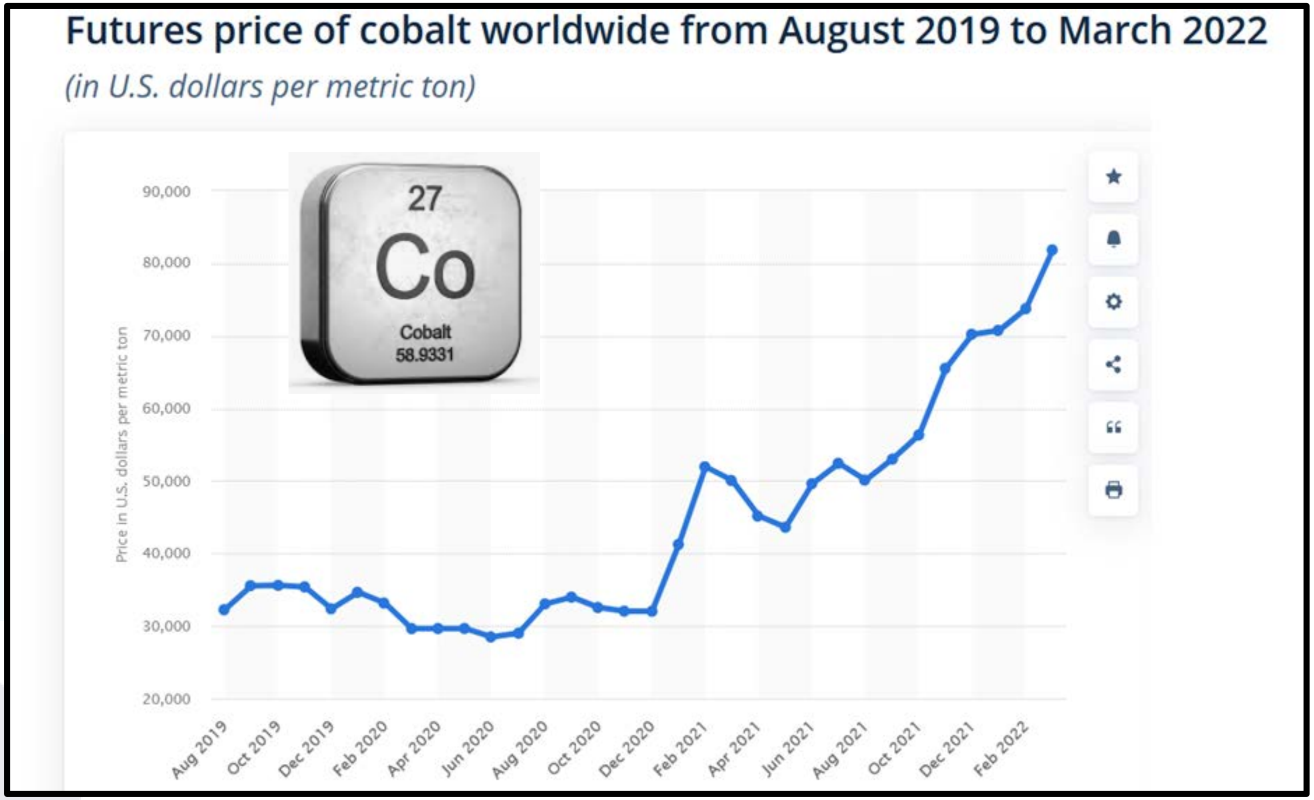
We may tend to think that lithium is the major component of lithium-ion batteries (LIBs). However, cobalt generally makes up a greater percentage of the total. Various types of LIBs are currently used in electric vehicles (EVs), but the most important is the lithium nickel-manganese-cobalt oxide (NMC) type.

Lithium cobalt oxide (LCO) batteries, which contain about 89 per cent cobalt, are used in mobile phones, laptops and cameras. Lithium nickel-manganese-cobalt oxide (NMC) batteries, which typically contain between 9 and 31 per cent cobalt, are used in e-bikes and electric vehicles. Image: BGS © UKRI (based on figures by Olivetti et al., 2017).

From: https://www.bgs.ac.uk/news/cobalt-resources-in-europe-and-the-potential-for-new-discoveries/

… *promoting organic batteries?*

Can be seen as a possible alternative to <u>stabilize</u> the pressure on redox-active metals vs. global demand



Futures price of cobalt worldwide from August 2019 to March 2022

(in U.S. dollars per metric ton)

https://www.statista.com/statistics/1171975/global-monthly-price-of-cobalt/, last accessed April 2022

… *promoting organic batteries?*

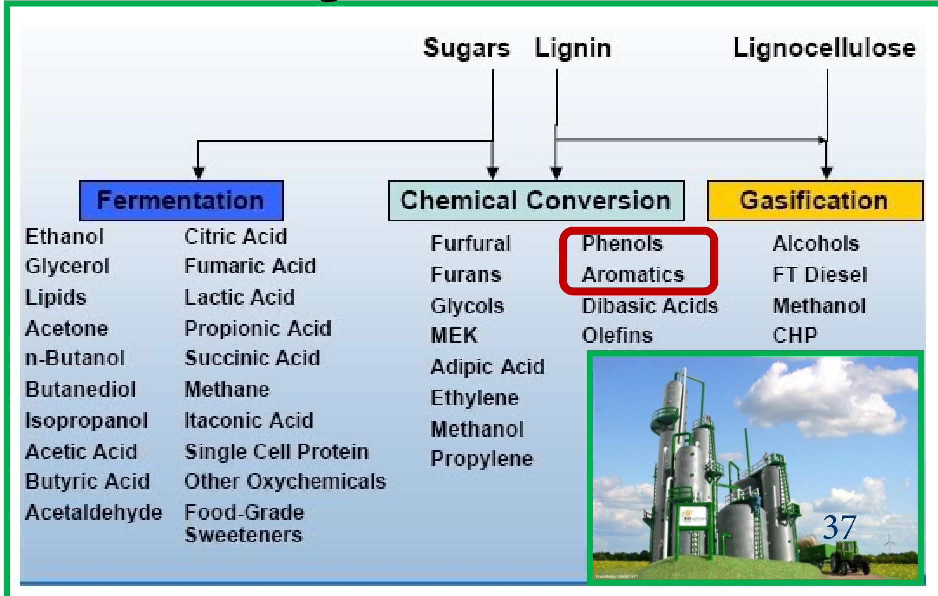
Can be seen as a possible alternative to <u>stabilize</u> the pressure on redox-active metals vs. global demand

Co, Ni, Mn, Fe, Ti, …

More abundant (“cheaper?”) elements

C, O, N, H …

Emergence of Biorefineries



Fermentation

- Ethanol
- Glycerol
- Lipids
- Acetone
- n-Butanol
- Butanediol
- Isopropanol
- Acetic Acid
- Butyric Acid
- Acetaldehyde
- Citric Acid
- Fumaric Acid
- Lactic Acid
- Propionic Acid
- Succinic Acid
- Methane
- Itaconic Acid
- Single Cell Protein
- Other Oxychemicals
- Food-Grade Sweeteners

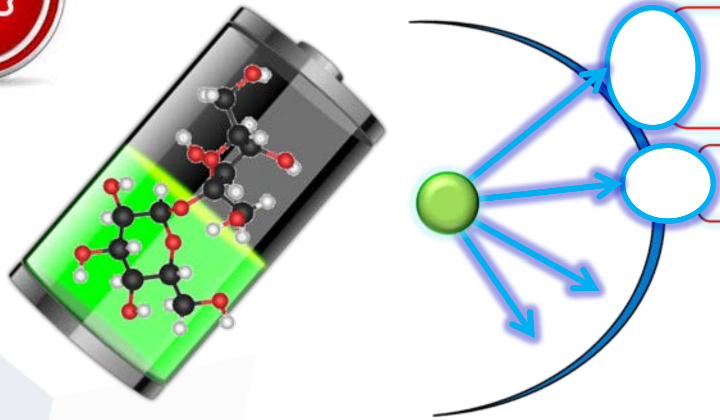
Chemical Conversion

- Furfural
- Furans
- Glycols
- MEK
- Adipic Acid
- Ethylene
- Methanol
- Propylene
- Phenols
- Aromatics
- Dibasic Acids
- Olefins

Gasification

- Alcohols
- FT Diesel
- Methanol
- CHP

Organic electrode materials, CONS



Low thermal stability
(but not systematically)

Lower volumetric energy density

- **Typical volumetric mass density of inorganic host materials:**

$LiCoO_2$: 4.92 g/cm^3
$LiFePO_4$: 3.47 g/cm^3

>

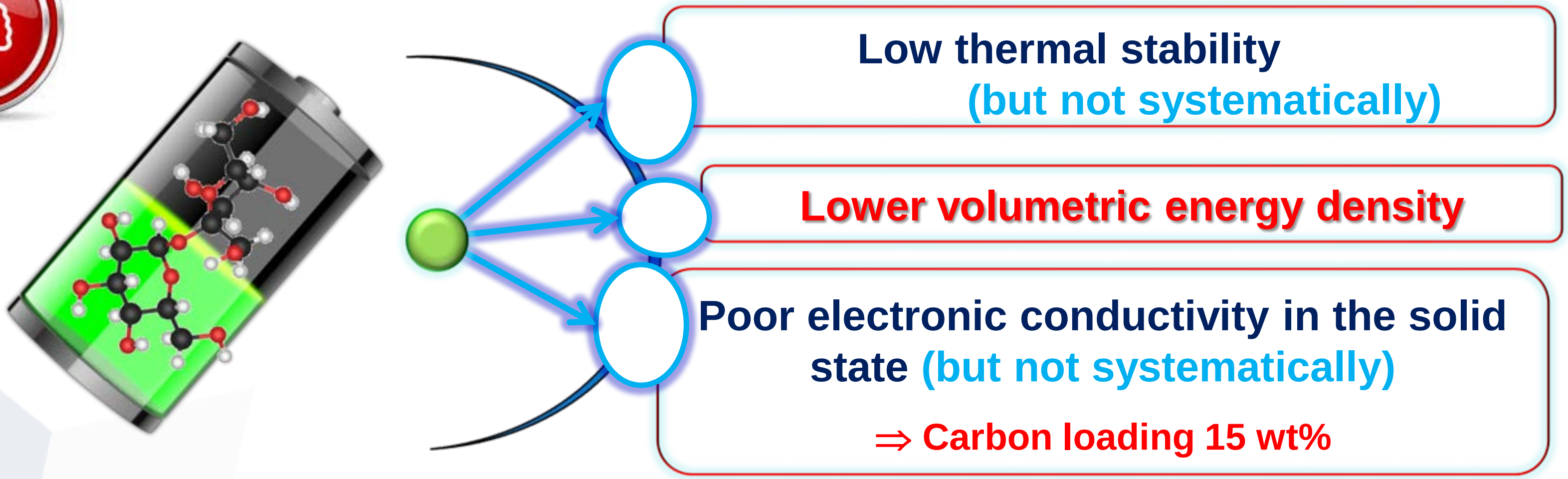
- **Typical volumetric mass density of organique electrode materials:**

1-2 g/cm^3 (only)

**Dense crystal packing
(iono-covalent bonding)
1 atom = 1 redox center, mostly**

**Less dense crystal packing
(van der Walls bonding)
several atoms = 1 redox center, mostly**

Organic electrode materials, CONS



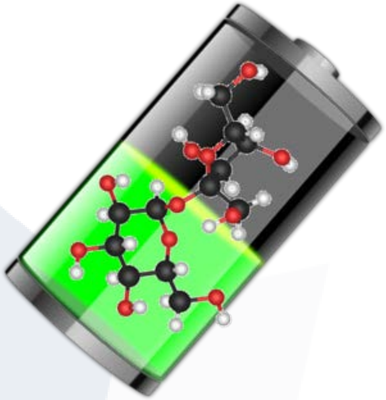
Low thermal stability
(but not systematically)

Lower volumetric energy density

Poor electronic conductivity in the solid state (but not systematically)

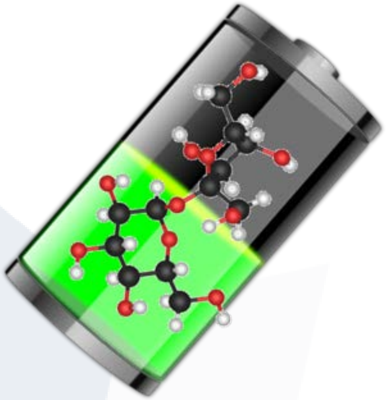
⇒ **Carbon loading 15 wt%**

Organic electrode materials, PROS



- **More abundant elements (C, H, O, N, S in particular)**
  Potentially generated from renewable resources (biomass)
- **Low Temperature synthesis (generally)**
- **Numerous chemical combinations**
- **Multi-electron reaction materials**
- **Ease of recycling (e.g. combustion)**

Organic electrode materials, PROS



More abundant elements (C, H, O, N, S in particular)

Potentially generated from renewable resources (biomass)

Low Temperature synthesis (generally)

Numerous chemical combinations

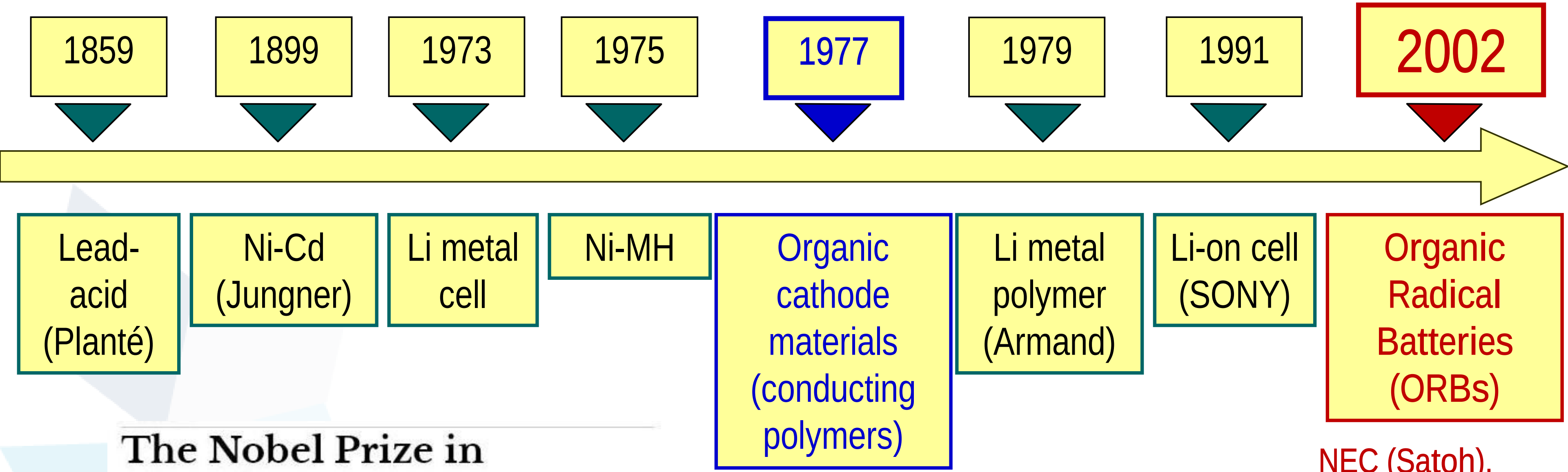
Multi-electron reaction materials

Ease of recycling (e.g. combustion)

DIFFERENT CELL CONFIGURATIONS:

Li-ion, Na-ion, Dual-ion cell,… in Aqueous or Non-aqueous electrolyte with <u>soluble redox species</u> (RFB) or <u>solid electrode materials</u>

… *promoting organic batteries?*



1859 – Lead-acid (Planté)

1899 – Ni-Cd (Jungner)

1973 – Li metal cell

1975 – Ni-MH

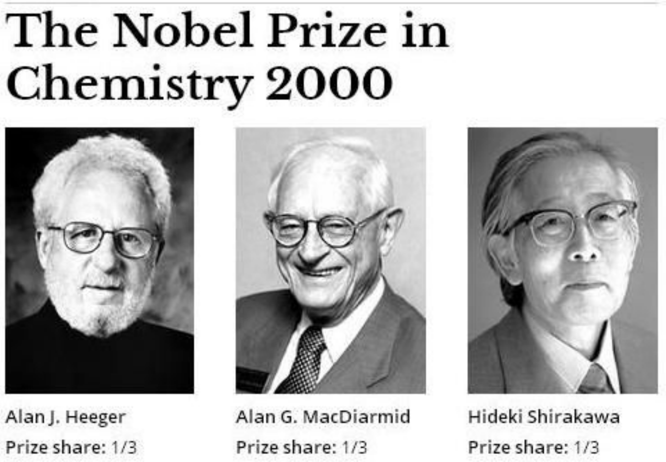
1977 – Organic cathode materials (conducting polymers)

1979 – Li metal polymer (Armand)

1991 – Li-on cell (SONY)

2002 – Organic Radical Batteries (ORBs)

NEC (Satoh), Nishide’s group

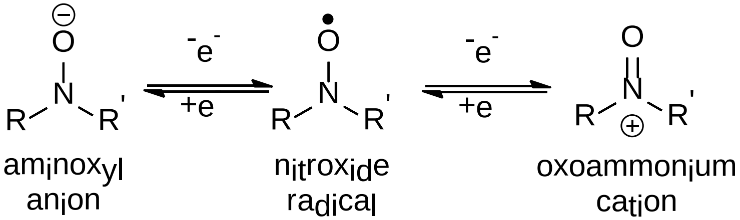


The Nobel Prize in Chemistry 2000

Alan J. Heeger
Prize share: 1/3

Alan G. MacDiarmid
Prize share: 1/3

Hideki Shirakawa
Prize share: 1/3



1977

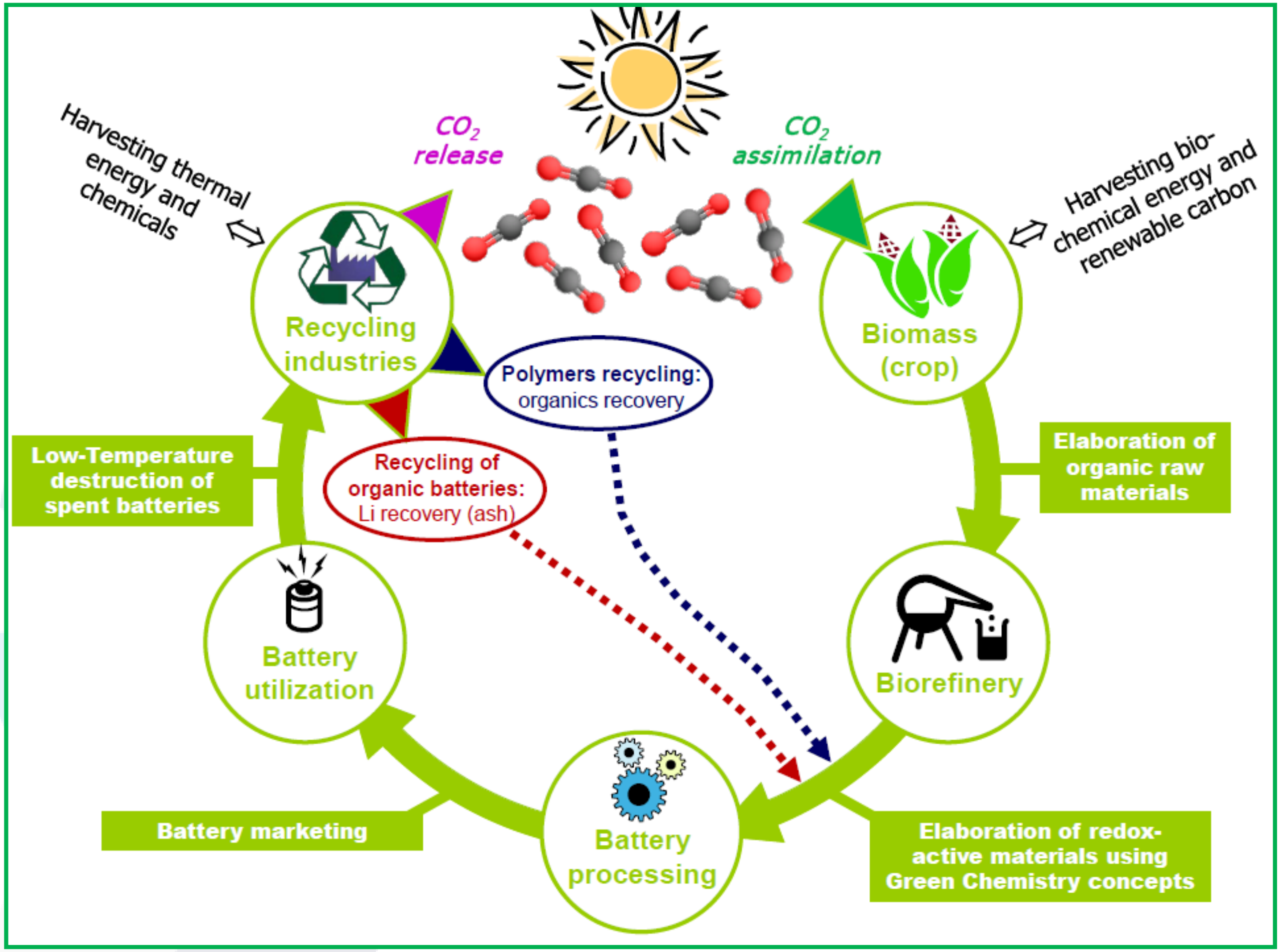
1979

1991

2002

2008

“Renewable” Li-ion Organic Batteries



Virtuous circle

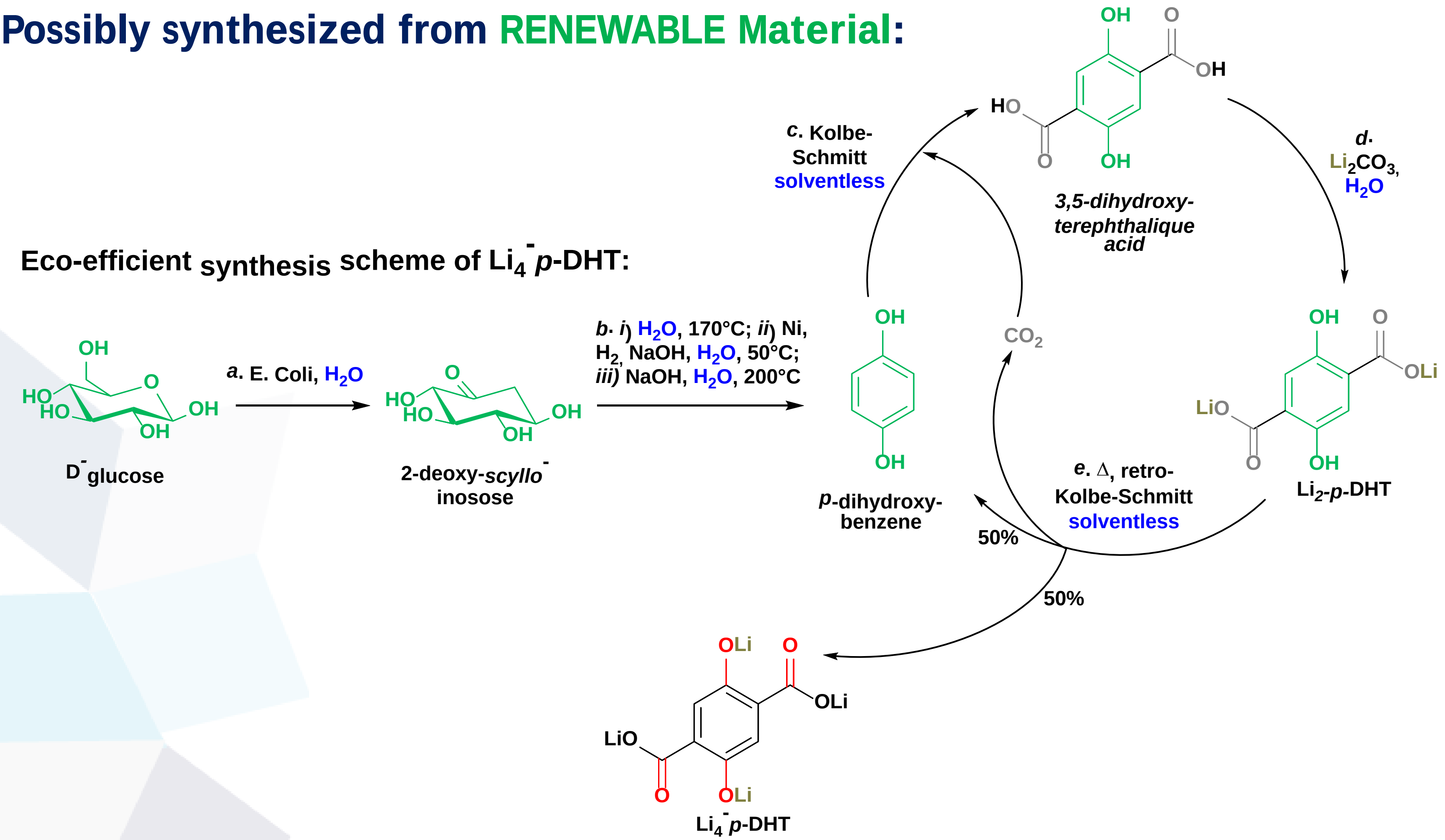
ChemSusChem, 2008
Energy Environ. Sci., 2011

n-type Li cathode: case of Li$_4$-p-DHT

Dilithium (2,5-dilithium-oxy)-terephthalate

⇒ **Possibly synthesized from RENEWABLE Material:**

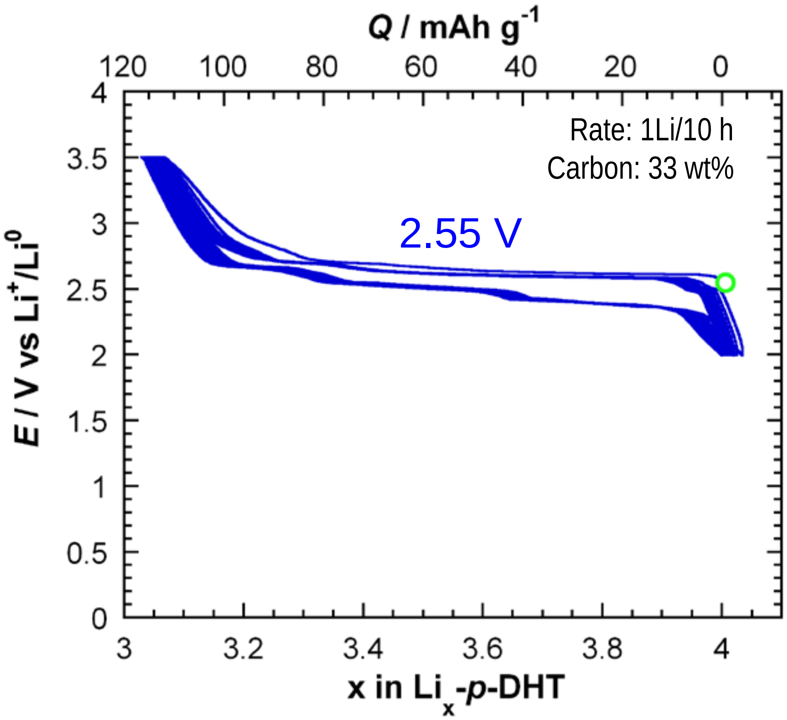
Eco-efficient synthesis scheme of Li$_4$-*p*-DHT:

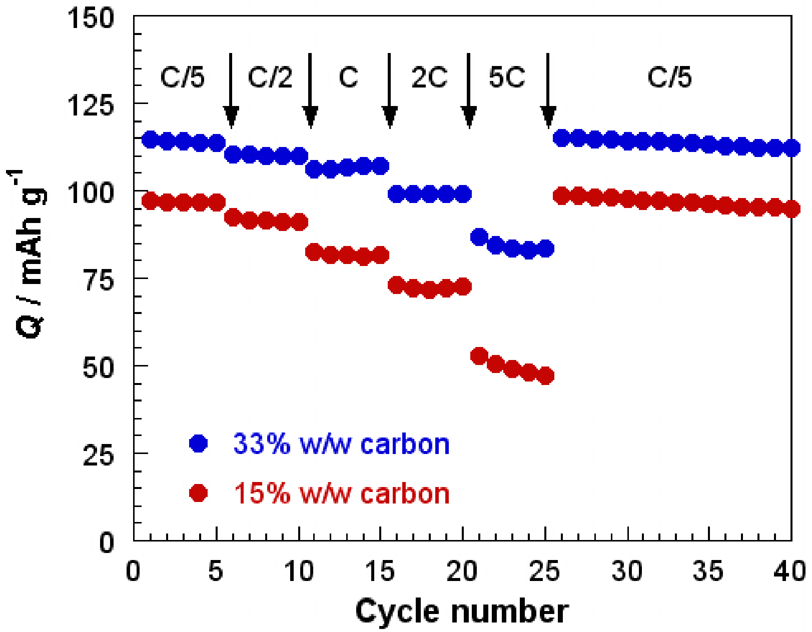


❑ *Energy Environ. Sci.*, **6**, 2124 (2013).

n-type Li cathode: case of Li_4-p-DHT

Dilithium (2,5-dilithium-oxy)-terephthalate



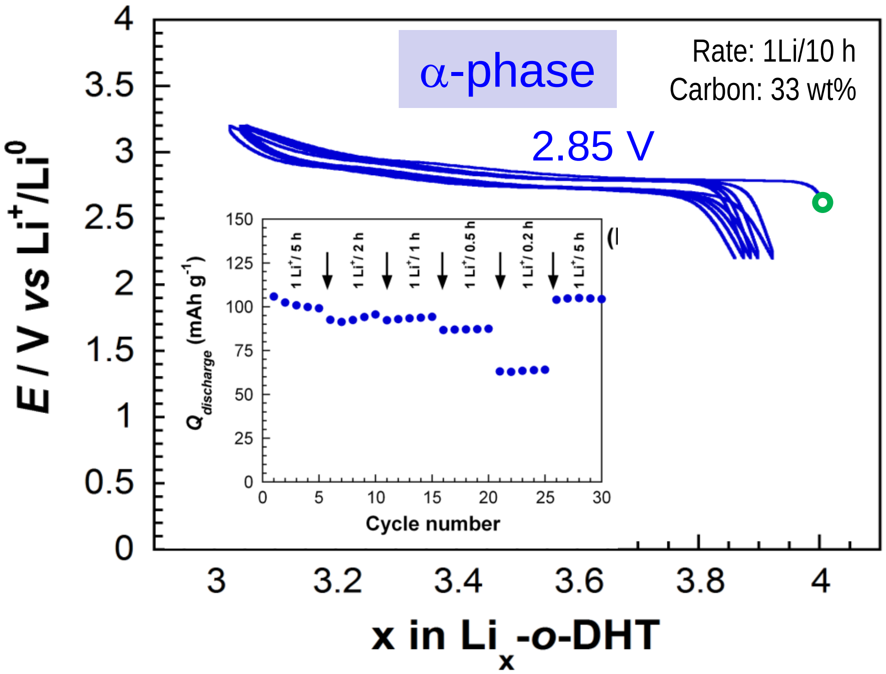


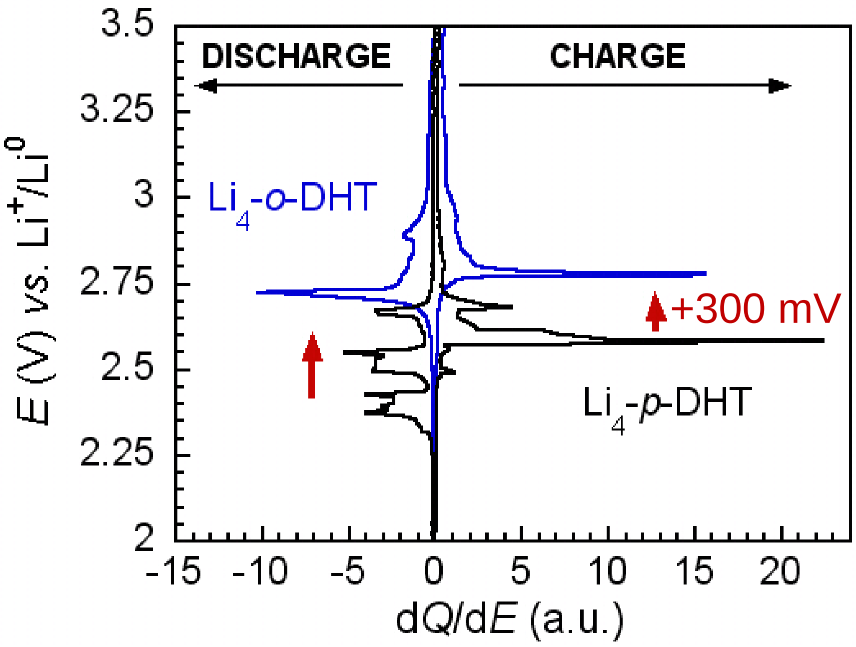
- Good electrochemical performance upon cycling including at high rate with no optimization (no binder, no complex formulation)

☐ *Energy Environ. Sci.*, **6**, 2124 (2013).

n-type Li cathode: case of Li_4-o-DHT

Dilithium (2,3-dilithium-oxy)-terephthalate

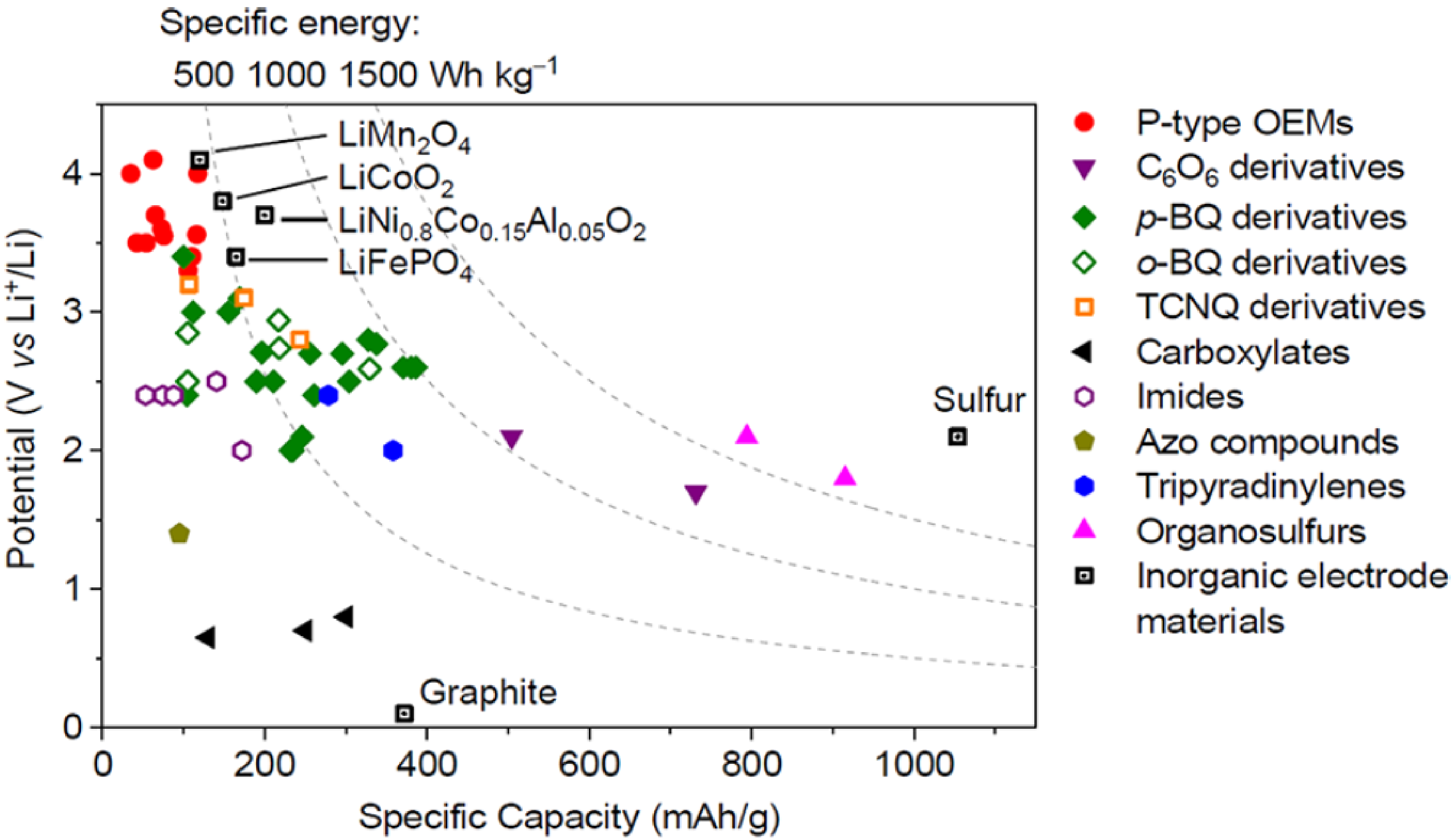




→ Voltage gain at least of + 300 mV

- ❑ *ACS Appl. Mater. Interfaces*, **6**, 10870 (2014).

Comparison with the state-of-the-art Organic vs Inorganic electrode materials for Li batteries



❑ *Chem. Rev.*, **120**, 6490−6557 (2020)

Summary

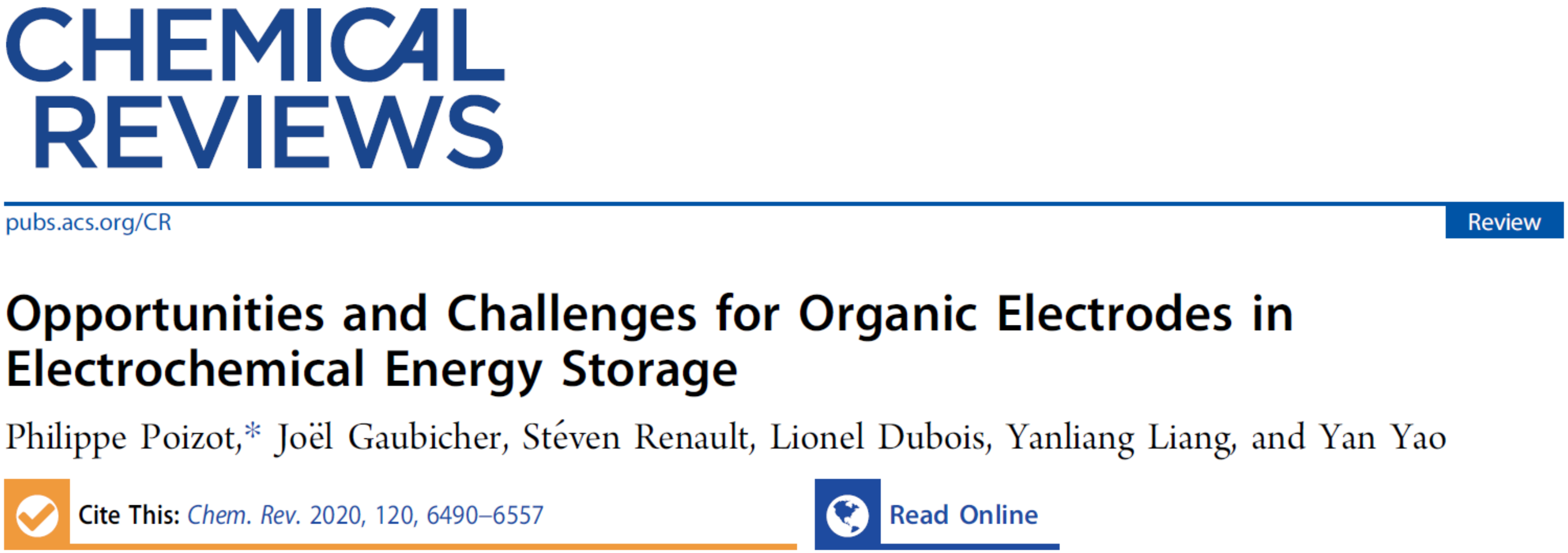
Organic materials can be considered as an alternative chemistry vs metals and other inorganic compounds

⇒ Richness of Organic structures and beyond!

Developing anion-ion batteries (potentially free of metals = molecular batteries) is possible

⇒ Proof of concept for an anion-ion battery made of crystalized organic materials

This research field is still in its infancy, and in terms of electrochemical performance, we cannot compete with regular Li-ion cells
PERFORMANCE vs ABUNDANCE?



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Review

Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage

Philippe Poizot,* Joël Gaubicher, Stéven Renault, Lionel Dubois, Yanliang Liang, and Yan Yao

Cite This: *Chem. Rev.* 2020, 120, 6490−6557

Read Online

Thank you for your attention

Selected contributions //
Organic Batteries & Perspective:

- ***Clean energy new deal for a sustainable world: from non-CO$_2$ generating energy sources to greener electrochemical storage devices***, *Energy Environ. Sci.*, **4**, 2003 (2011)
- ***Progress in all-organic rechargeable batteries using cationic and anionic configurations: Toward low-cost and greener storage solutions?***, *Curr. Op. in Electrochem.*, **9**, 70 (2018)
- ***Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage***, *Chem. Rev.*, **120**, 6490−6557 (2020)
- **A perspective on organic electrode materials and technologies for next generation batteries**, *J. Power Sources*, **482**, 228814 (2021).
- **2021 roadmap for sodium-ion batteries**, *J. Phys-Energy*, **3**, 031503 (2021).