Electrochemistry
Energy
Sustainability

Materials for electrochemical energy storage and conversion devices

UNICAM

School of Science and Technology, Chemistry Division

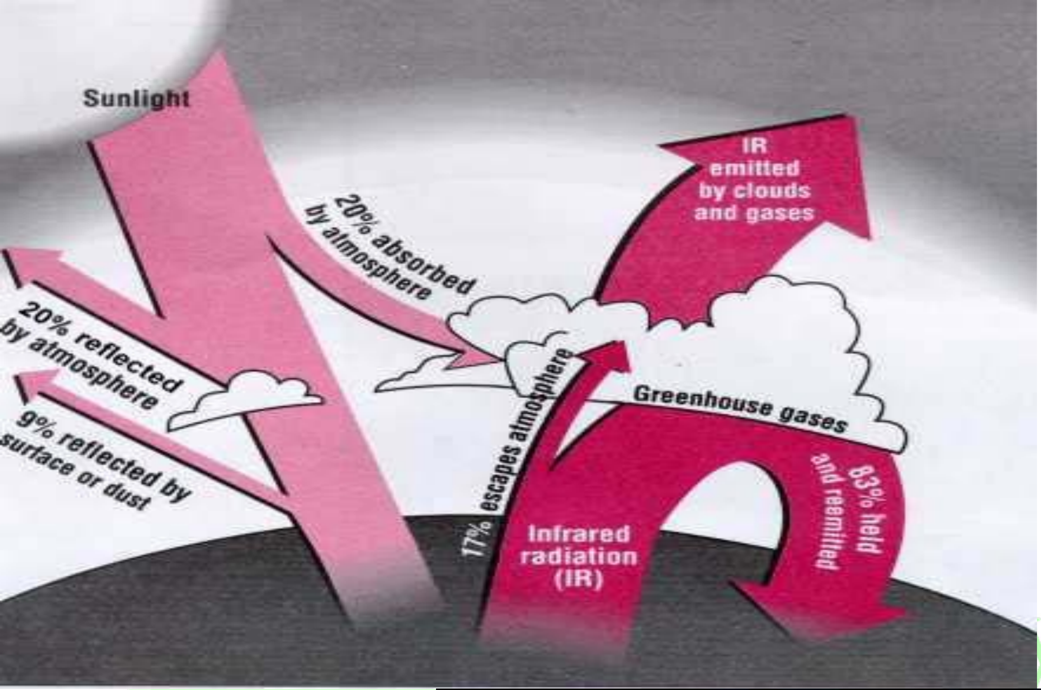
Electrochemistry /Physical Chemistry Lab

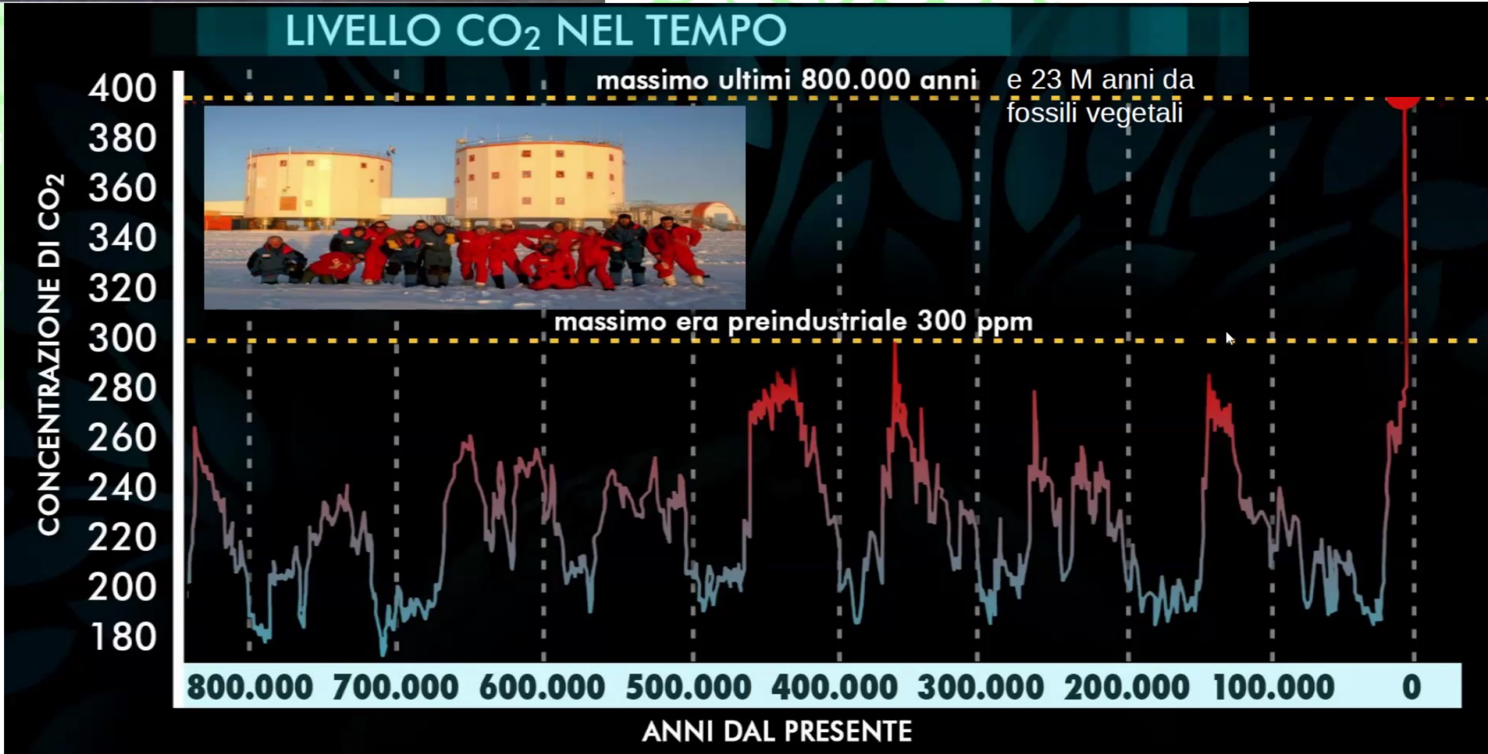
prof. Francesco Nobili and collaborators

francesco.nobili@unicam.it

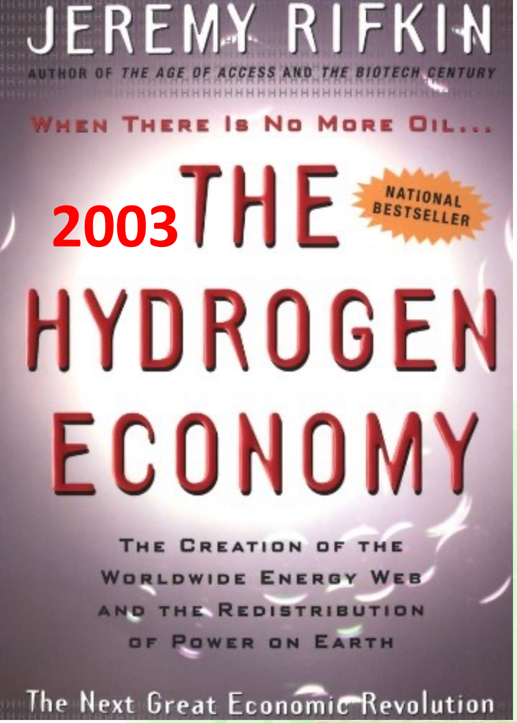
THE FRAMEWORK

First hints at relationship between CO_2 levels and global warming issues
→ Arrhenius 1887





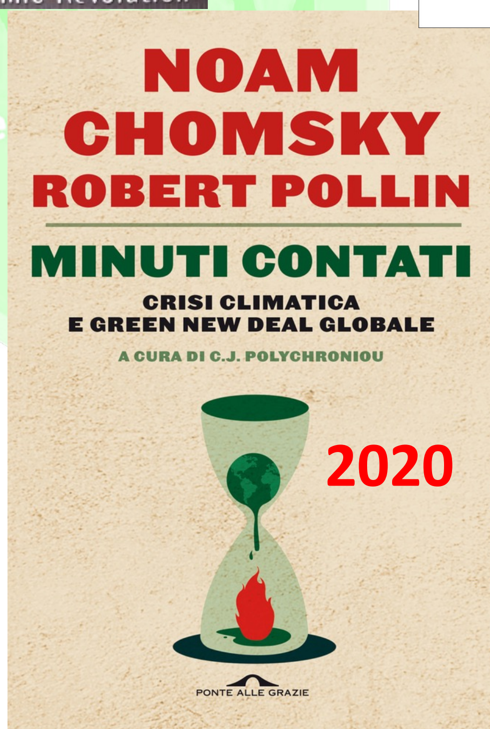
2003



2018

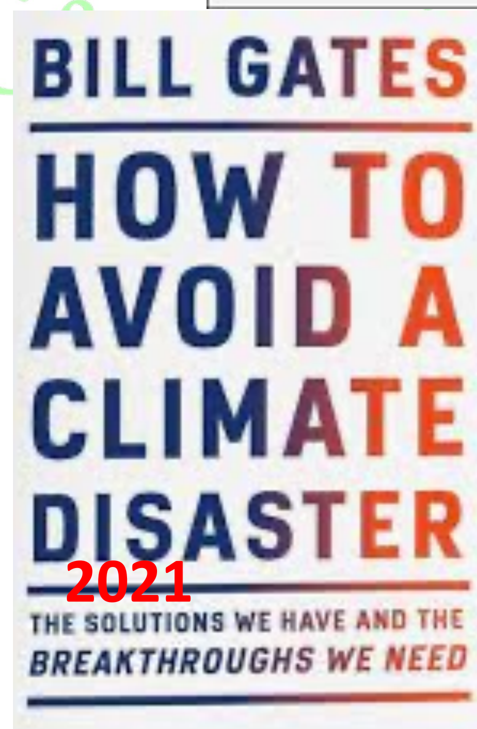
2019

2020



IT'S A HOT TOPIC!

2021



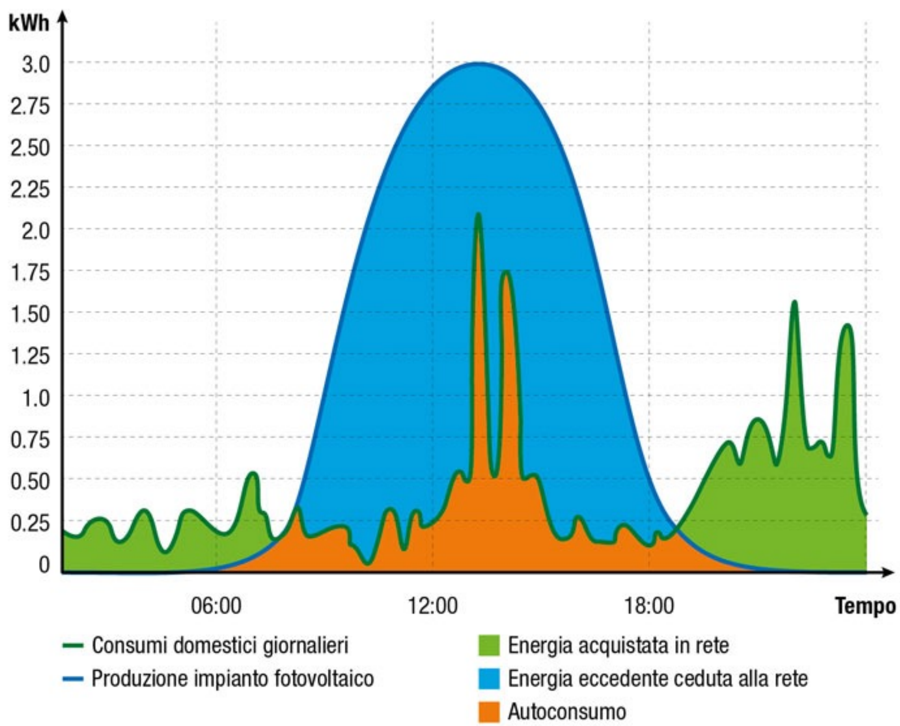
UNICAM
Università di Camerino
1336

SUSTAINABLE DEVELOPMENT GOALS

REVENEWABLE SOURCES AND ENERGY STORAGE

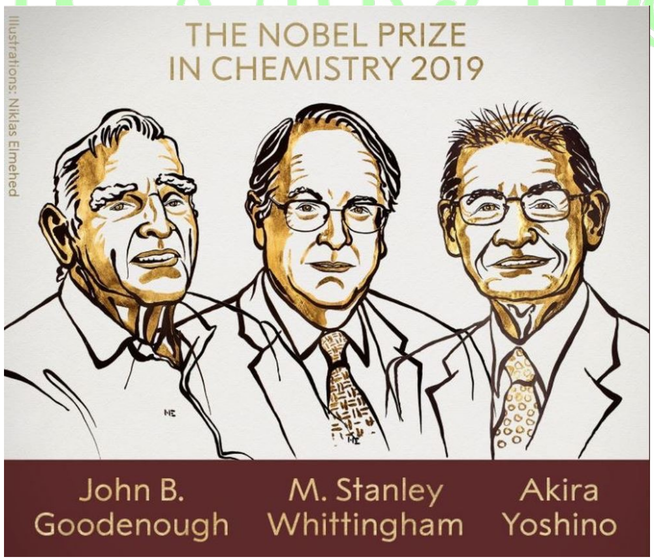
PROBLEM

Production and consumption of RENEWABLE ENERGY are ASYMMETRICAL on daily an seasonal scales



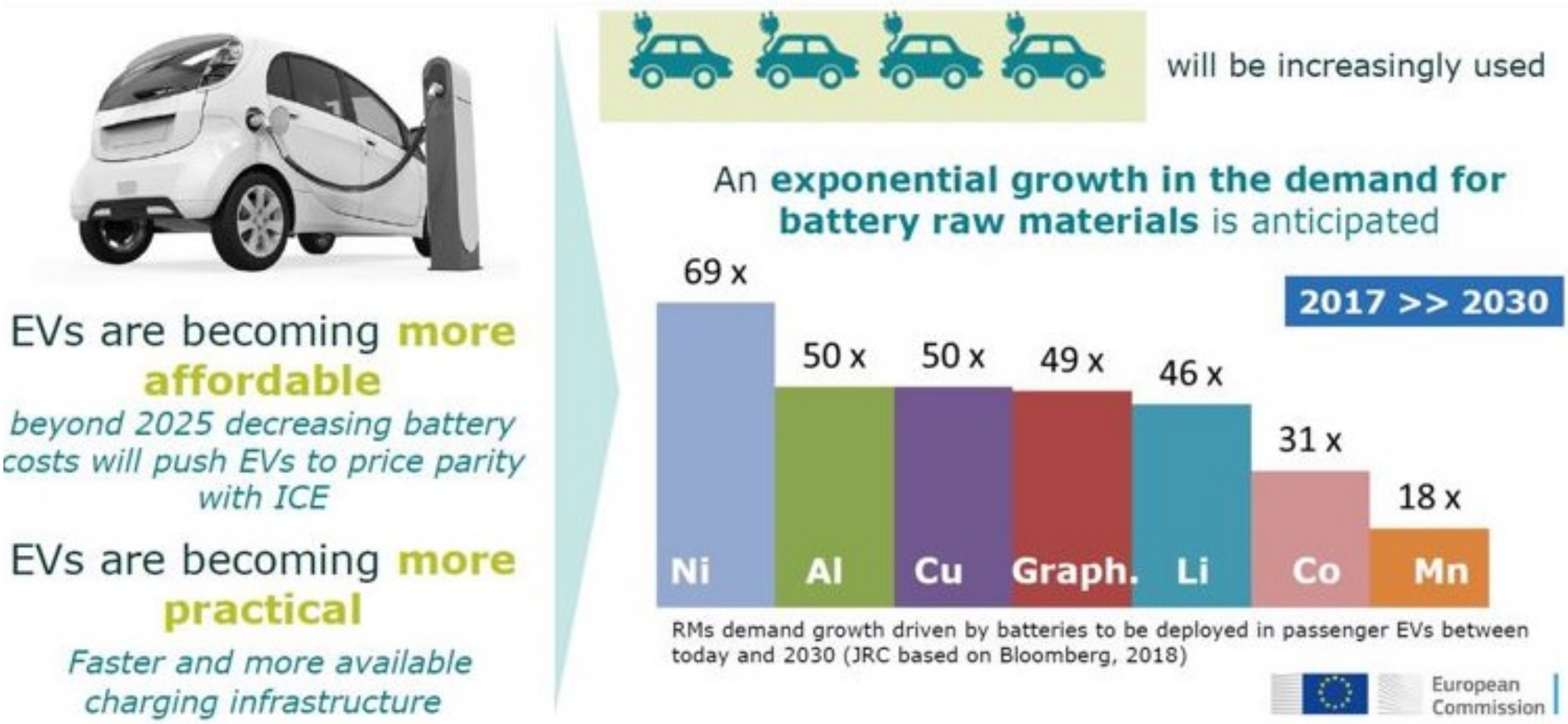
SOLUTION

Use of STORAGE SYSTEMS that store excess energy when generated, and release it when needed

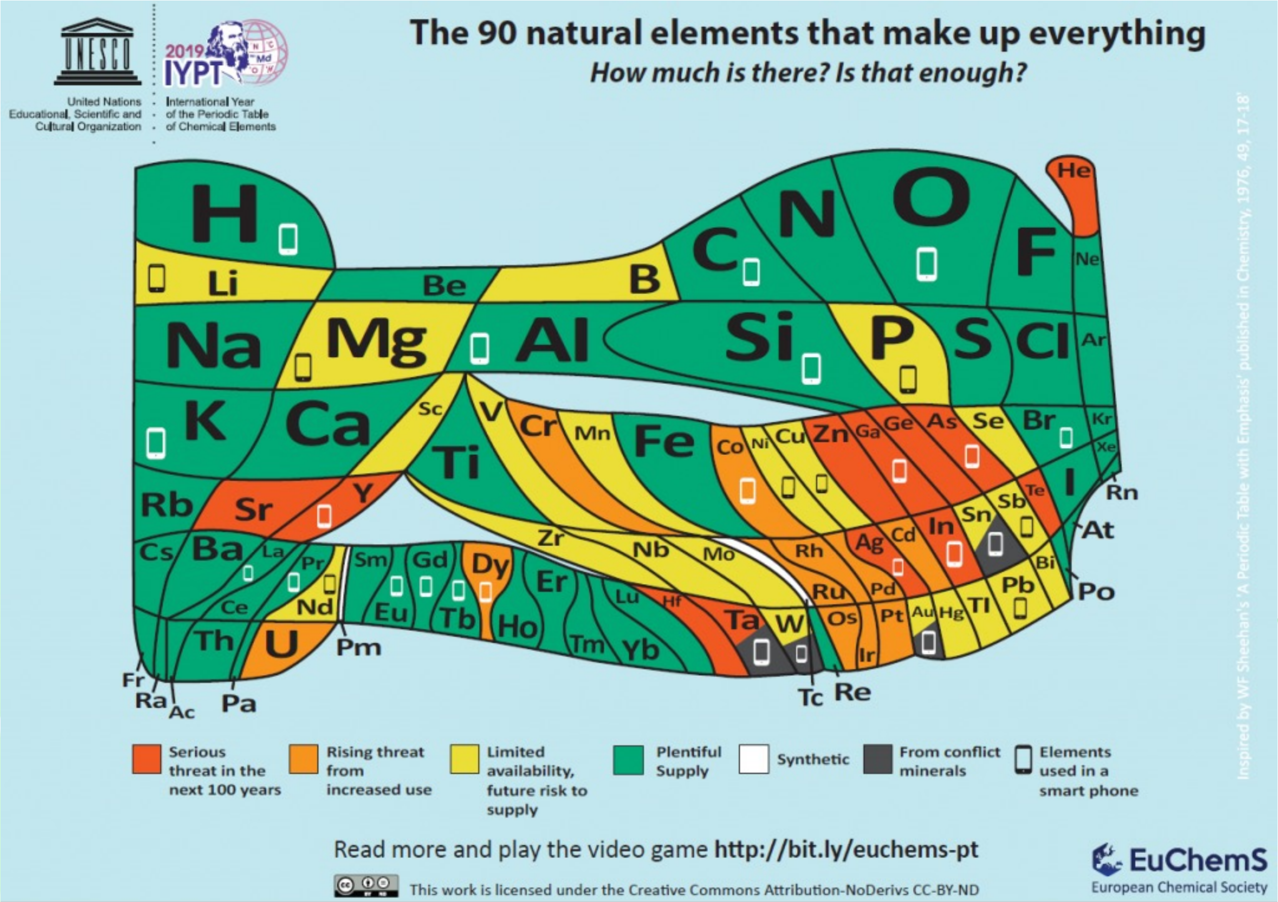


for the discovery of Li-ion batteries!

ARE BATTERIES SUSTAINALBE?
the case-study of ELECTRIFIED VEHICLES



SUSTAINABILITY



- Supply and cost of raw materials
- Energy costs
- Environmental impact
- Safety
- Performances
- Applications

- **SYNTHESIS AND CHARACTERIZATION (SEM, TGA, FTIR, Raman) of functional materials for electrochemical energy STORAGE AND CONVERSION: LIBs, NIBs, PEMFCs, SOFCs**

- **Sustainability** plays a central role
  - **Alternative materials** for HIGHER PERFORMANCES and reducing DEPENDENCY ON RAW MATERIALS
  - **Hard carbons** da economia circolare
  - **GREEN electrode formulations** (solvente/binder alternative combinations)
  - **Reuse/recycle /upcycle** strategies

- **Electrochemical characterizations**
  - **Redox processes**
  - **Charge/discharge performances**
  - **Interfacial phenomena**

Reduction of Co content in LIB cathodes

$LiCoO_2$

NMC 333
(30% Co)

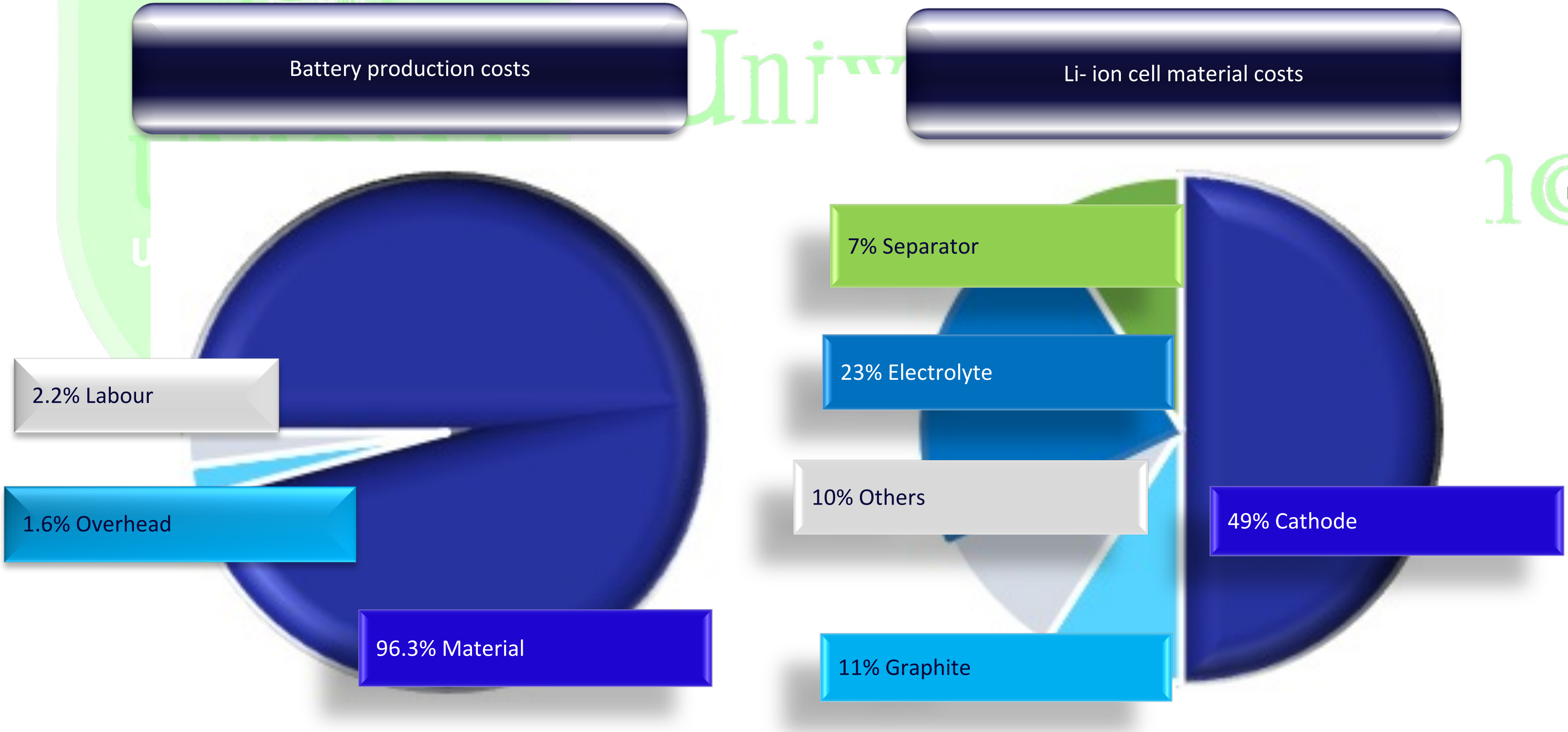
NMC 811
(10% Co)

LNMO
(Co free)

less Co also means higher redox potential → higher cell voltage

Why cathode materials?

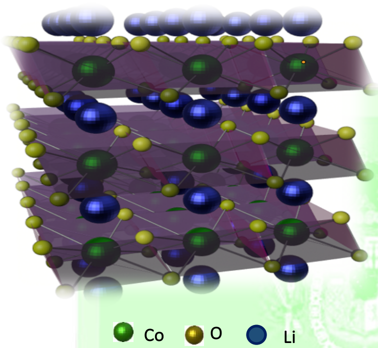
Why the right choice of cathode materials has significant attention?



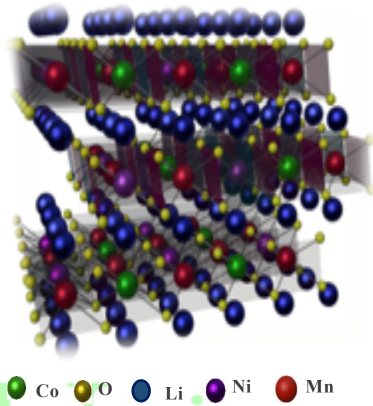
NMC(333) → 33% Co → Nowadays are used in the market

$LiNi_xMn_yCo_zO_2$ (NMC)

$LiCoO_2$

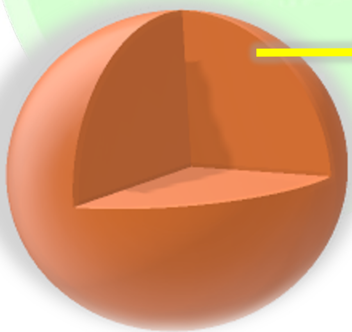


Replace partially with Mn & Ni

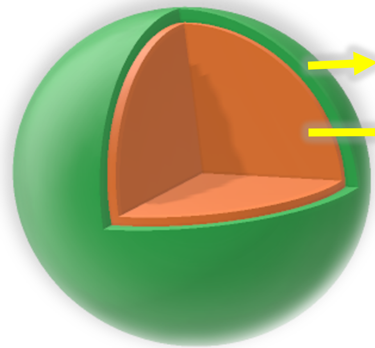


- The cost of cobalt
- The toxicity of the material

NMC(811) → 10% Co → Are considered as next generation cathodes

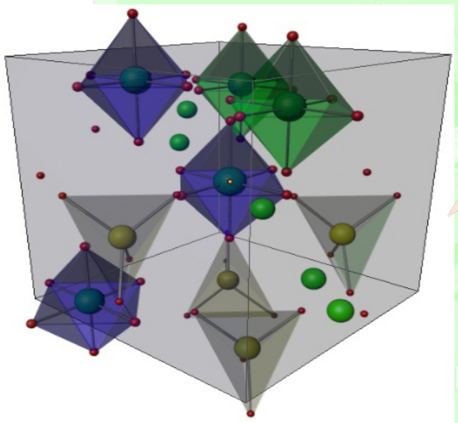


Modification



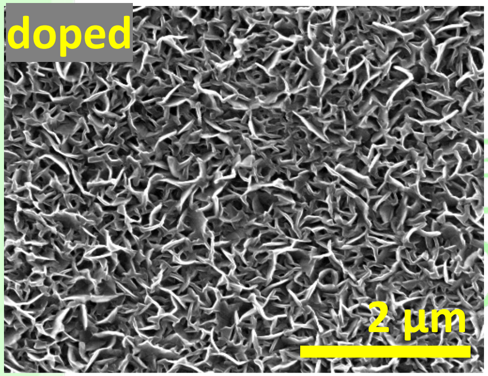
- ❑ Improving the chemical stability.
- ❑ Improving the ion and electron transport.
- ❑ Enhancing the thermal stability.

$LiMn_{1.5}Ni_{0.5}O_4$ (Co-free)



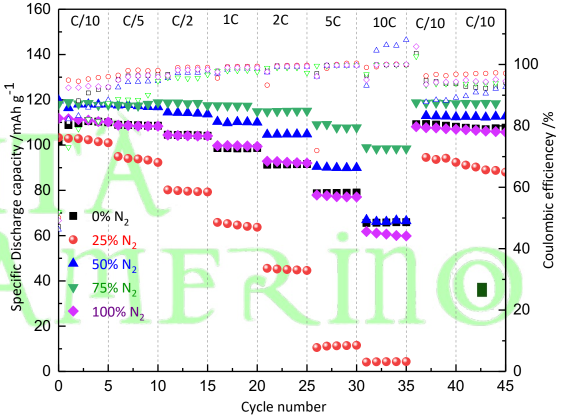
With *Fd3m* space group

Doping



Nano flake

High performance



✓ High voltage (5 V)

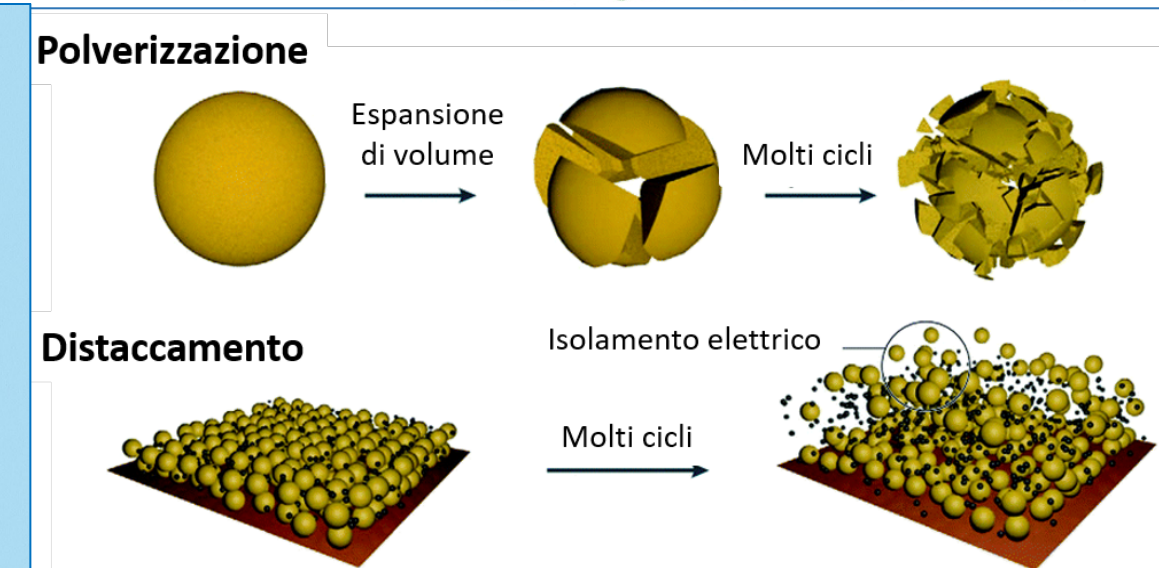
Higher energy densities

Next-generation anodes: Silicon

Advantages:
- 10x capacity with respect to state-of-the-art graphite
- Low cost, high abundance, envinronmentally friendly

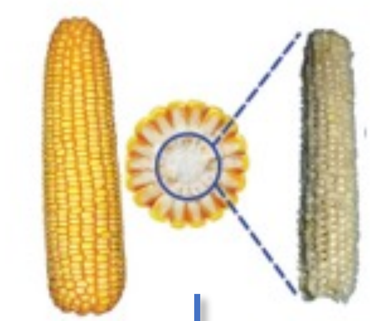
Drawbacks:
- Large volume variations and mechanical unstability
- Performance loss upon cycling

UNICAM
Università di Camerino



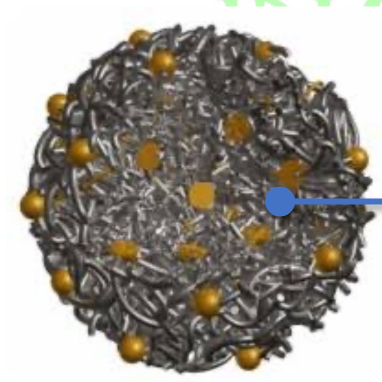
Next-generation anodes: Silicon

Si/C composite anodes



- Food-waste largely available raw materials
- Facile synthesis with no pre-treatment needed

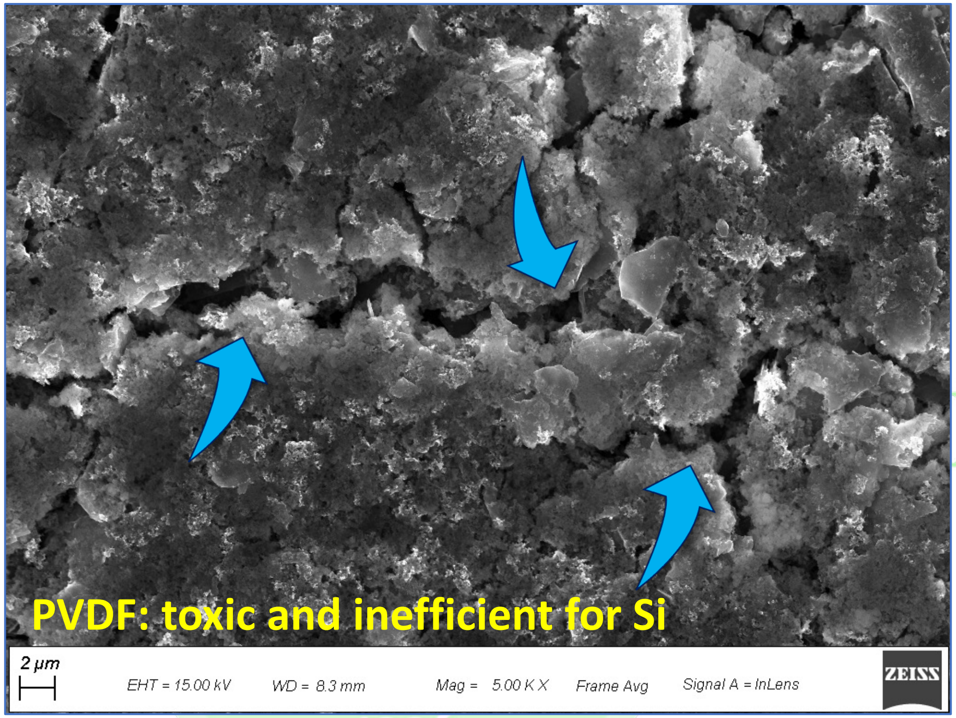
CIRUCULAR ECONOMY

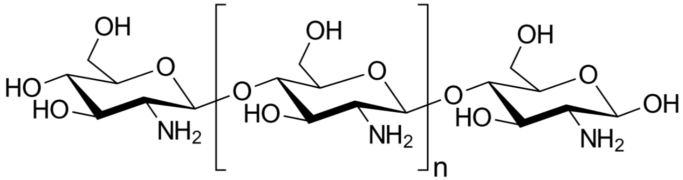


C matrix buffering Si volume changes

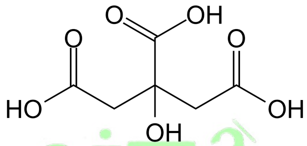
Eco-friendly binders as substitues for PVDF

UNICAM
Università di Camerino
1336

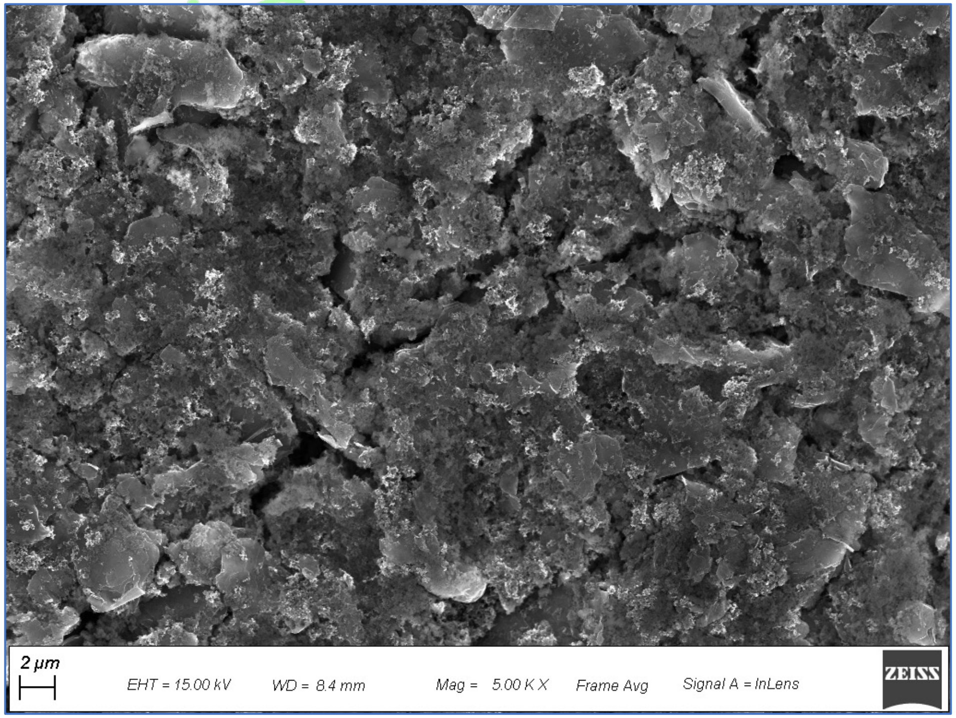


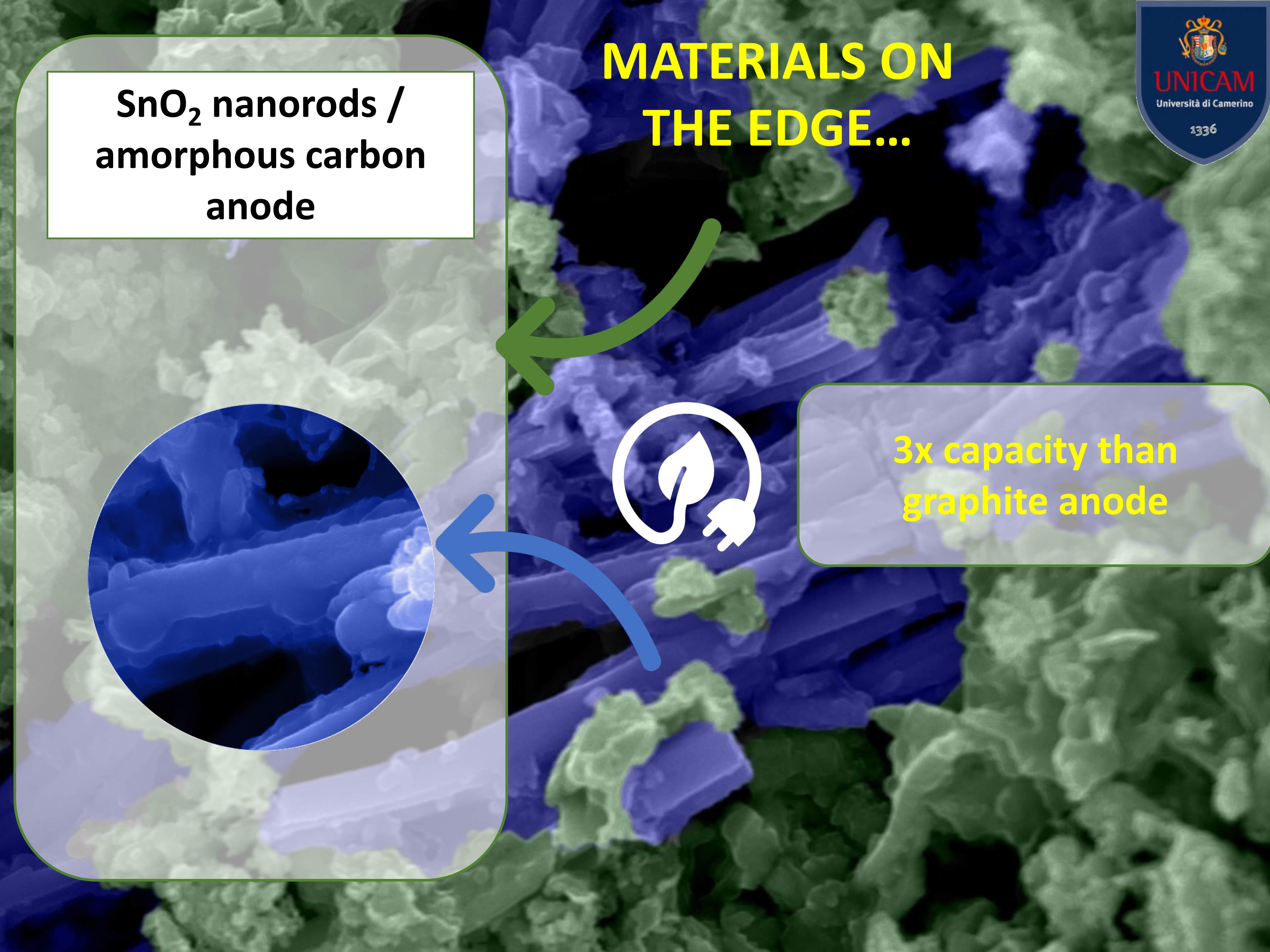


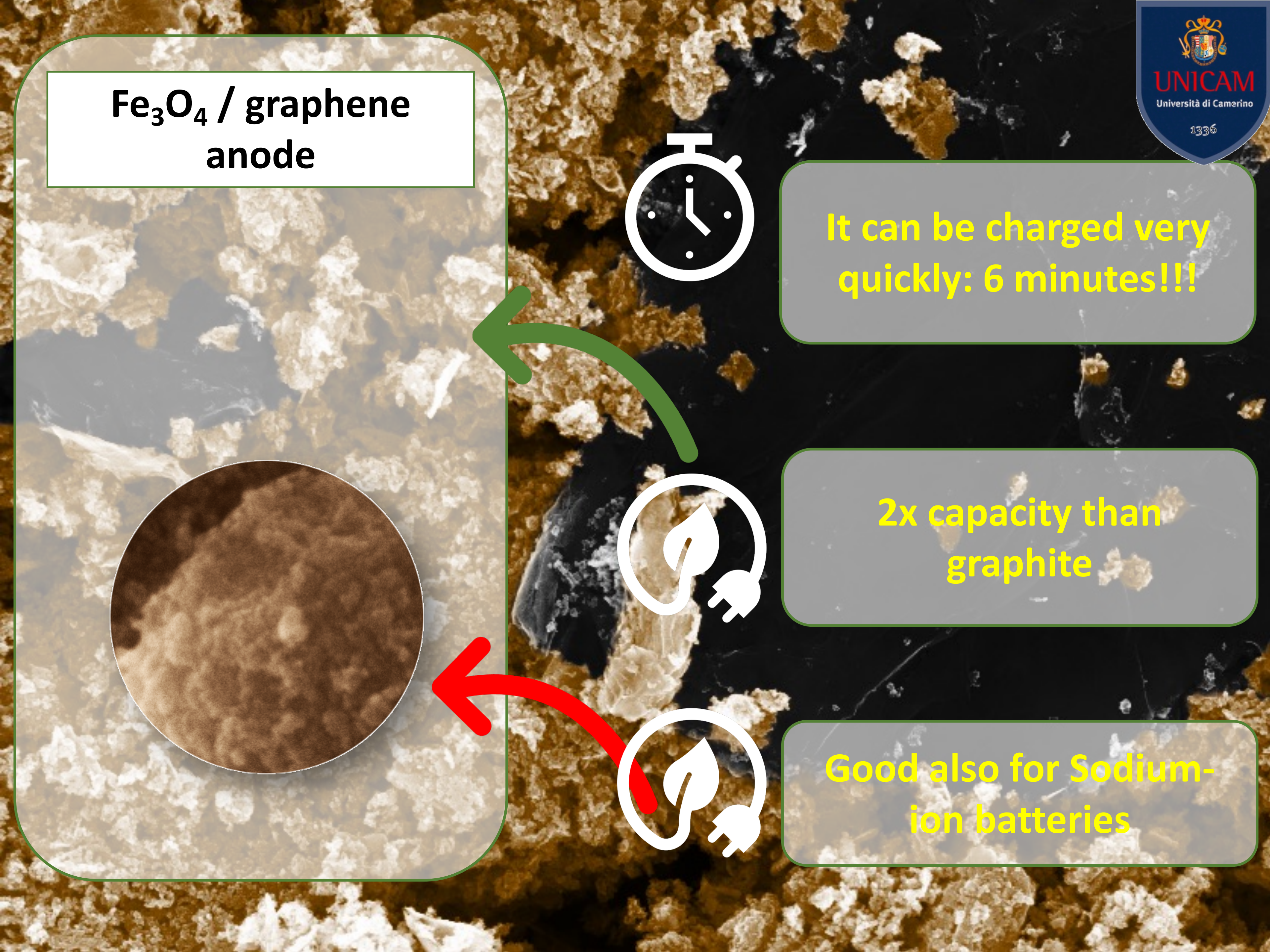
Chitosan



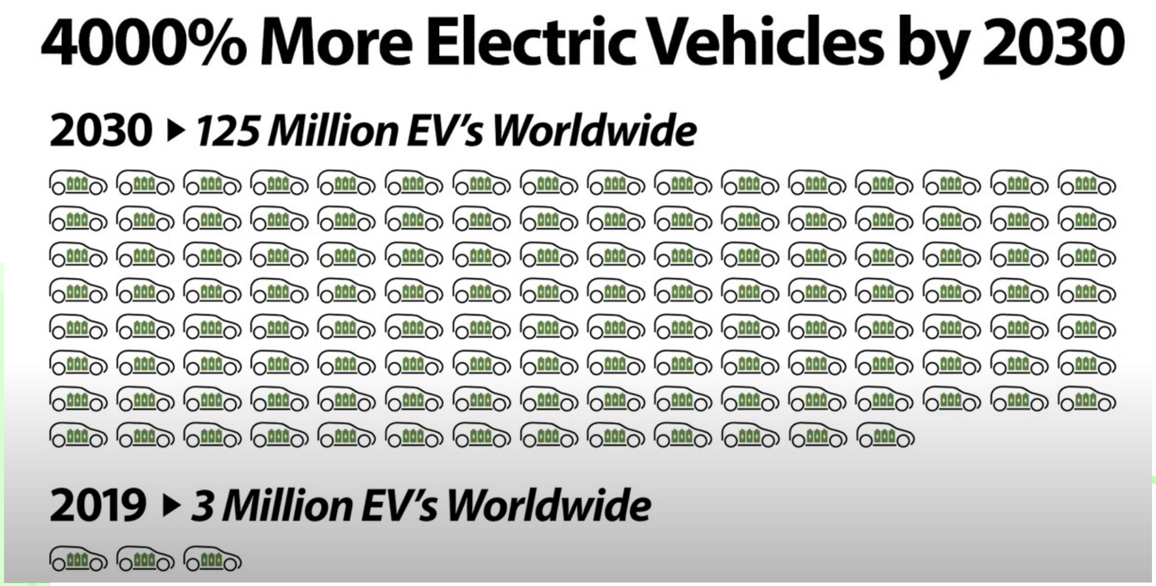
Acido citrico

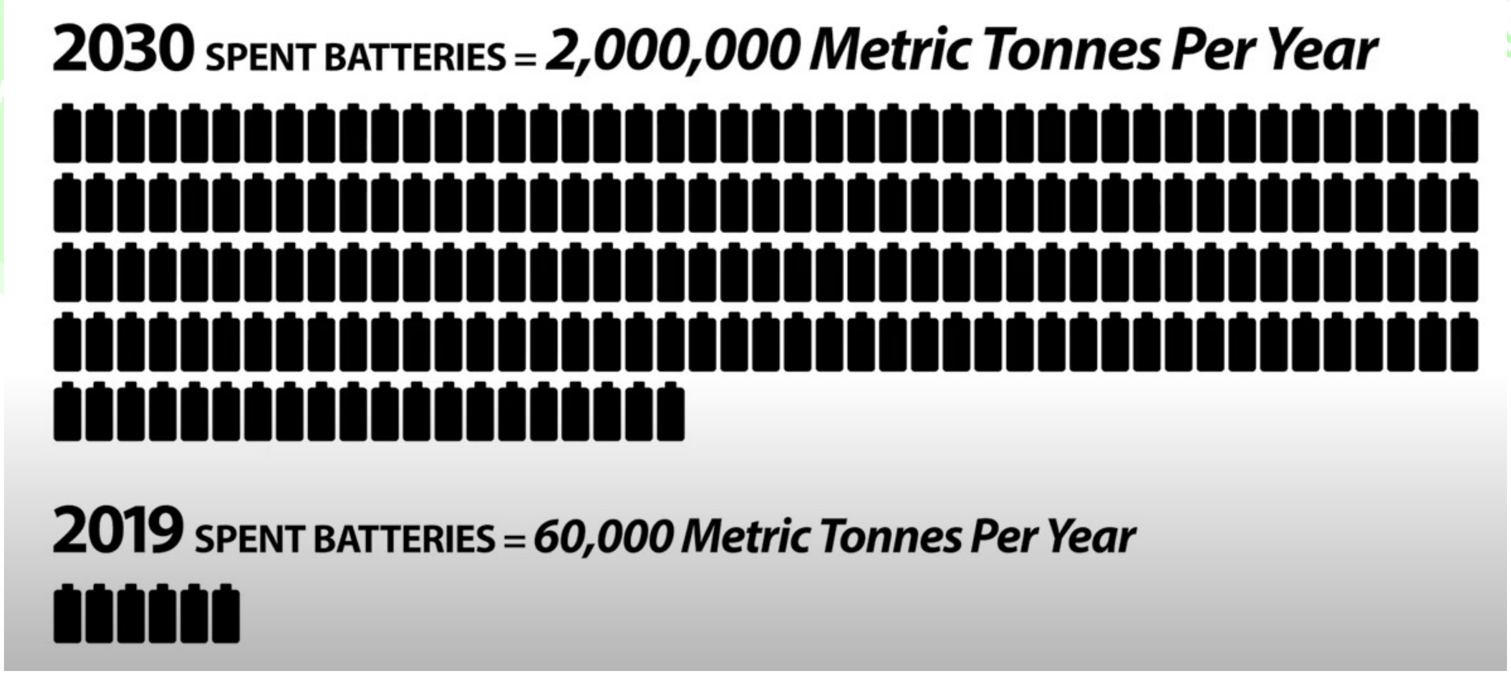



MATERIALS ON THE EDGE…
SnO_2 nanorods / amorphous carbon anode
3x capacity than graphite anode
UNICAM
Università di Camerino
1336

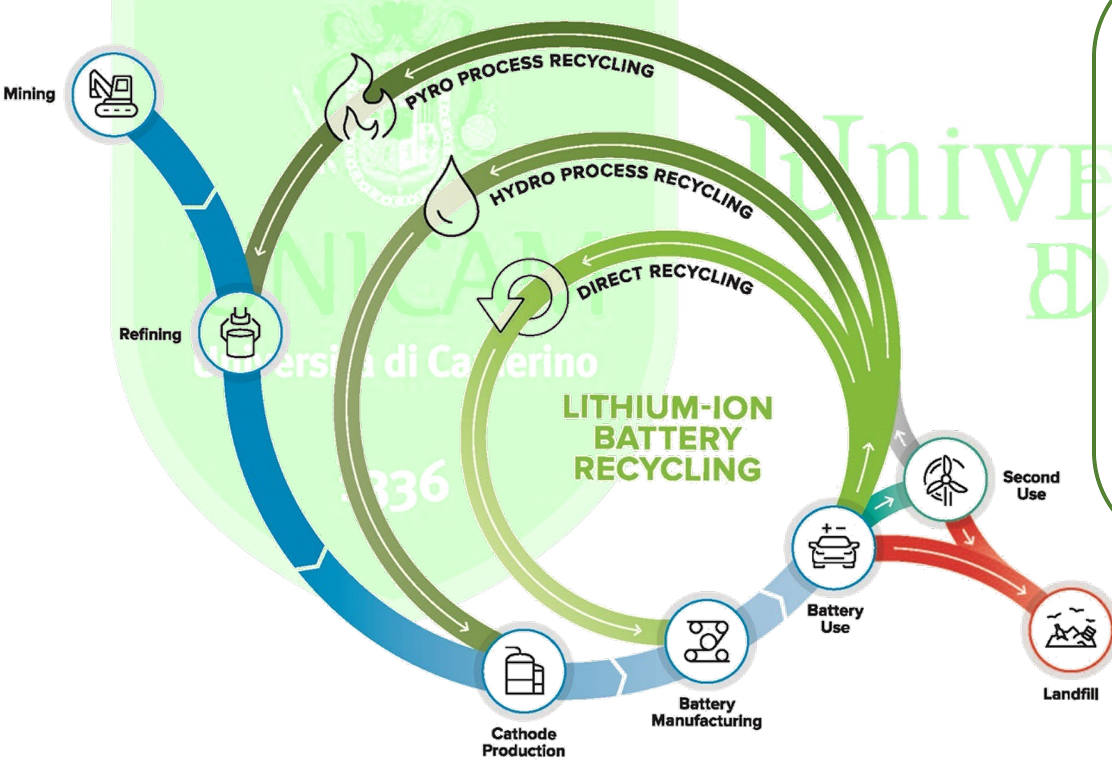

Fe3O4 / graphene anode
It can be charged very quickly: 6 minutes!!!
2x capacity than graphite
Good also for Sodium-ion batteries
UNICAM
Università di Camerino
1336

Recycling and upcycling of Li-ion batteries





Upcycling of Li-ion batteries



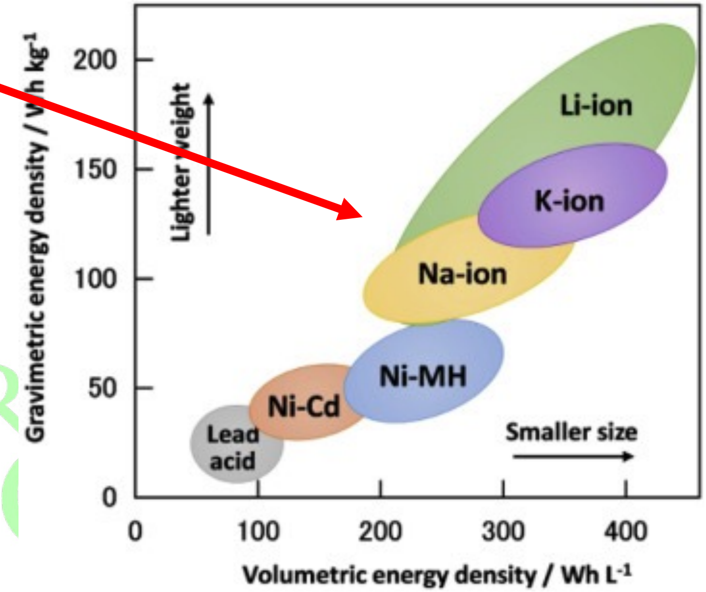
Why **UP**cycling?

- Direct recycling → Shorter cycle
- Recovery of materials with enhanced performances
- Removaol of critical materials (Co, F-based polymers…)

Sodium-Ion Batteries (NIBs)

UNICAM
Università di Camerino
1336

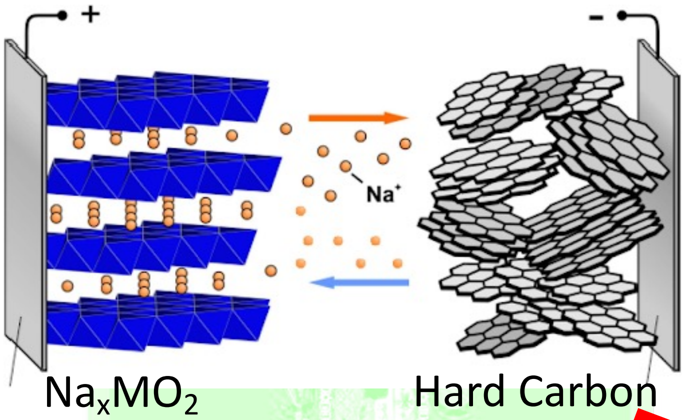
Parameters	Lead Acid Batteries	Lithium-ion Batteries	Sodium-ion Batteries
Cost	Low	High	Low
Energy Density	Low	High	Moderate/High
Safety	Moderate	Low	High
Materials	Toxic	Scarce	Earth-abundant
Cycling Stability	Moderate (high self-discharge)	High (negligible self-discharge)	High (negligible self-discharge)
Efficiency	Low (< 75%)	High (> 90%)	High (> 90%)
Temperature Range	-40 °C to 60 °C	-25 °C to 40 °C	-40 °C to 60 °C
Remarks	Mature technology; fast charging not possible	Transportation restrictions at discharged state	Less mature technology; easy transportation

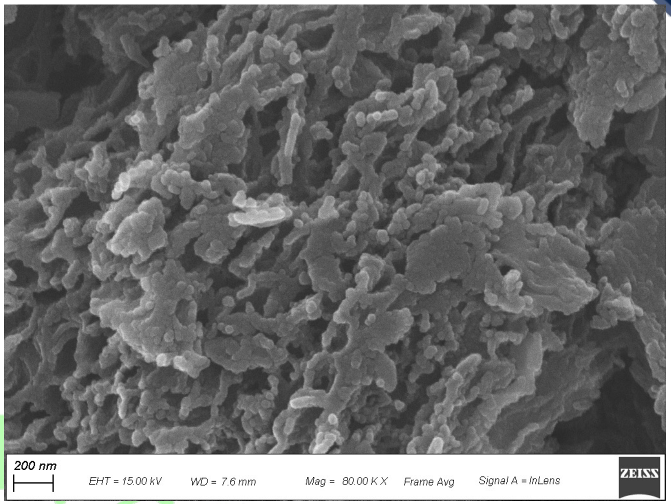


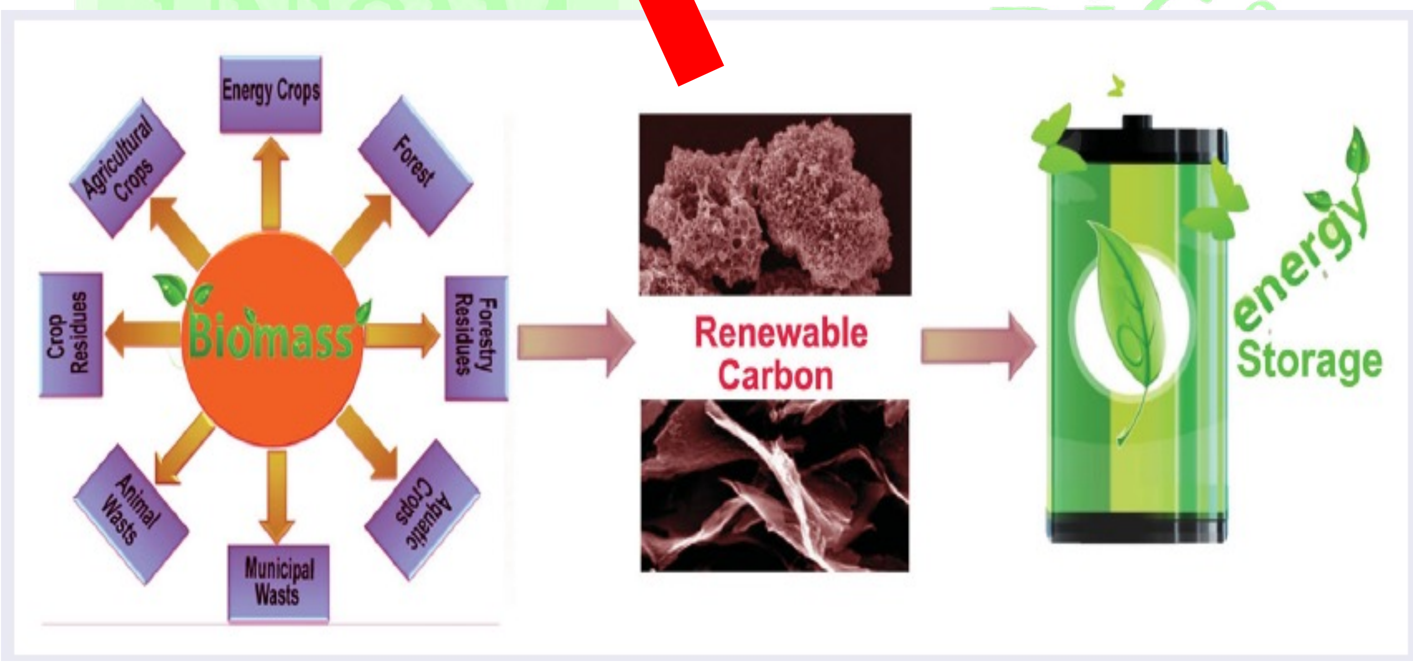
Due to its abundance on Earth's crust and low-cost, Na is an ideal candidate for substituting Li in efficient rechargeable batteries.

BUT… lower performances (Na heavier than Li, higher anode potential)

Hard Carbon anode necessary (graphite not usable)
→ can be prepared from waste biomass (food/forest)







yieLding added valuE to Apennine Forest resources