

Electrochemistry Energy

Sustainability

**Materials for electrochemical energy
storage and conversion devices**

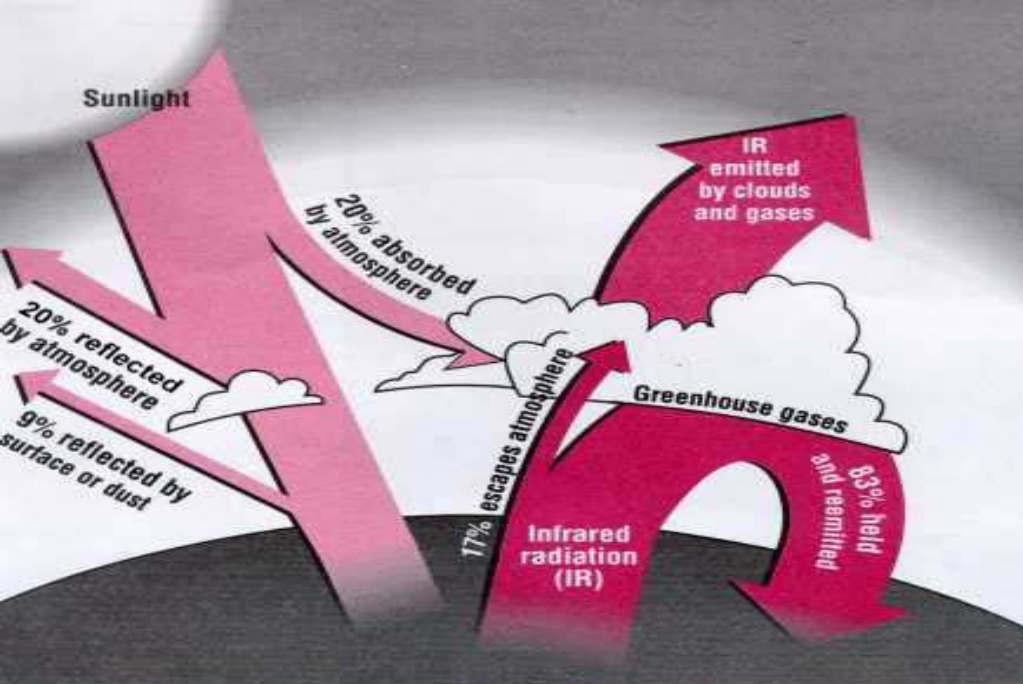
UNICAM

School of Science and Technology, Chemistry Division

Electrochemistry /Physical Chemistry Lab

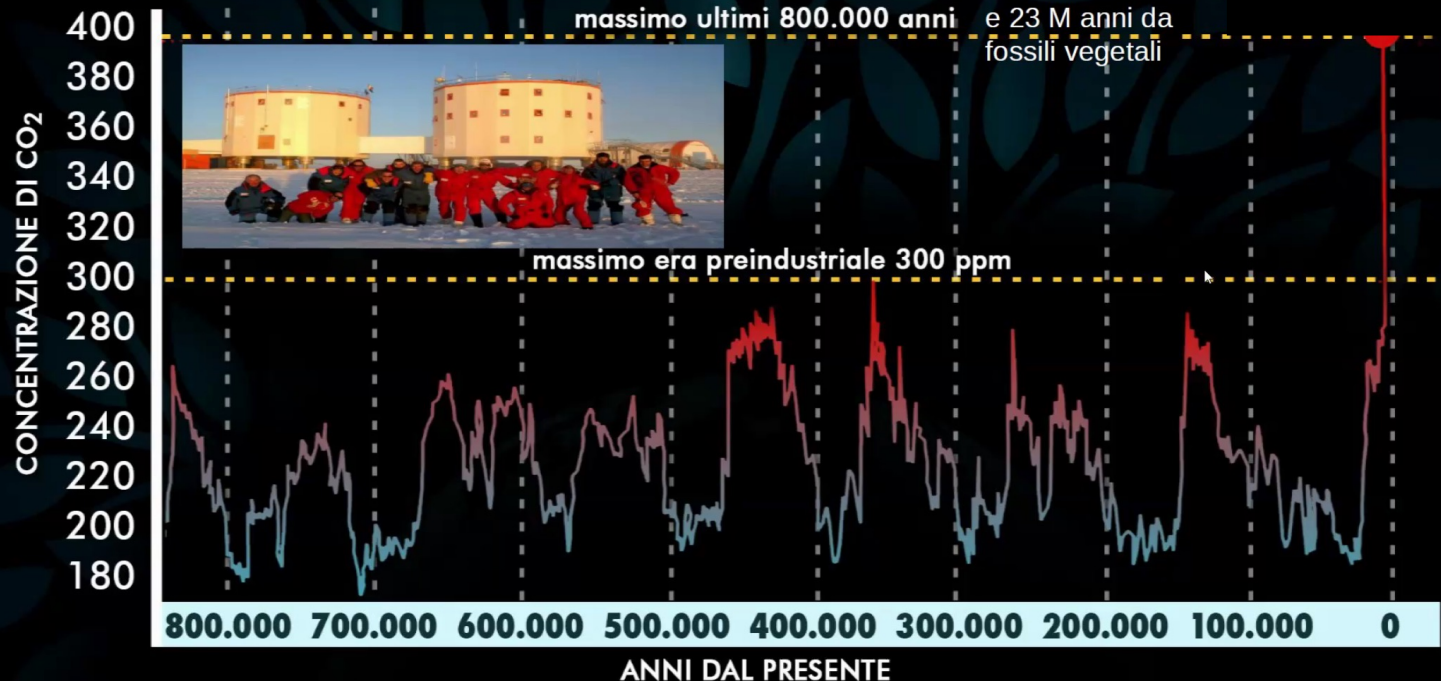
prof. Francesco Nobili and collaborators
francesco.nobili@unicam.it

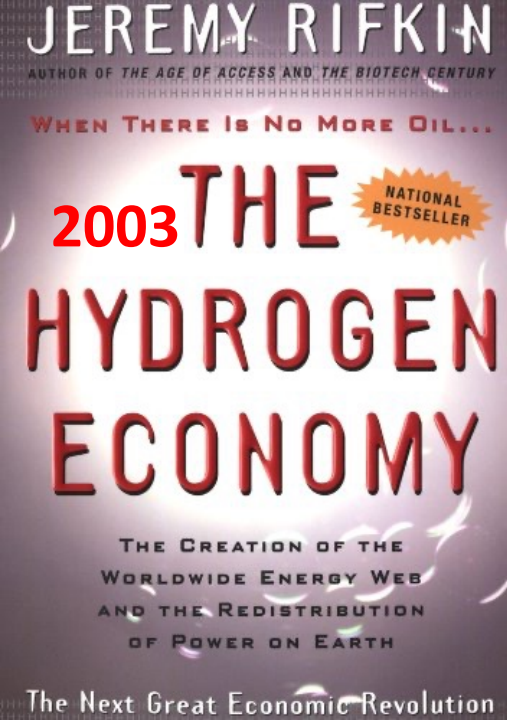
THE FRAMEWORK



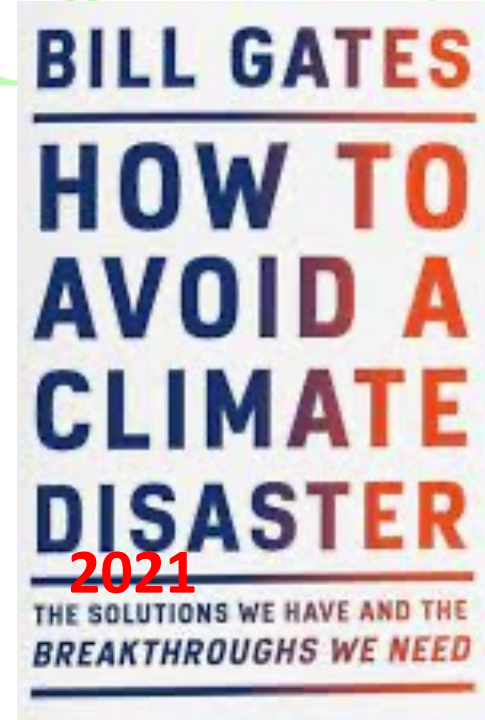
First hints at relationship
between CO₂ levels and
global warming issues
→ Arrhenius 1887

LIVELLO CO₂ NEL TEMPO





**IT'S A
HOT
TOPIC!**





SUSTAINABLE DEVELOPMENT GOALS



1 NO POVERTY



2 ZERO HUNGER



3 GOOD HEALTH AND WELL-BEING



4 QUALITY EDUCATION



5 GENDER EQUALITY



6 CLEAN WATER AND SANITATION



7 AFFORDABLE AND CLEAN ENERGY



8 DECENT WORK AND ECONOMIC GROWTH



9 INDUSTRY, INNOVATION AND INFRASTRUCTURE



10 REDUCED INEQUALITIES



11 SUSTAINABLE CITIES AND COMMUNITIES



12 RESPONSIBLE CONSUMPTION AND PRODUCTION



13 CLIMATE ACTION



14 LIFE BELOW WATER



15 LIFE ON LAND



16 PEACE, JUSTICE AND STRONG INSTITUTIONS



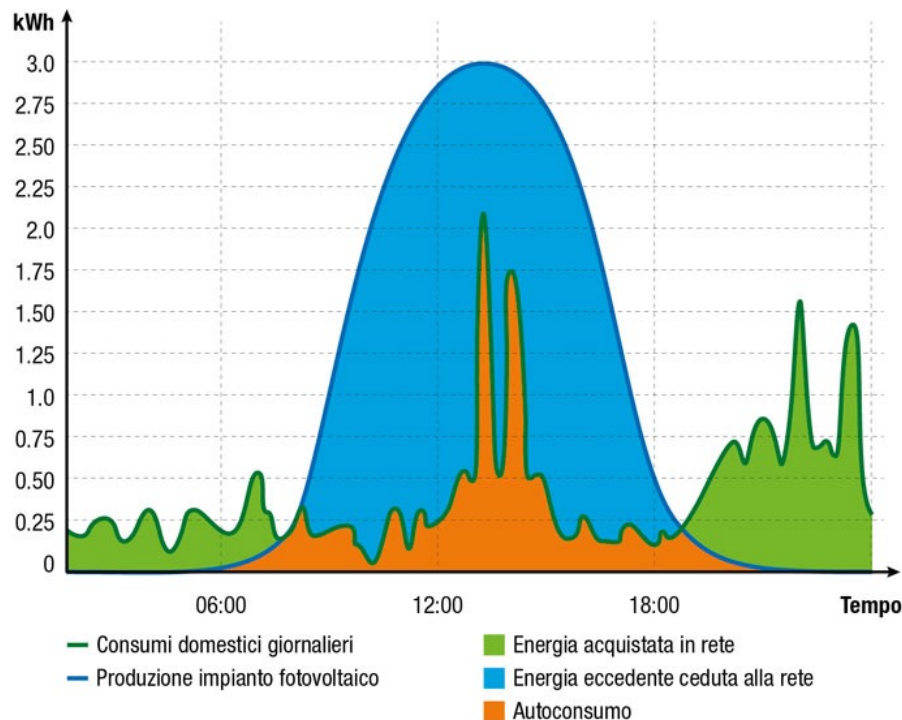
17 PARTNERSHIPS FOR THE GOALS



RENEWABLE SOURCES AND ENERGY STORAGE

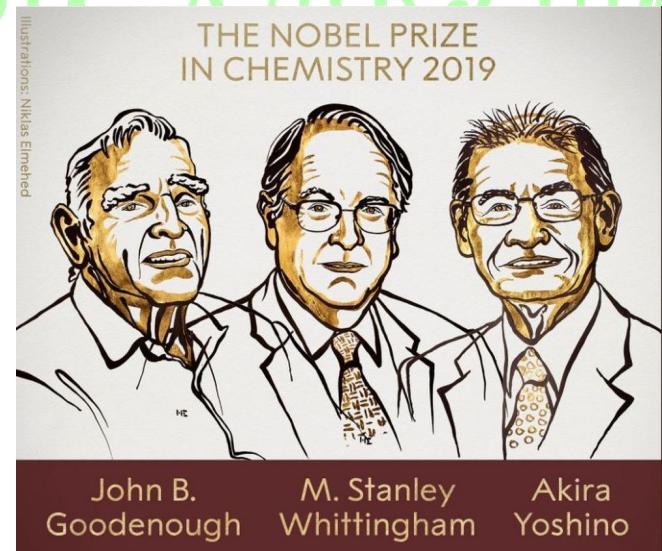
PROBLEM

Production and consumption of RENEWABLE ENERGY are ASYMMETRICAL on daily and 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 SUSTAINABLE?

the case-study of ELECTRIFIED VEHICLES



EVs are becoming **more affordable**

beyond 2025 decreasing battery costs will push EVs to price parity with ICE

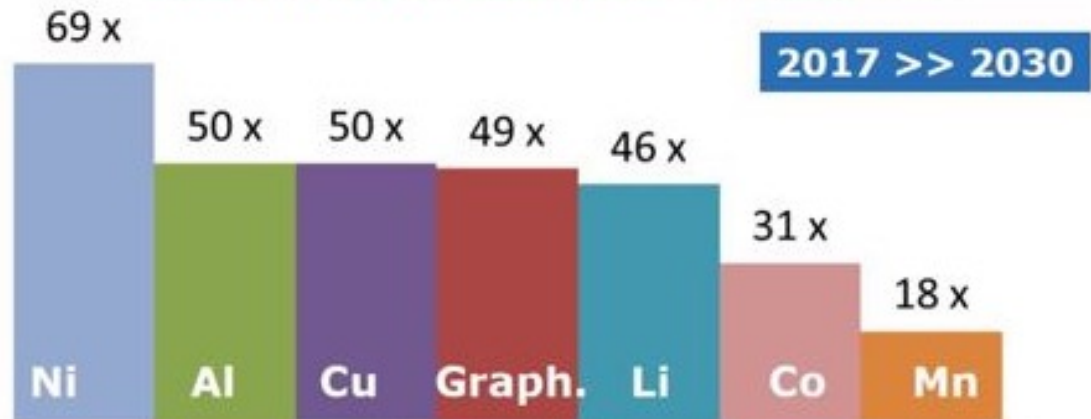
EVs are becoming **more practical**

Faster and more available charging infrastructure



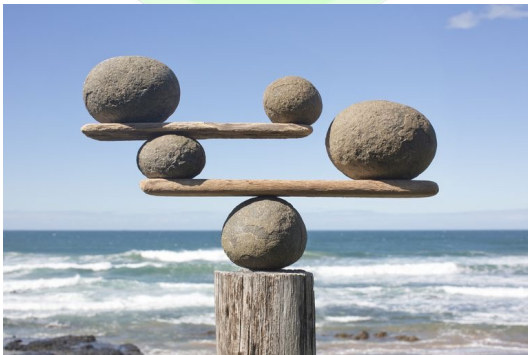
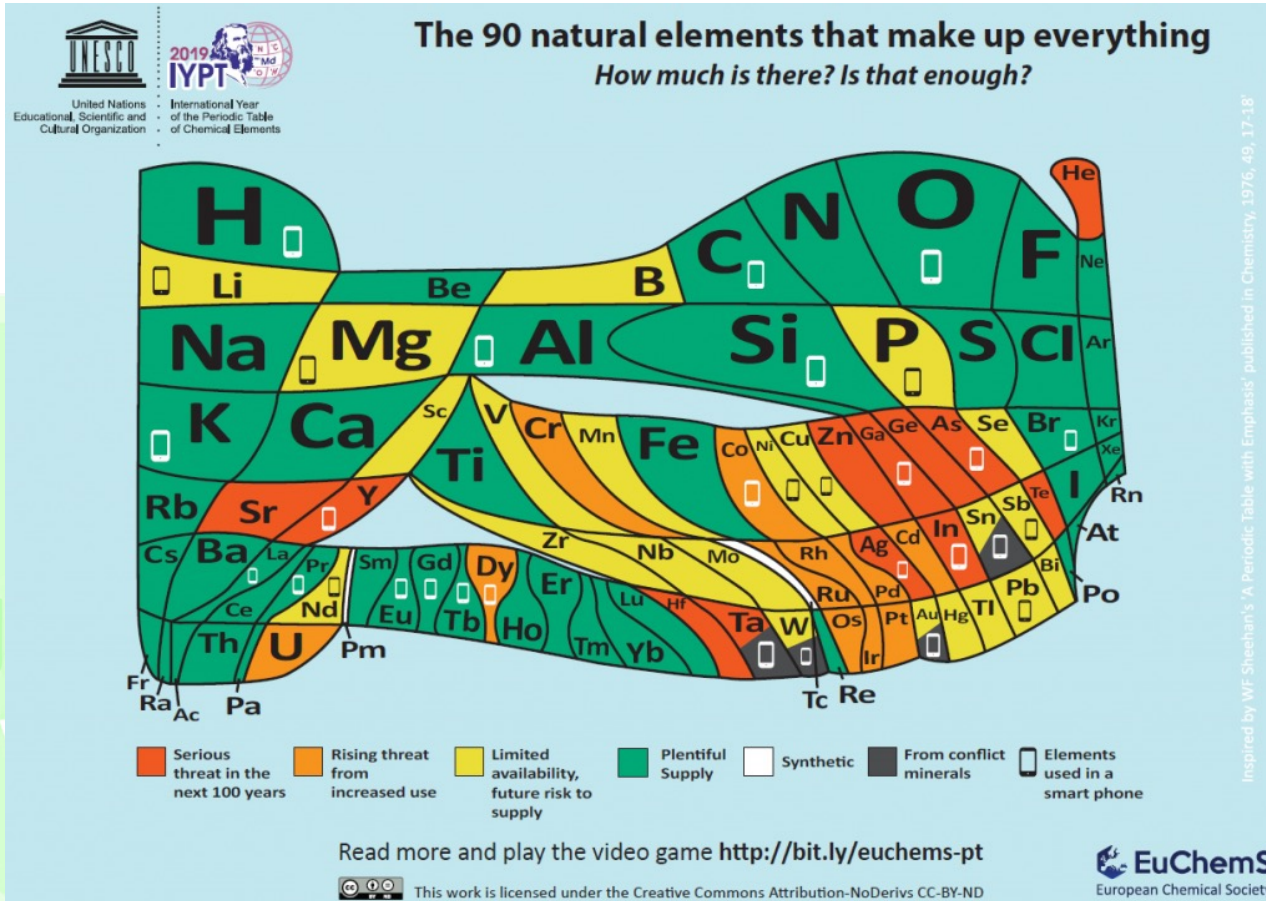
will be increasingly used

An **exponential growth in the demand for battery raw materials** is anticipated



RM's demand growth driven by batteries to be deployed in passenger EVs between today and 2030 (JRC based on Bloomberg, 2018)

SUSTAINABILITY



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

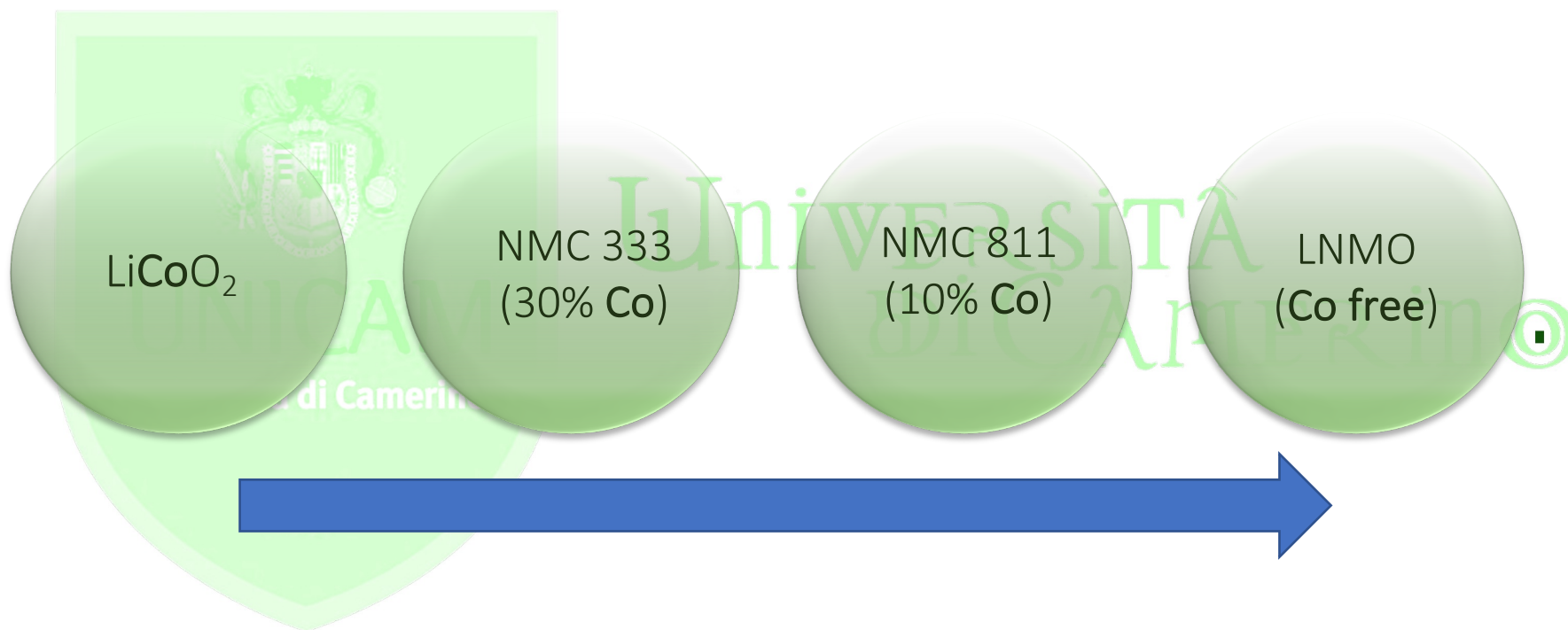
- **SYNTHESIS AND CHARACTERIZATION (SEM, TGA, FTIR, Raman)** of functional materials for electrochemical energy **STORAGE AND CONVERSION: LIBs, NIBs, PEMFCs, SOFCs**

- **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

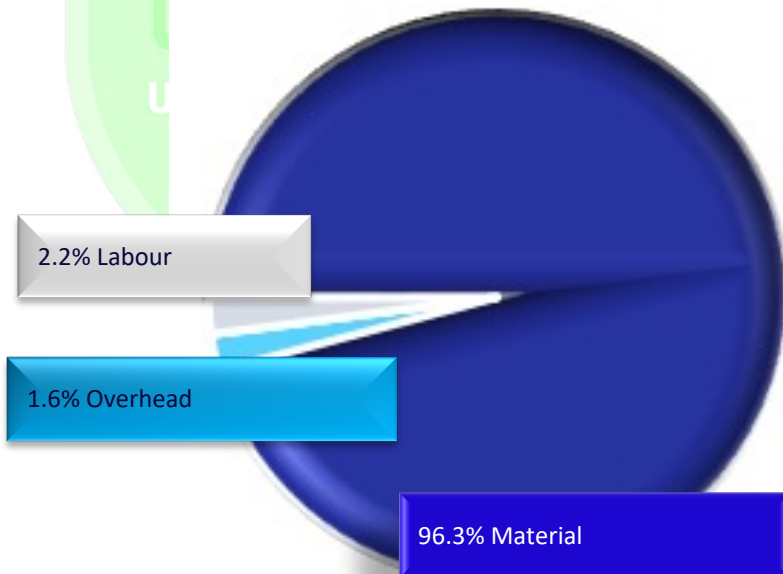


less Co also means higher redox potential → higher cell voltage

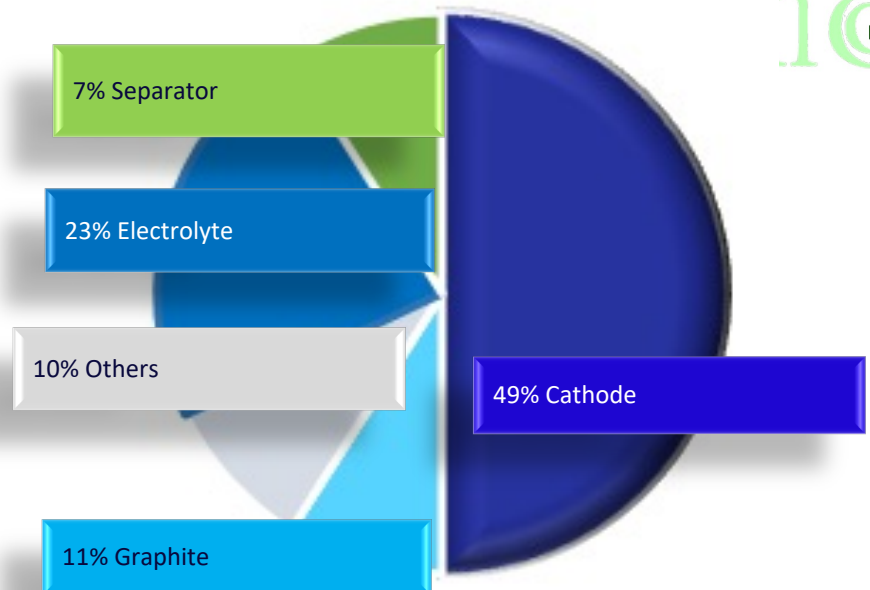
Why cathode materials?

Why the right choice of cathode materials has significant attention?

Battery production costs



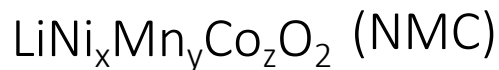
Li-ion cell material costs



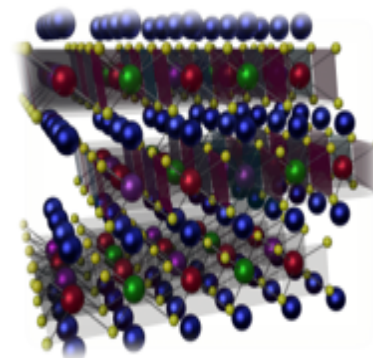
NMC(333)

33% Co

Nowadays are used in the market



Replace partially
with Mn & Ni



Co O Li Ni Mn

NMC(811)

10% Co

Are considered as next generation
cathodes

- The cost of cobalt
- The toxicity of the material

Università di Camerino

NMC

Coating layer

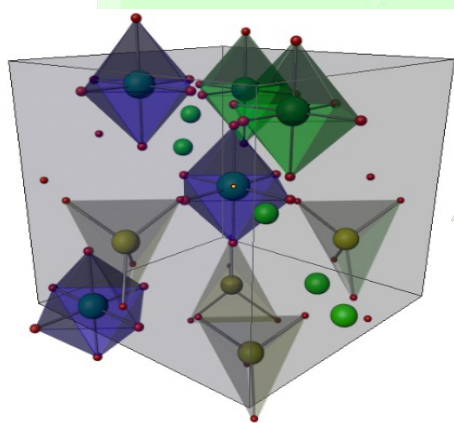
Doped-NMC

Modification

☐ Improving the chemical stability.

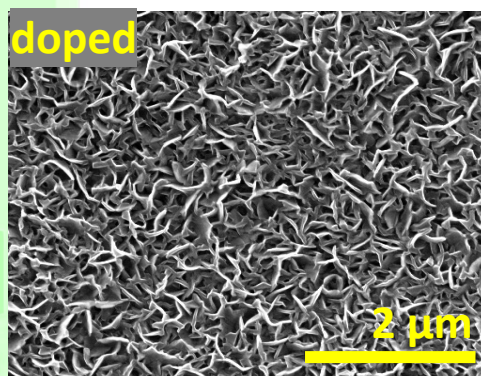
☐ Improving the ion and electron transport.

☐ Enhancing the thermal stability.



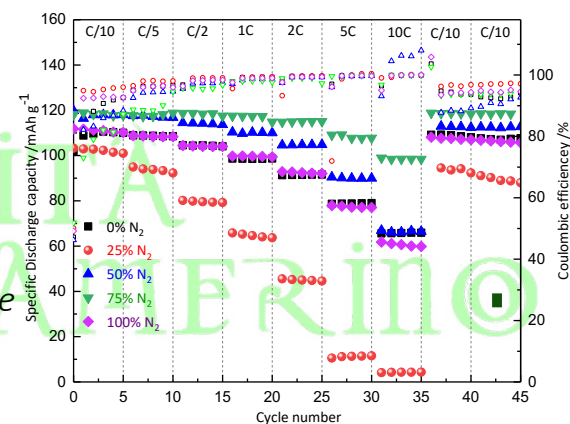
Doping

merino



Nano flake

High
performance



✓ High voltage (5 V)

Higher energy
densities

With $Fd3m$ space group

Next-generation anodes: Silicon

Advantages:

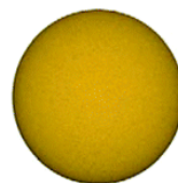
- 10x capacity with respect to state-of-the-art graphite
- Low cost, high abundance, environmentally friendly

Drawbacks:

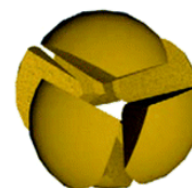
- Large volume variations and mechanical unstability
- Performance loss upon cycling



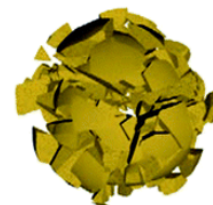
Polverizzazione



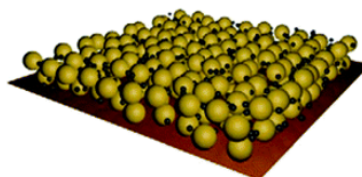
Espansione
di volume



Molti cicli

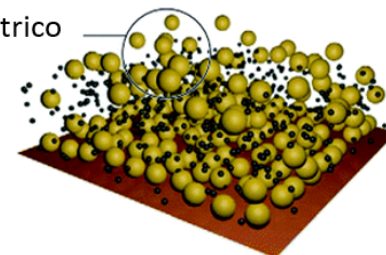


Distaccamento



Isolamento elettrico

Molti cicli

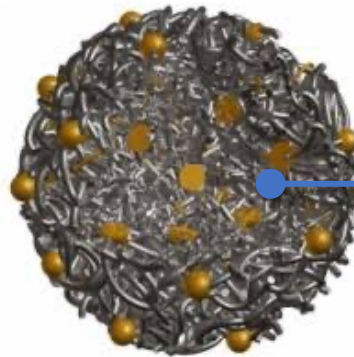
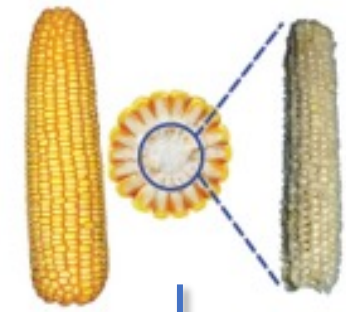


Next-generation anodes: Silicon

Si/C composite anodes

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

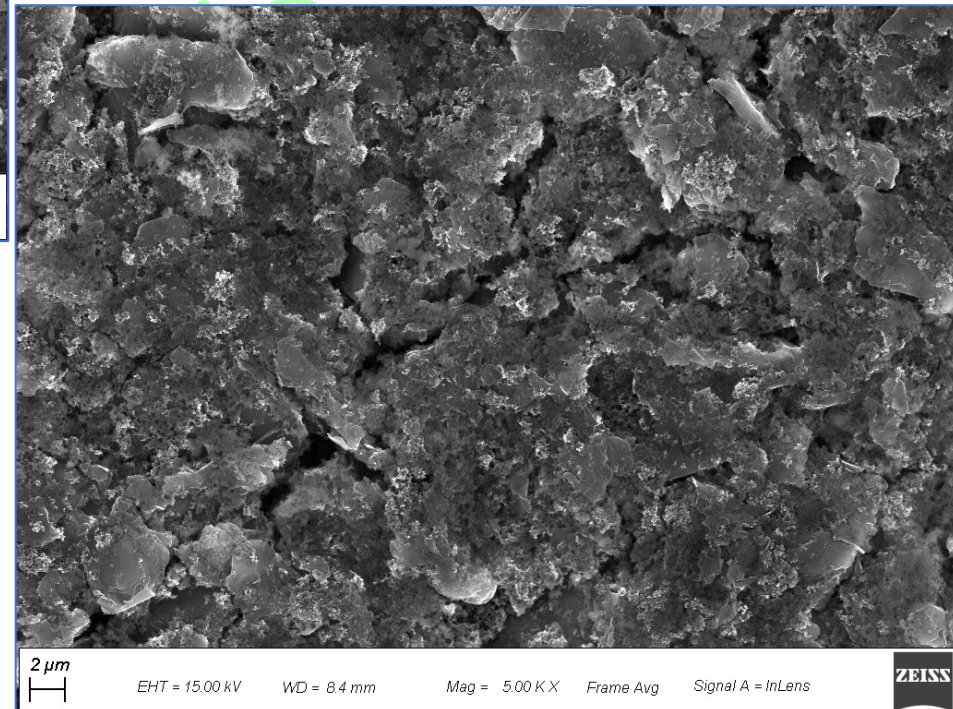
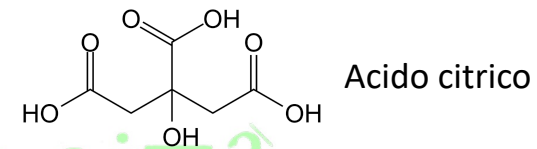
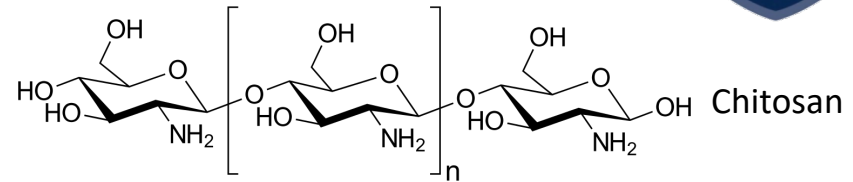
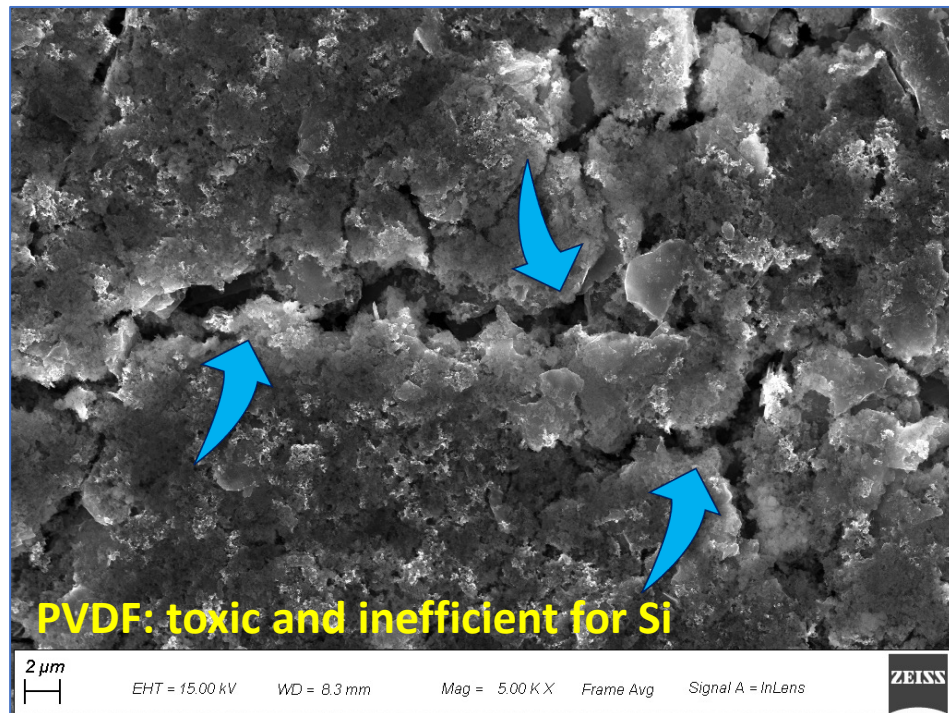
CIRUCULAR ECONOMY



C matrix buffering Si
volume changes



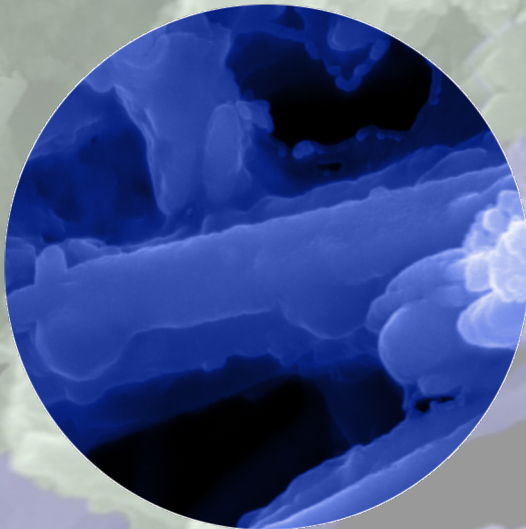
Eco-friendly binders as substitutes for PVDF



MATERIALS ON THE EDGE...

**SnO₂ nanorods /
amorphous carbon
anode**

**3x capacity than
graphite anode**



Fe_3O_4 / graphene
anode



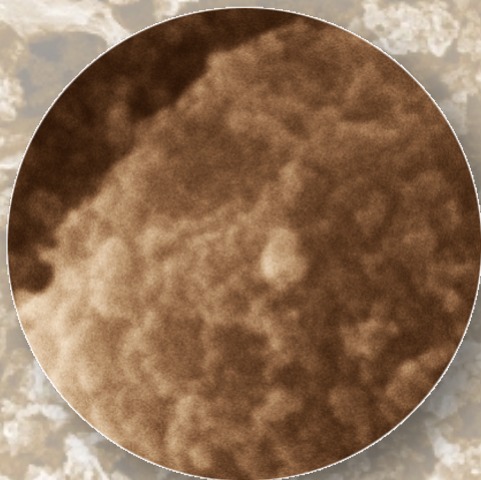
It can be charged very
quickly: 6 minutes!!!

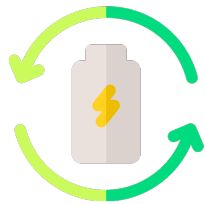


2x capacity than
graphite



Good also for Sodium-
ion batteries





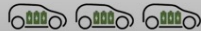
Recycling and upcycling of Li-ion batteries

4000% More Electric Vehicles by 2030

2030 ► 125 Million EV's Worldwide



2019 ► 3 Million EV's Worldwide



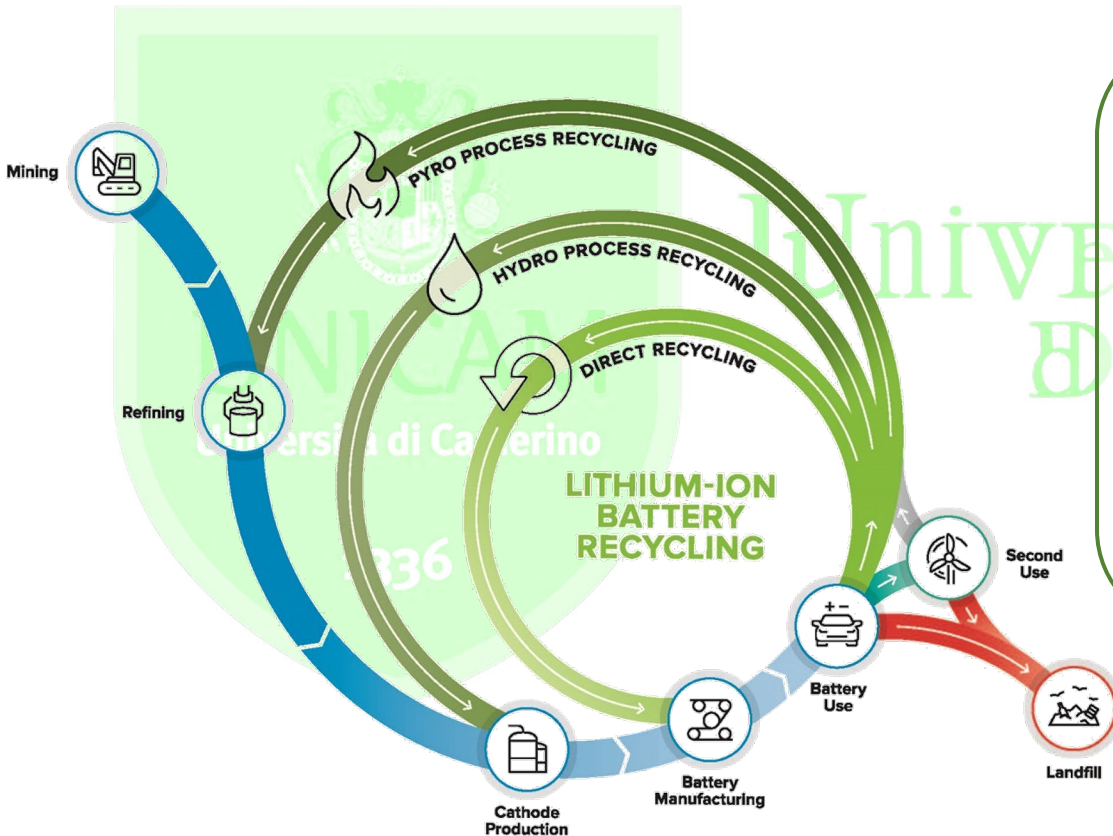
2030 SPENT BATTERIES = 2,000,000 Metric Tonnes Per Year



2019 SPENT BATTERIES = 60,000 Metric Tonnes Per Year



Upcycling of Li-ion batteries

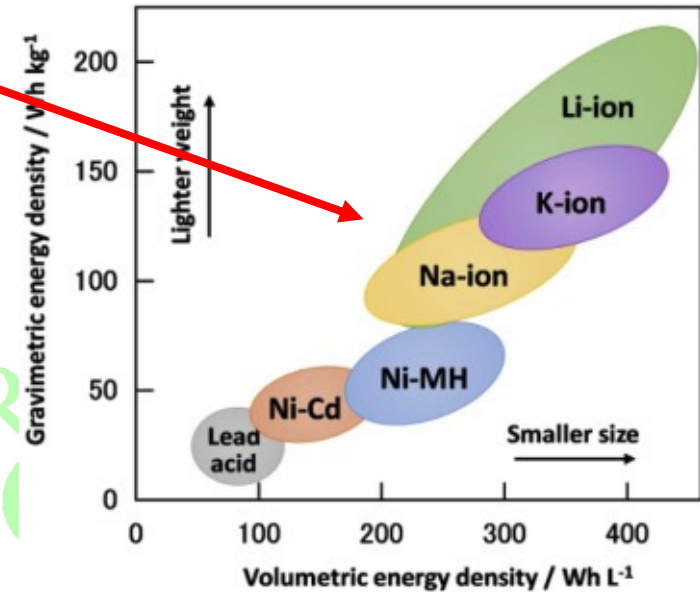


Why **UP**cycling?

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

Sodium-Ion Batteries (NIBs)

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



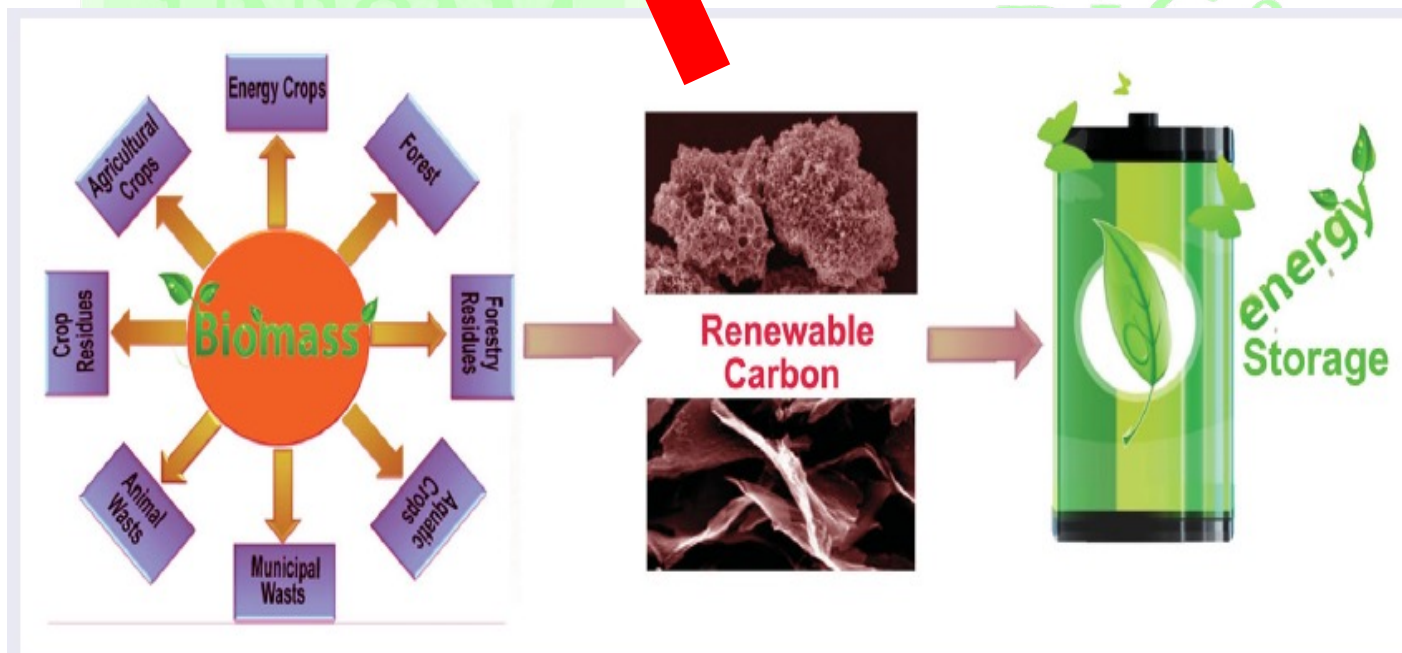
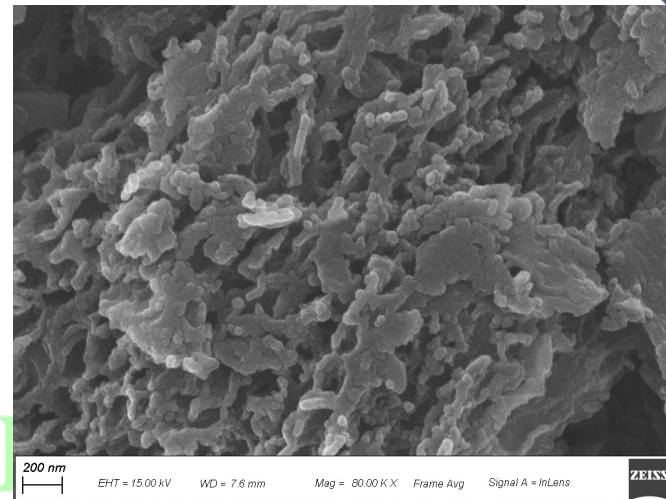
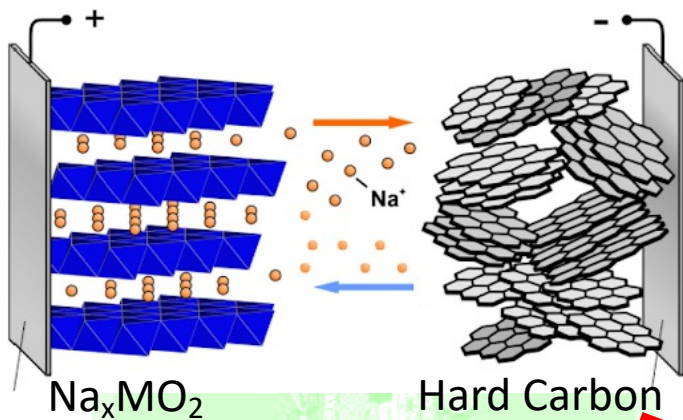
Due to its abundance on Earth's crust and low-cost, Na is an ideal candidate for substituting Li in efficient rechargeable batteries.

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

