Batteries

Design of electrode materials for electrochemical energy storage

Jacob OLCHOWKA

Groupe: “Energie: Matériaux et Batteries”
Institut de Chimie de la Matière Condensée de Bordeaux
CNRS, Université de Bordeaux, Bordeaux INP

EL NANO: ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy, 11-16 Jun 2023 Aussois (73500) (France)

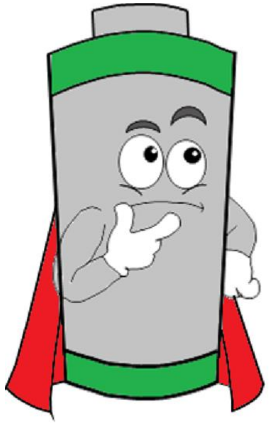
Menu of the day

Introduction to the electrochemical energy storage

- Principles of an accumulator
- Different types of batteries
- Li-ion battery: principle and different technologies
- Na-ion versus Li-ion batteries – advantages and drawbacks

How to optimize an electrode material from its elaboration

- Playing on the composition
- Nano-structuration
- Surface functionalization
- Developing composite materials

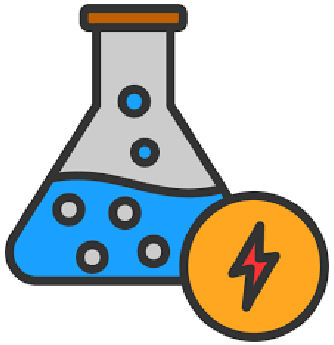


General conclusion

***Battery or accumulators*:**

Device that generates **electrical energy** by **direct conversion of chemical energy**

chemical energy

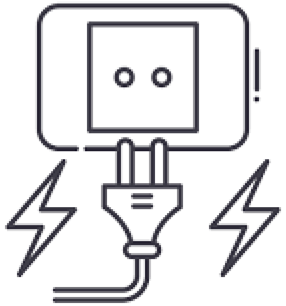


Primary battery

Secondary battery

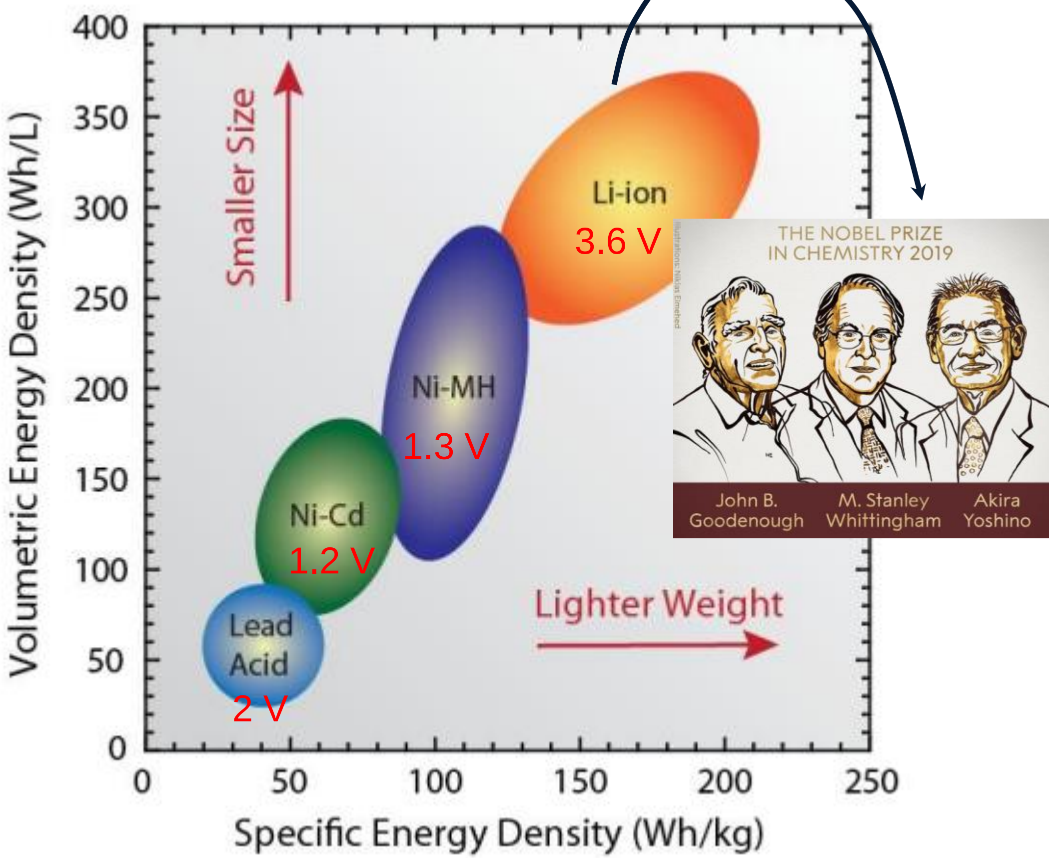
(reversible reaction)

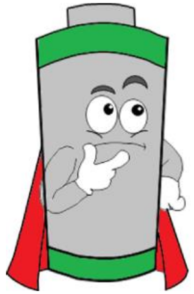
electrical energy

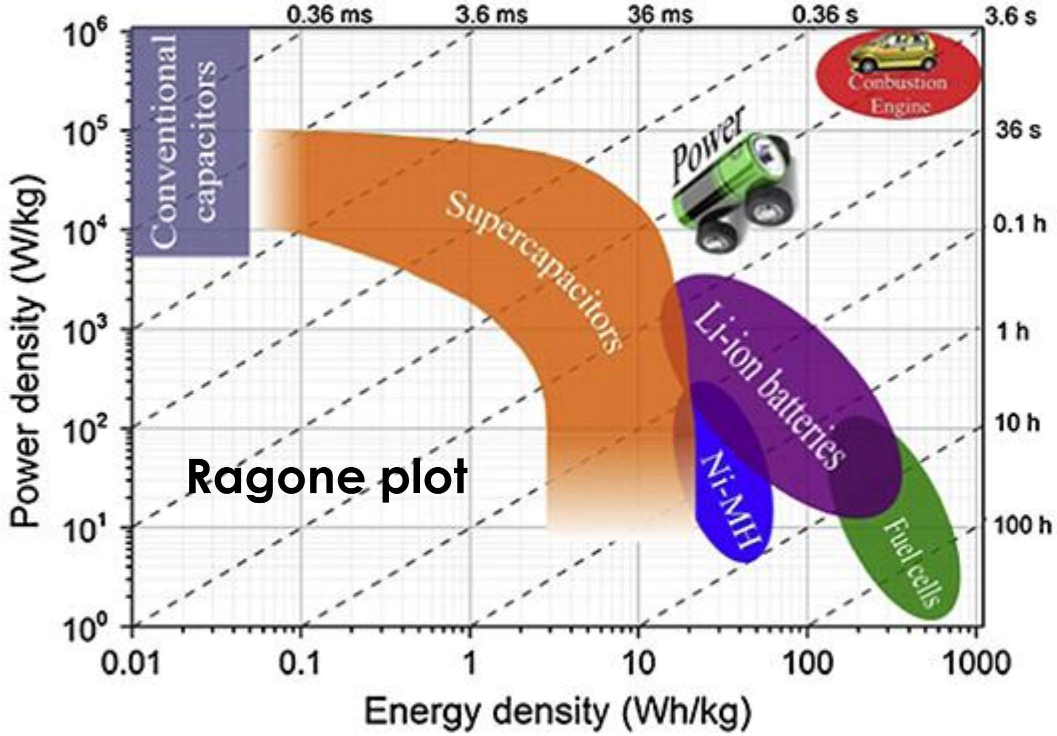


Generalities on Batteries

The most important breakthrough in electrochemistry of last century

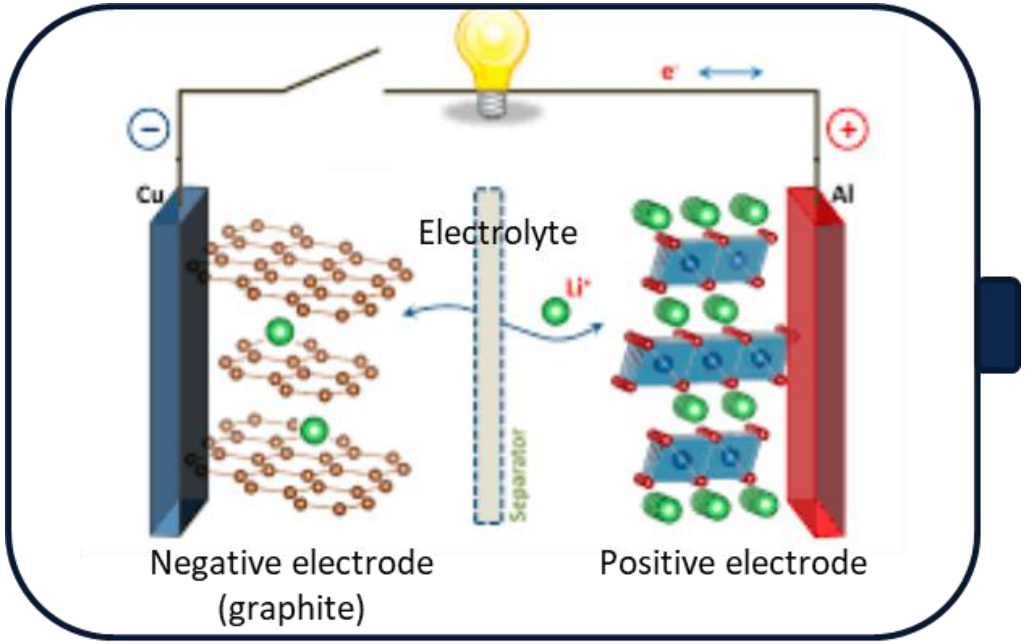


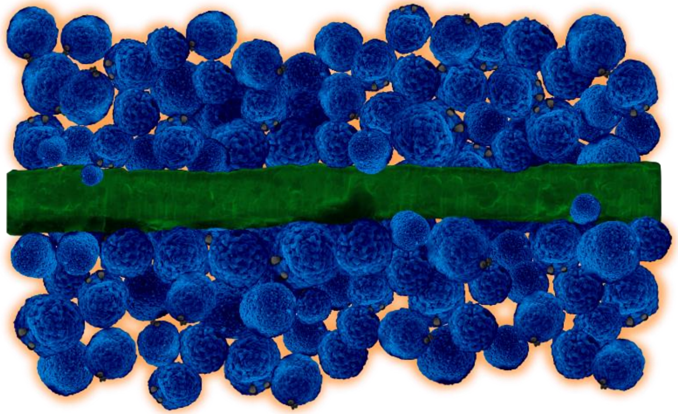




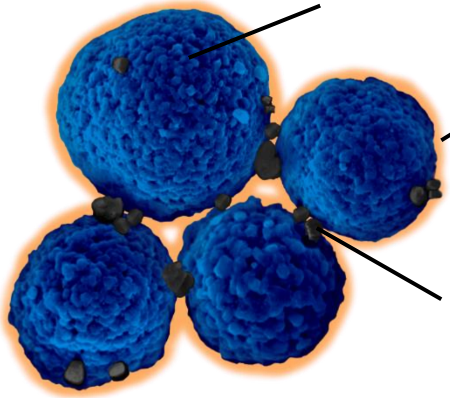
Dan Wu et al., *Front. Mater.* (2020)

Generalities on Li-ion Batteries





Schematic of positive electrode Thickness ~100 µm



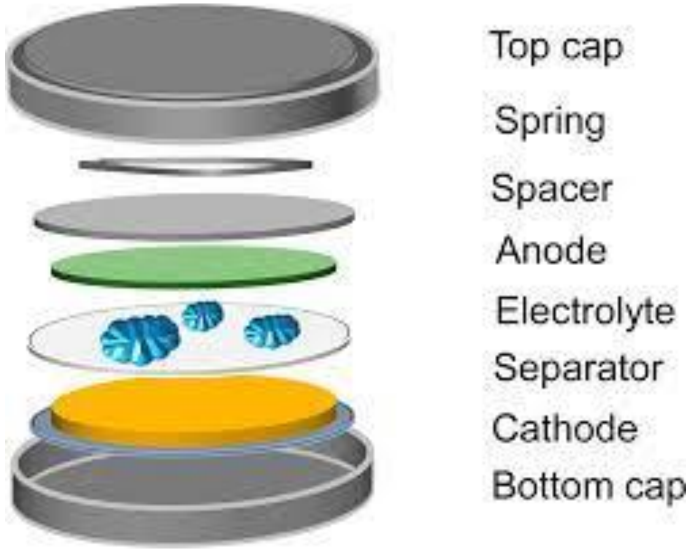
Organic electrolyte with Li salt (ionic conductor)

2 electrodes composed of materials that are both ionic and electronic conductor
(i) Reversible Intercalation of Li^+ (topotatic reaction)
(ii) Redox reactions

$$LiM^{3+}O_2 \leftrightarrow Li_{1-x}M^{3+,4+}O_2 + xLi^+ + 1e^-$$

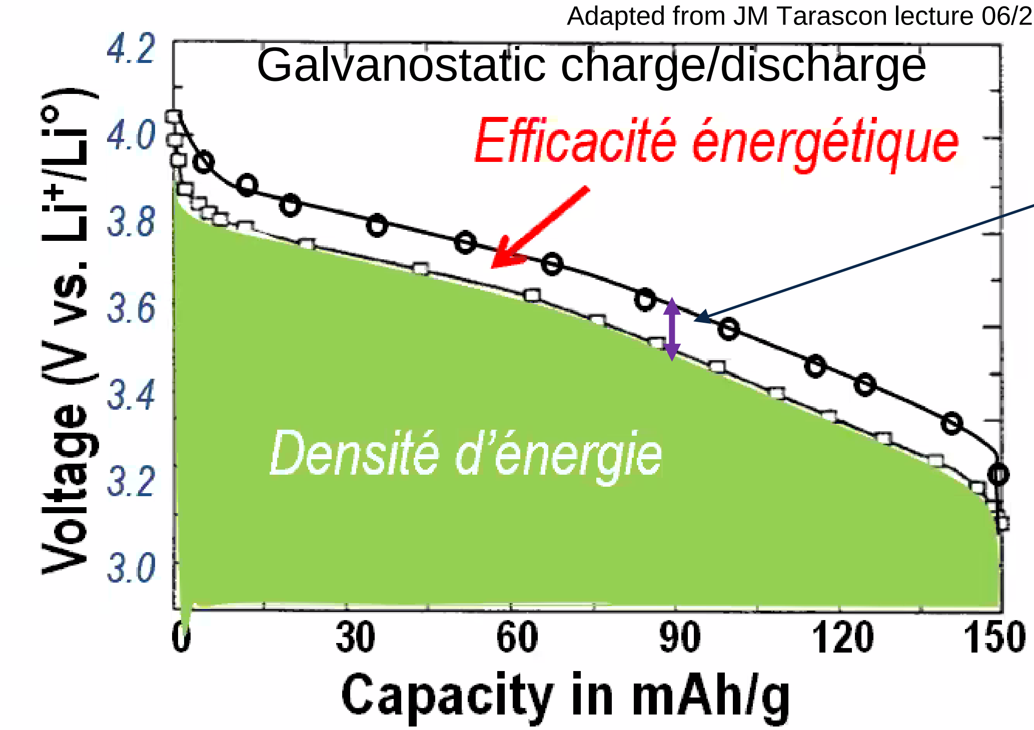
$$C + xLi^+ + xe^- \leftrightarrow Li_xC$$

How to evaluate cathode materials performance

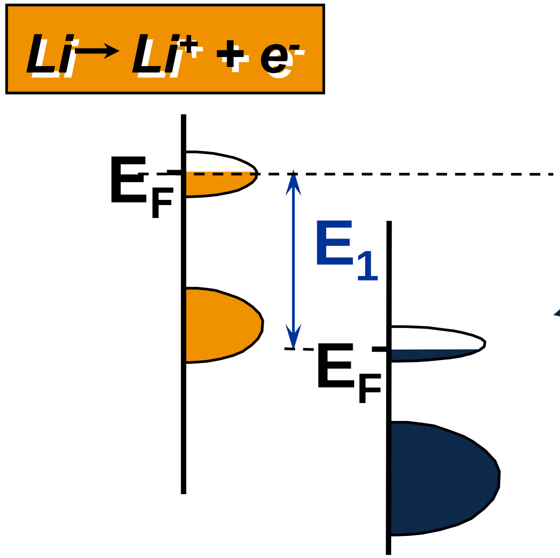


Full cells or half cells

Adapted from JM Tarascon lecture 06/2023



Polarization (resistance)



Energy density (Wh/kg) = Voltage (V) x Capacity (Ah/kg)

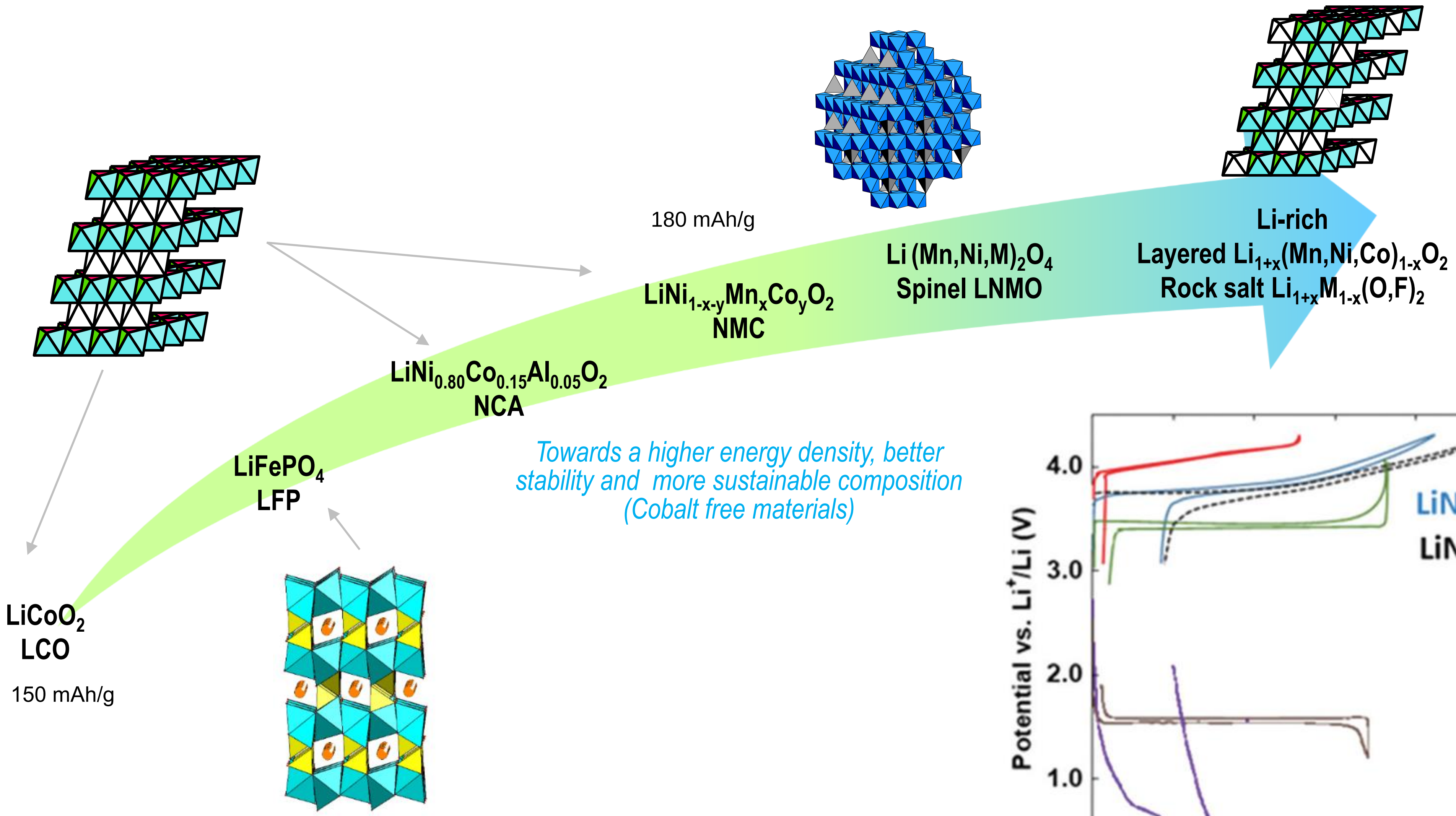
Electronic structure

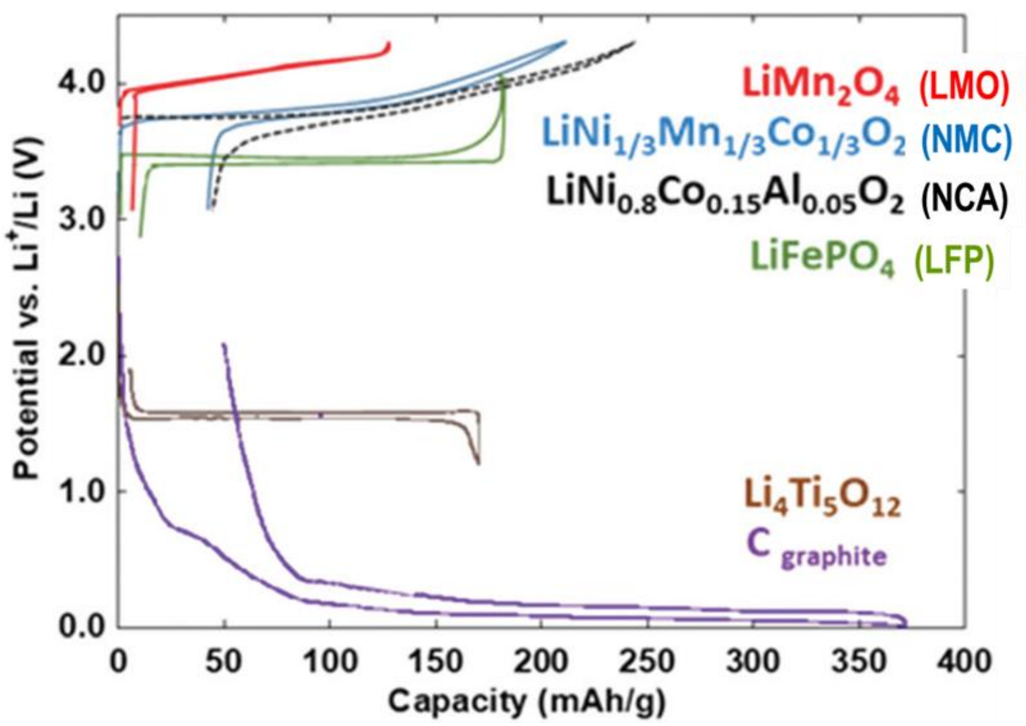
Nb electron /mol

$$\text{Capacity (Ah/kg)} = 26.8 \times \frac{n}{M}$$

Molecular weigth

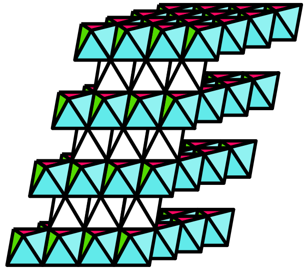
Various Li-ion Batteries technologies



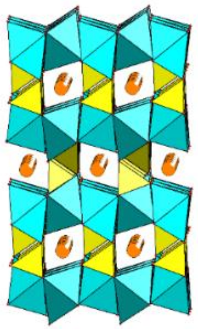


L.Croguennec and R. Palacin, *JACS*, 2015

Various Li-ion Batteries technologies



$LiCoO_2$
LCO
150 mAh/g

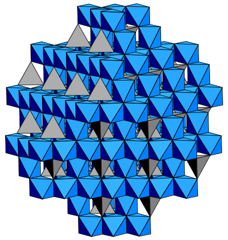


$LiFePO_4$
LFP

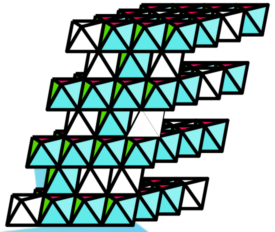
$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$
NCA

180 mAh/g

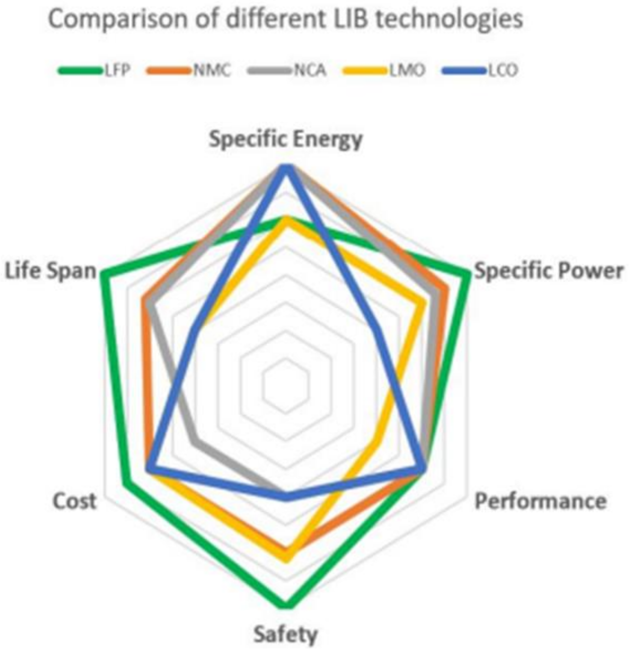
$LiNi_{1-x-y}Mn_xCo_yO_2$
NMC

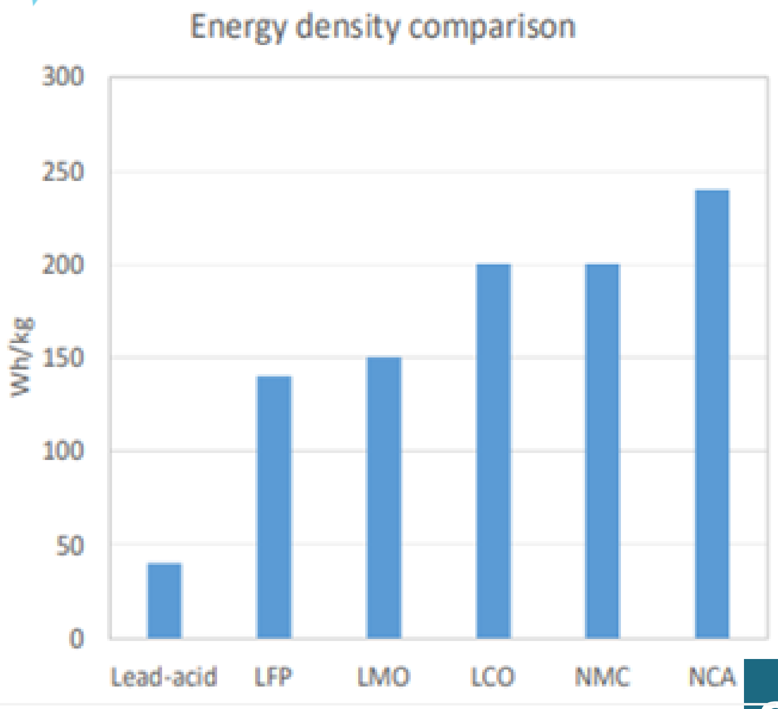


$Li(Mn,Ni,M)_2O_4$
Spinel LNMO

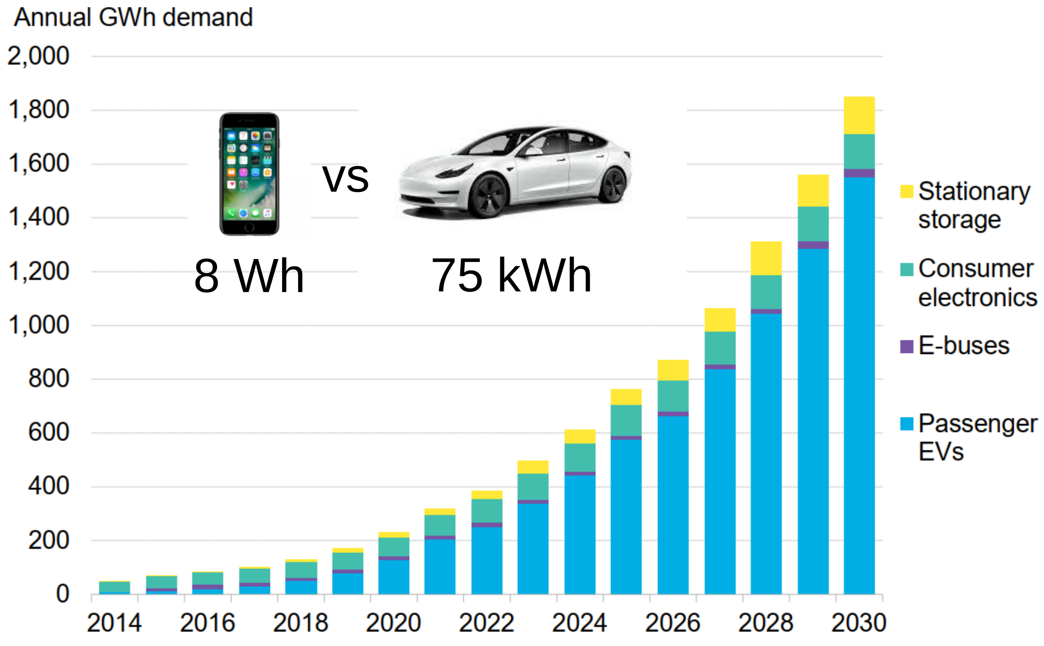


Li-rich
Layered $Li_{1+x}(Mn,Ni,Co)_{1-x}O_2$
Rock salt $Li_{1+x}M_{1-x}(O,F)_2$

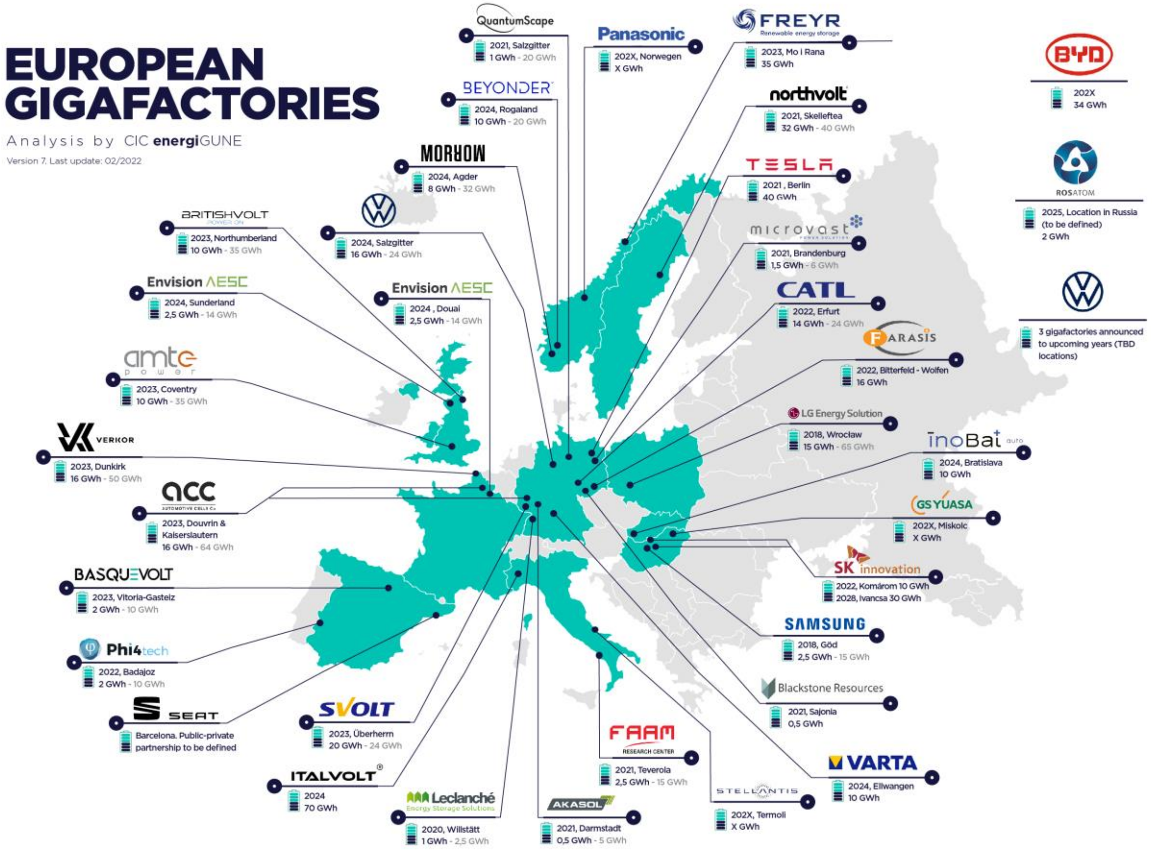




LI-ION BATTERIES MARKET EVOLUTION



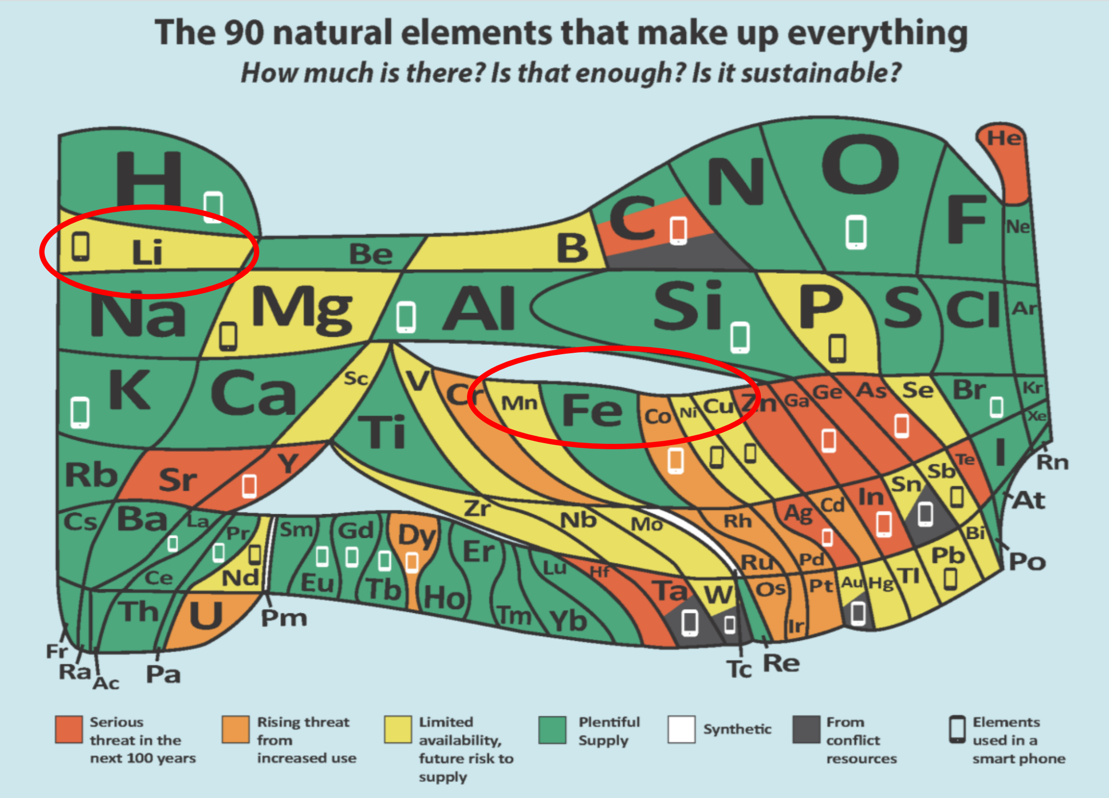
EU ban on sale of new petrol and diesel cars from 2035



Development of Gigafactories in Europe

LI-ION BATTERIES MARKET EVOLUTION

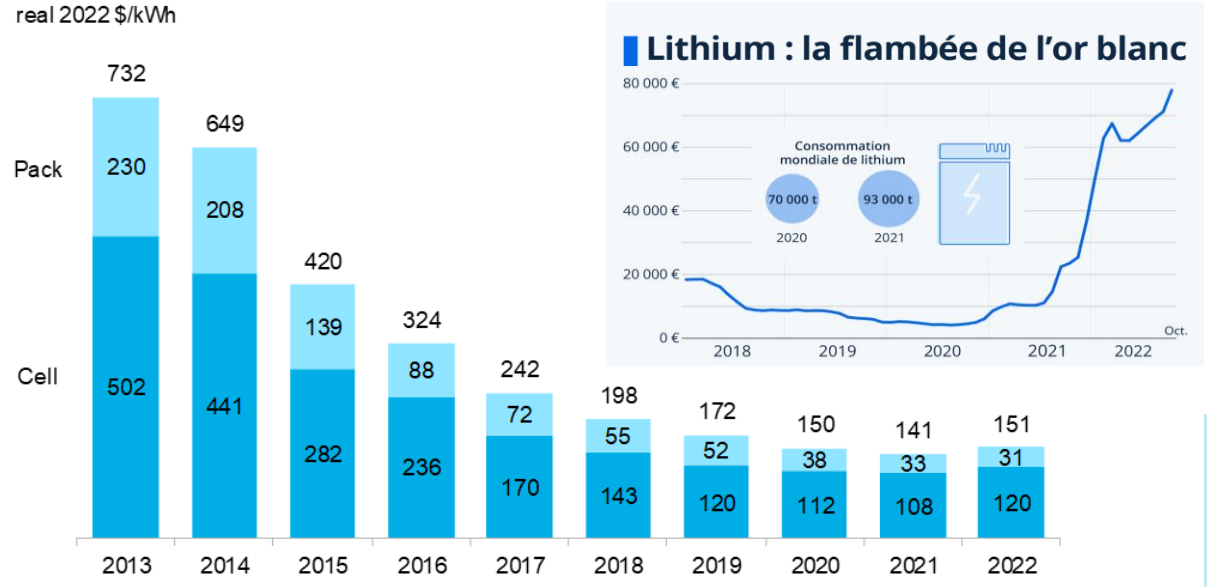
Sustainability concerns !!



Positive electrode: Li, Ni, Co, Mn, Fe …

Price of Positive electrode: 30 - 50% LiB

Figure 1: Volume-weighted average lithium-ion battery pack and cell price split, 2013-2022



Source: BloombergNEF. All values in real 2022 dollars. Weighted average survey value includes 178 data points from passenger cars, buses, commercial vehicles and stationary storage.

Na-ion batteries,
a reliable alternative to Li-ion batteries

COMPARISON BETWEEN NA-ION AND LI-ION BATTERIES

	Sodium	Lithium
Potential (V *vs.* S.H.E.)	−2.70	−3.04
Cation radii (Å)	0.97	0.68
Price (US$ per ton)	250–300	5800
Atomic weight (g)	23	6.9

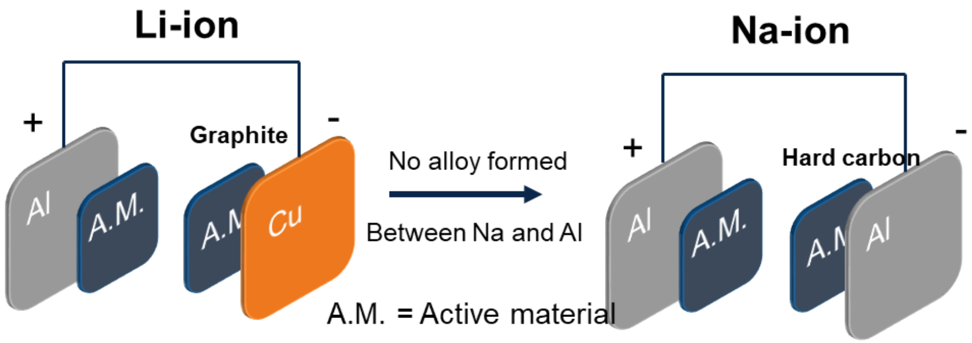
Lower ΔV for Na-ion

Energy density: $$E\ (Wh \cdot kg^{-1}) = \int_{x_{min}}^{x_{max}} \frac{F \cdot V_{OC}(x)}{3.6 \cdot M} dx$$

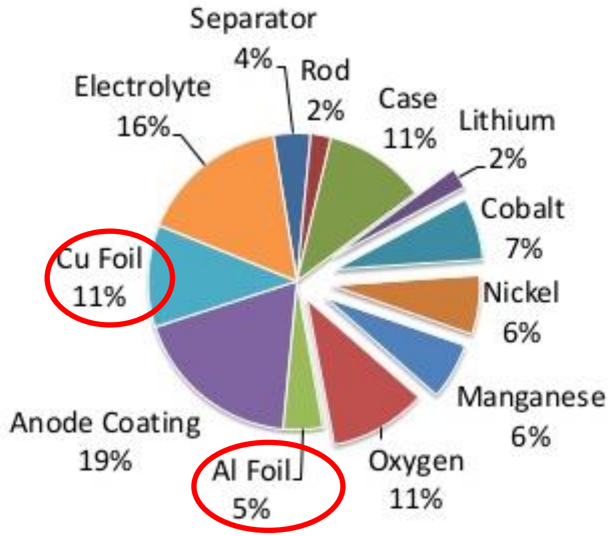
Higher mass for Na^{+}

For a similar chemistry: *Energy density Na-ion < Energy density of Li-ion*

ADVANTAGES OF NA-ION BATTERIES

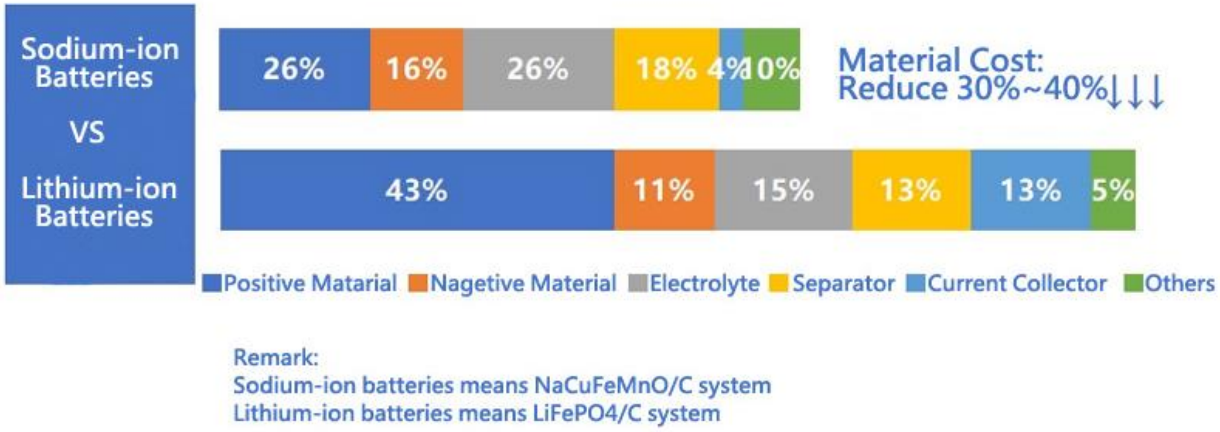


Composition d'une batterie Li-ion



Current collector	Price
Cu (11%)	10,000 US$/ton
Al (5%)	3,000 US$/ton

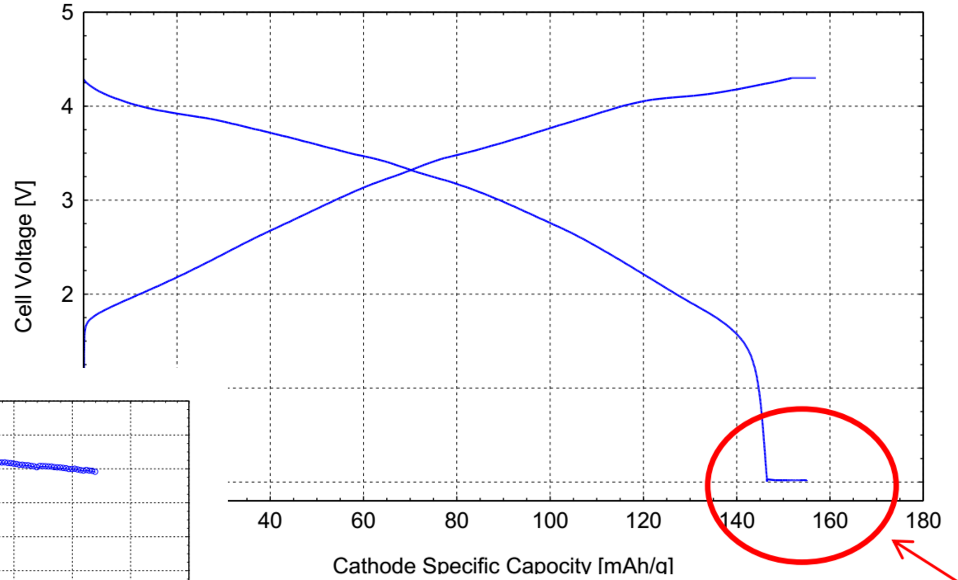
https://markets.businessinsider.com/. Barker, J. et al. (Faradion Ltd), US20170237270A1, 2017.

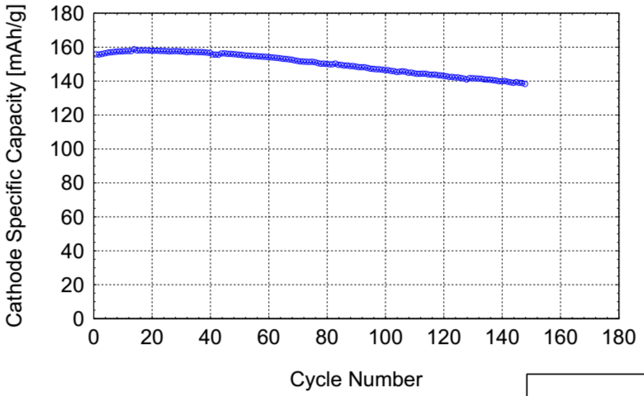


https://www.ecolithiumbattery.com/sodium-ion-battery/

WHY NA-ION BATTERIES ARE SAFER THAN LI-ION BATTERIES

All prototype cells stored and shipped physically shorted





0 V Voltage hold for 48 h

Max: 6 months at 0 V = No Degradation

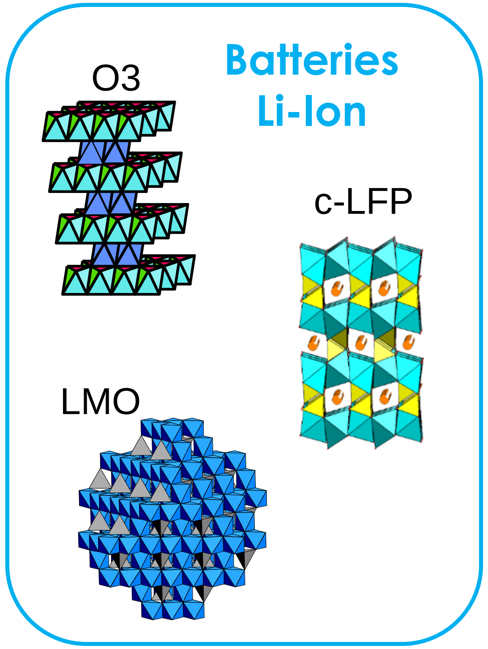
TIAMAT & STARTEC ENERGY

No propagation of **thermal runaway** from one cell to another

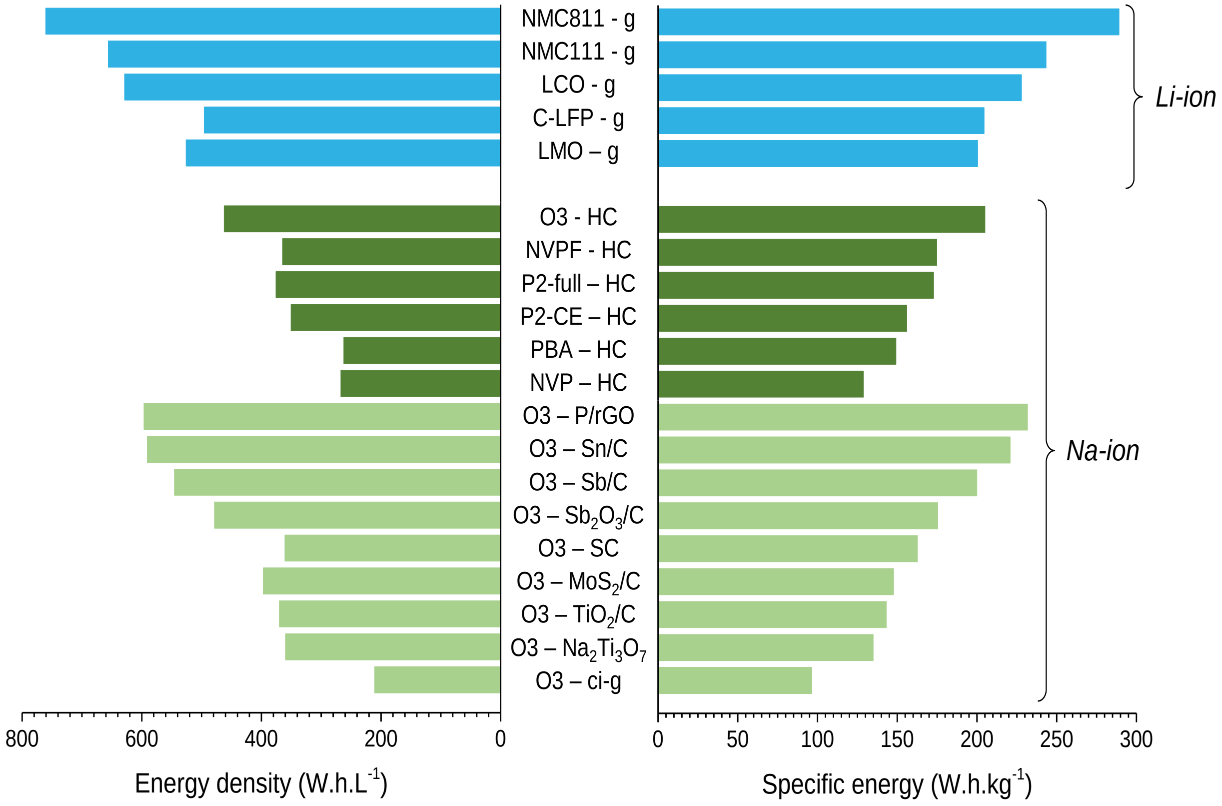
0 V safety storage

First generation of Na-ion Batteries competitive with Li-ion ones

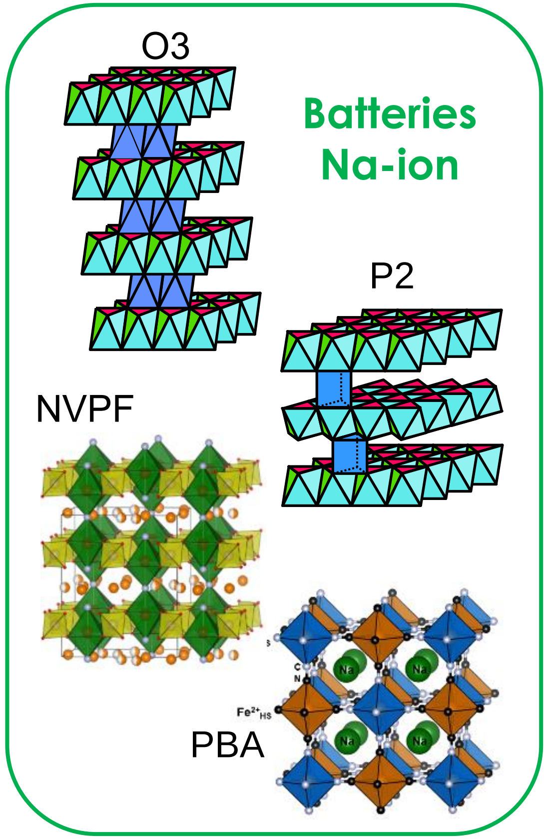
Abundance du Na



Similar intercalation chemistry between Li-ion and Na-ion batteries



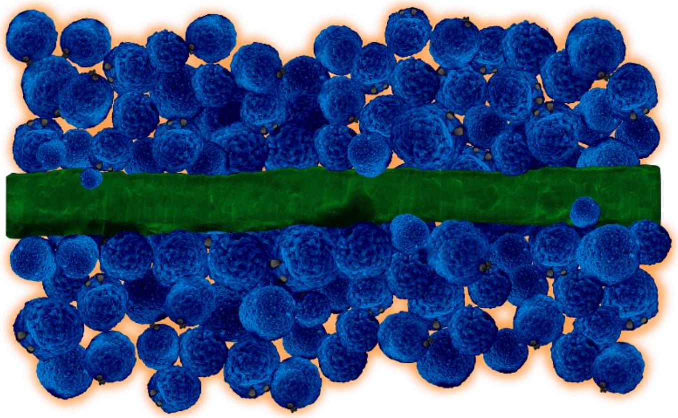
Cheaper and safer

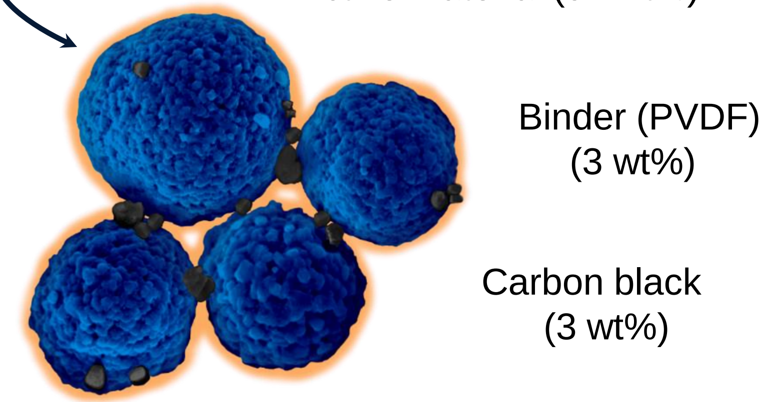


Hasa, Mariyappan, Saurel, Adelhelm, Koposov, Masquelier, Croguennec, Casas-Cabanas - J. Power Sources, 2021

How to optimize the positive electrode materials ?

What's a good cathode material ??





High Voltage

High Capacity

Easy to recycle

Stable upon cycling

Cheap

Non-toxic

Fast ionic Conductor

Good electronic conductivity

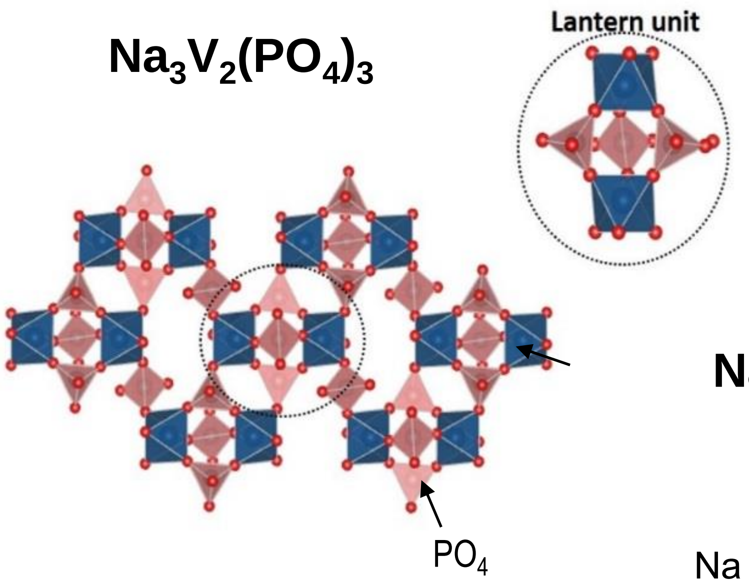
Playing with the chemical composition (solid-state chemistry)

Control of the particle's size and morphology

Applying a coating

Towards composite active materials

Different chemistry of polyanionic material

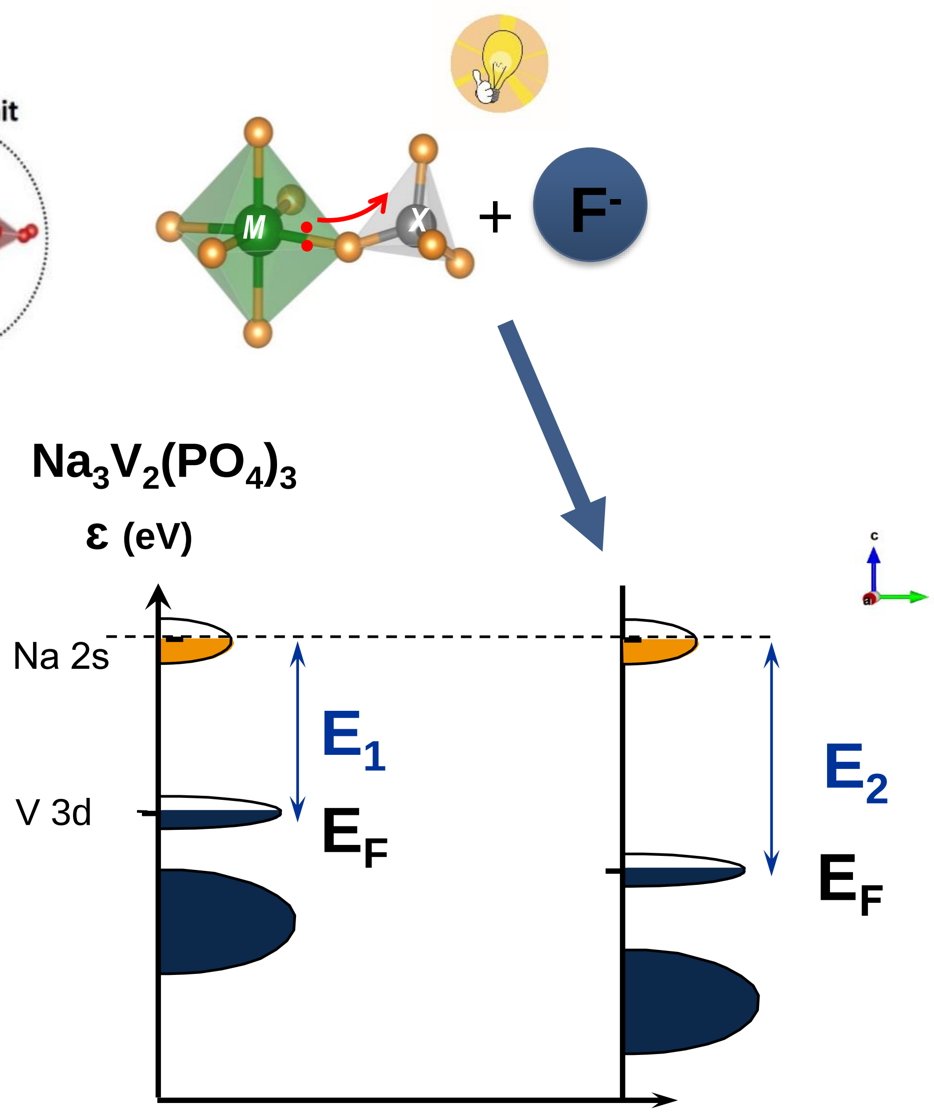


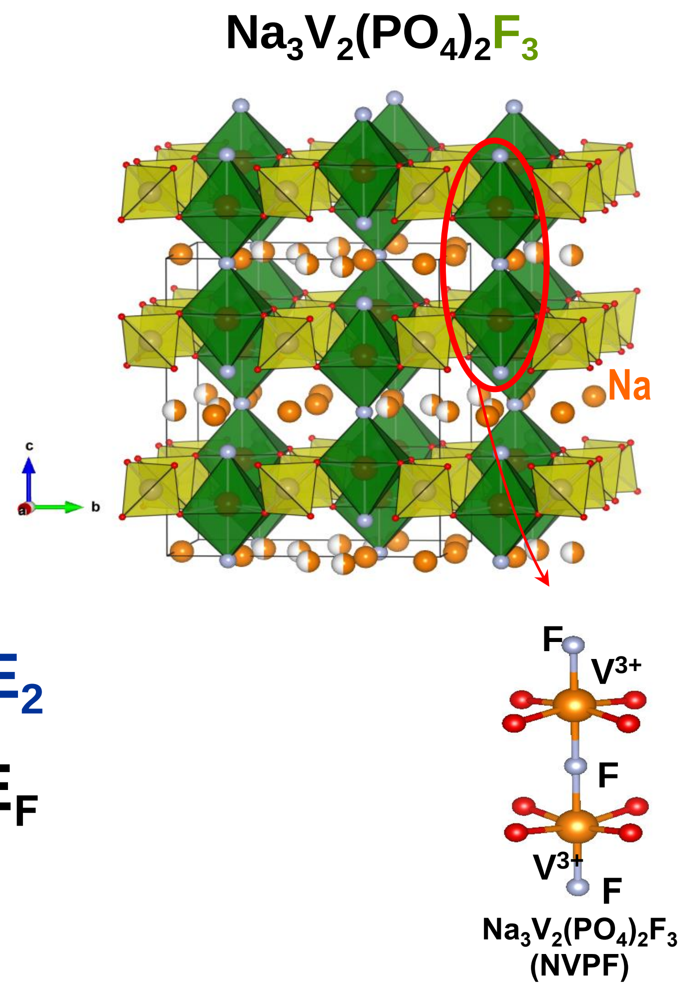
NASICON structure

High Na^+ conductivity

but low potential : 3.2 V vs Na^+/Na

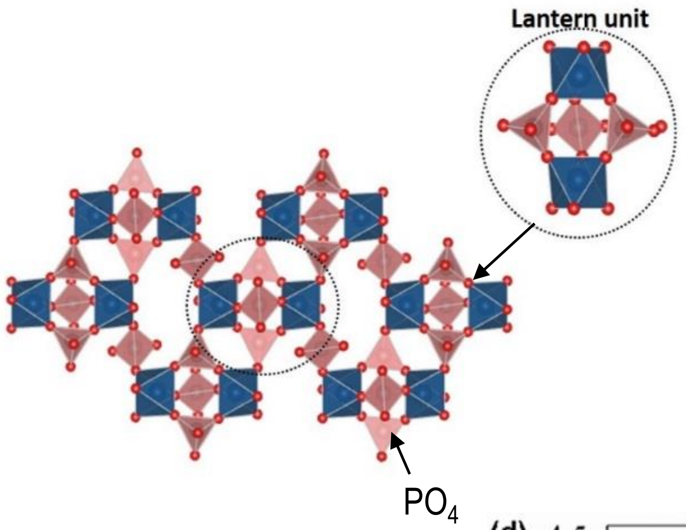
Widely studied, fundamental research on new NASICON chemical composition, new polymorphs …

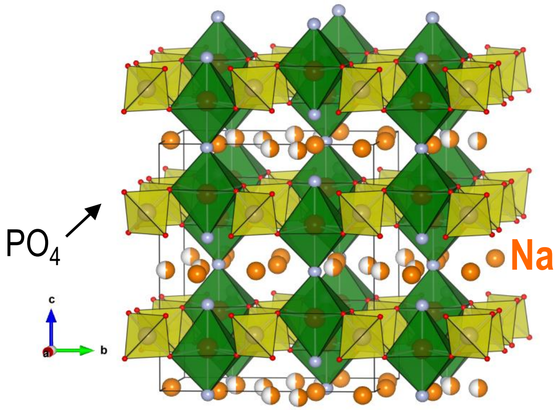


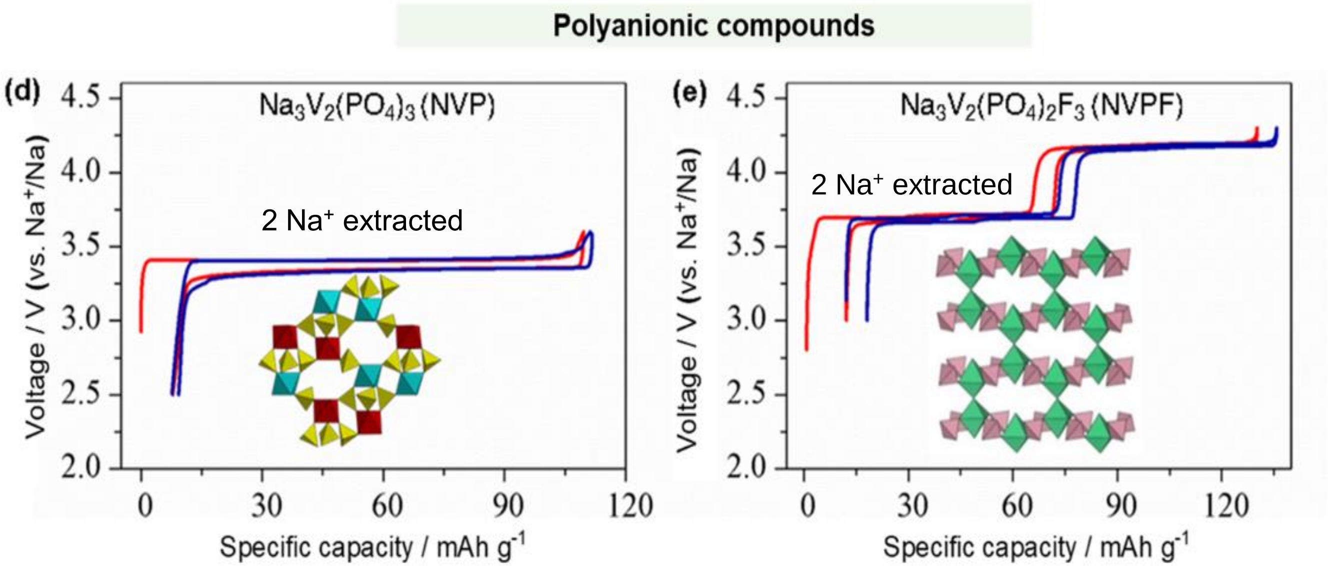


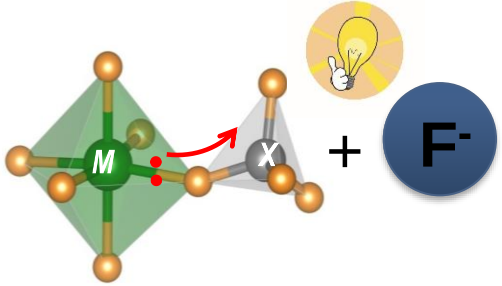
Croguennec and Masquelier, Chem. Rev. 2013

Different chemistry of polyanionic material









$1Na^+/V$, 3.2 V vs Na^+/Na

V^{3+}/V^{4+}

Capacité reversible
< 100 mAh/g

Limited Energy Density

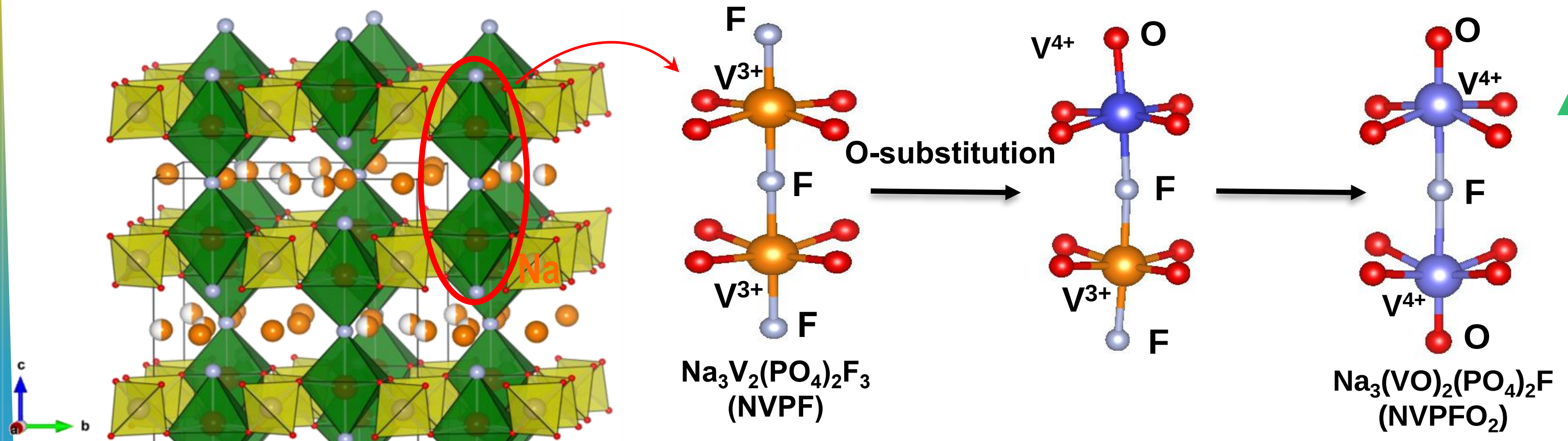
$1Na^+/V$, 3.95 V vs Na^+/Na

V^{3+}/V^{4+}

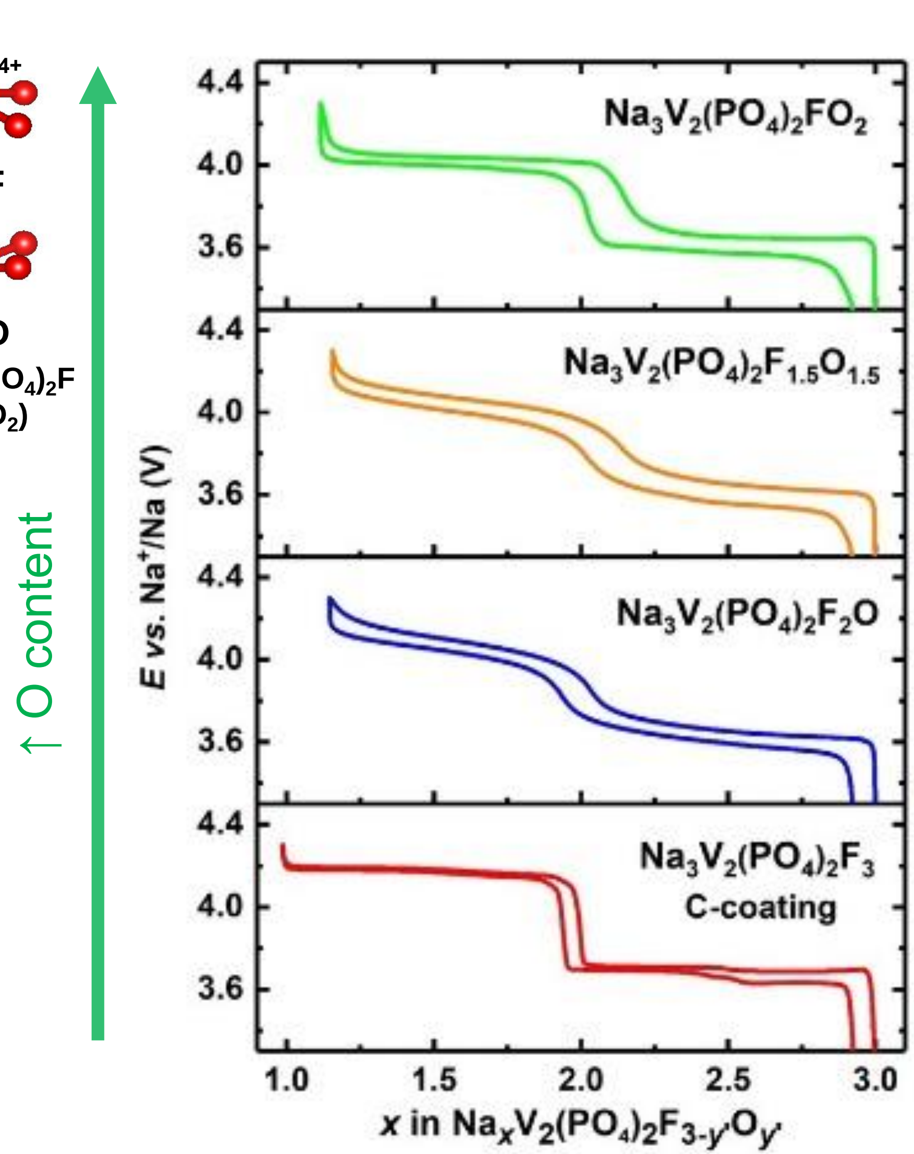
Reversible capacity
> 110mAh/g
Increased Energy Density

Croguennec and Masquelier, Chem. Rev. 2013

Different chemistry of polyanionic material

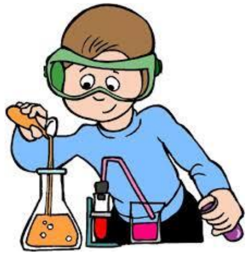


Full solid solution



When O content increases

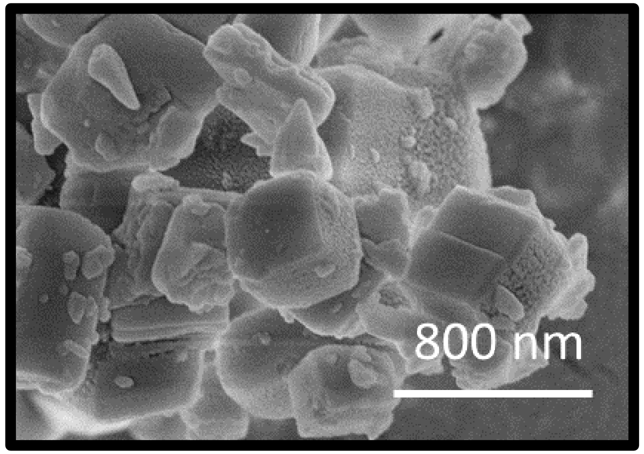
Potential decreases and thus energy density decreases



Important to control the composition during the synthesis

Nguyen et al. Energy Storage Materials, 2019

Particle's nanosizing



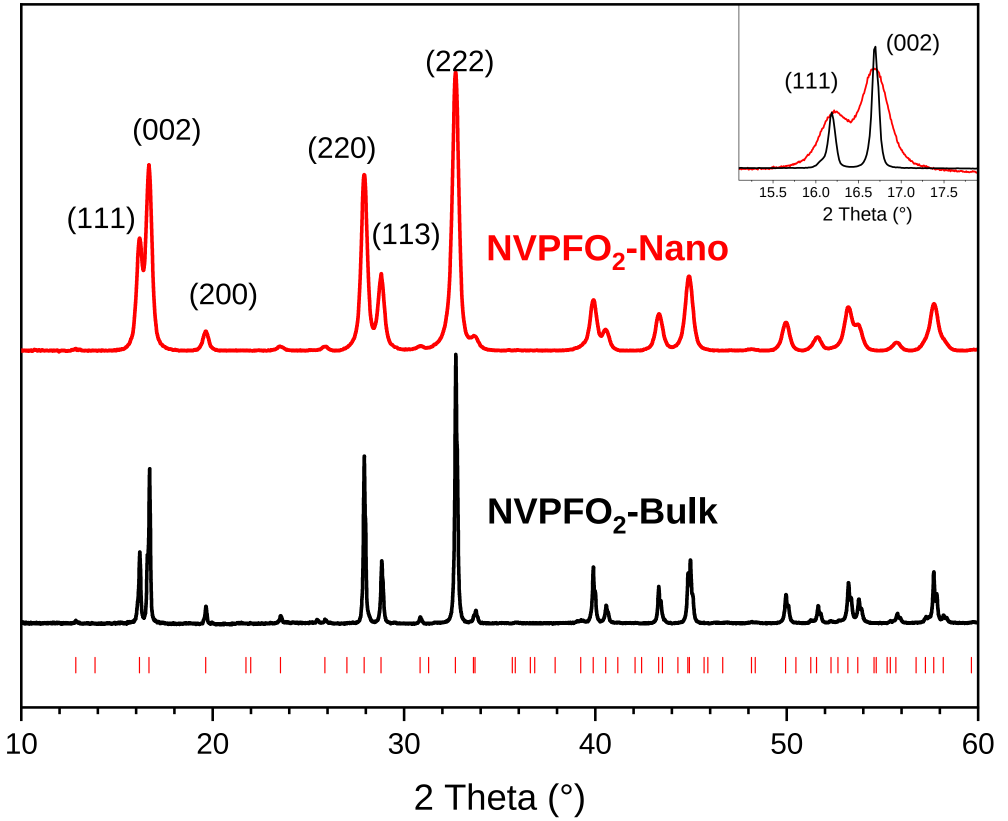
$NVPFO_2$-Bulk
Crystallite size: ~85 nm

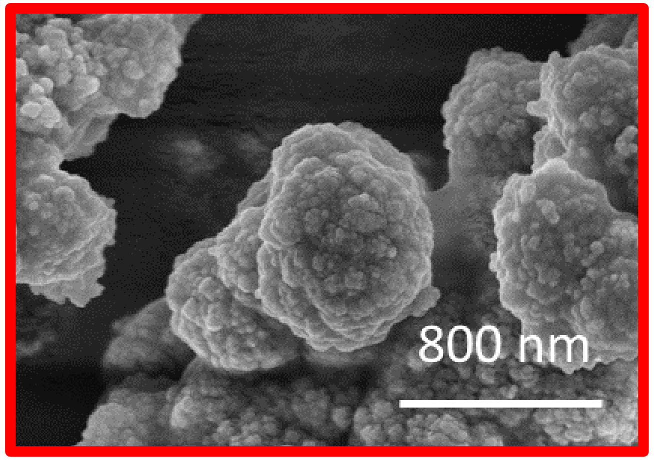
VPO_4, $VOPO_4$, NaF and Na_2CO_3 with a molar ratio 1:1:1:1

550° C 2 hours

Argon flow

Example: case of $Na_3V_2(PO_4)_2FO_2$





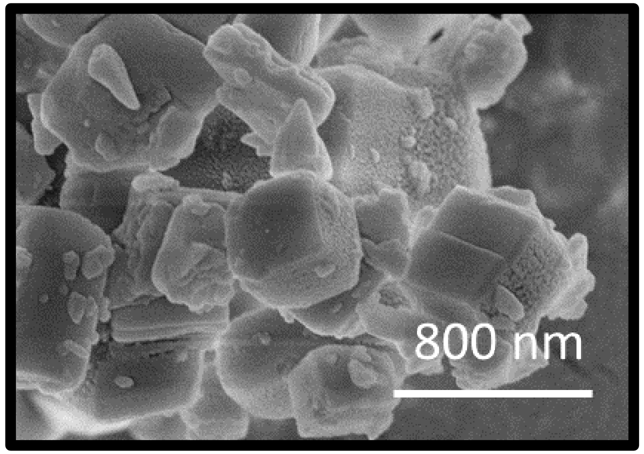
$NVPFO_2$-Nano
Crystallite size: ~30 nm

- $VO(acac)_2$, NaF and H_3PO_4 (molar ratio of 1/1.5/1)
- 4.5 mL ethanol / 4.5 mL H_2O
- Autoclave 180°C 10 hours

Same phase, same composition but different particles size and crystallinity

Olchowka et al. *Nanoscale*, 2022

Particle's nanosizing



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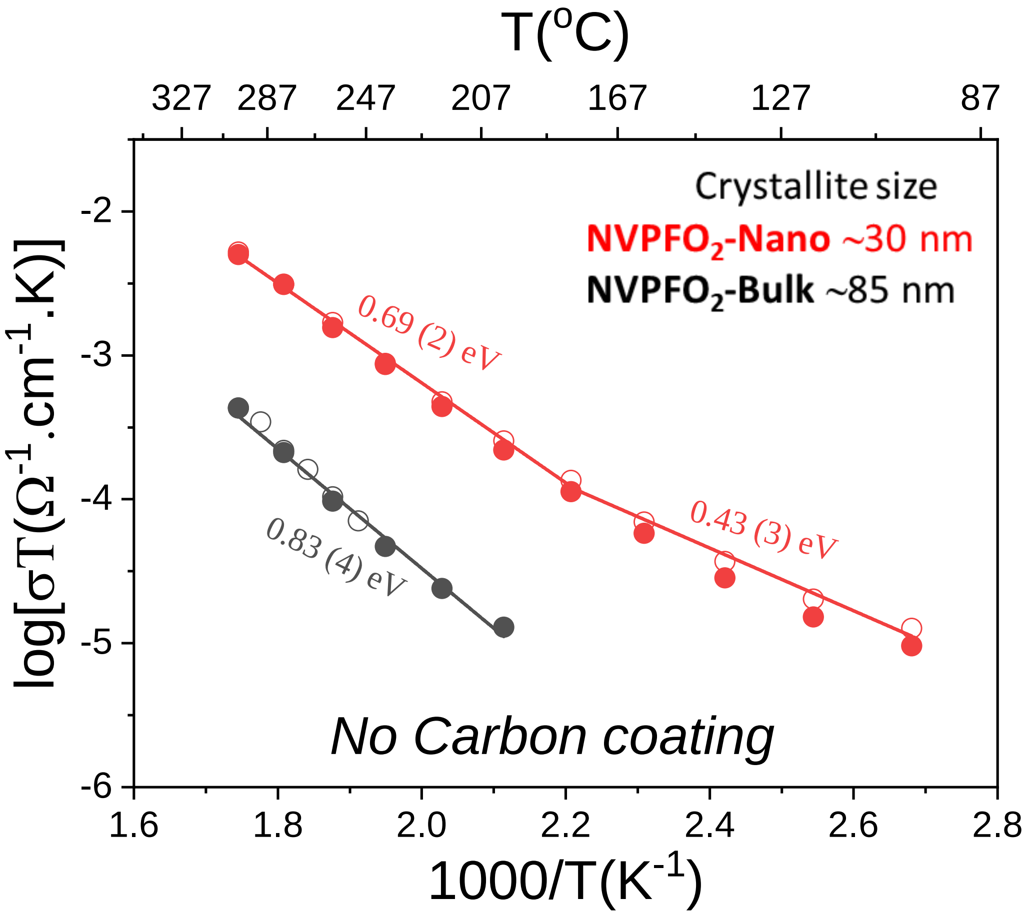

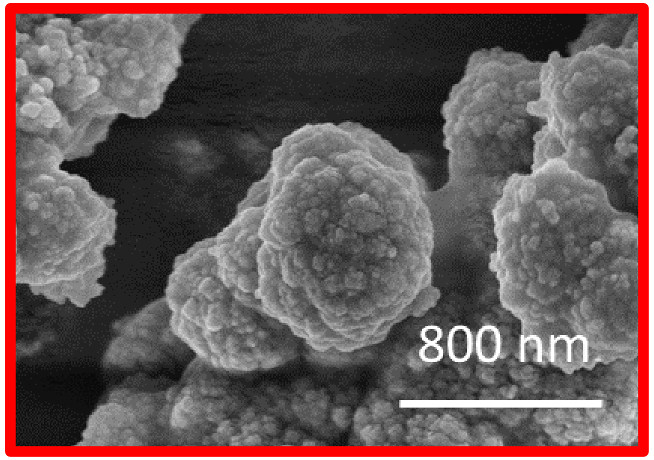

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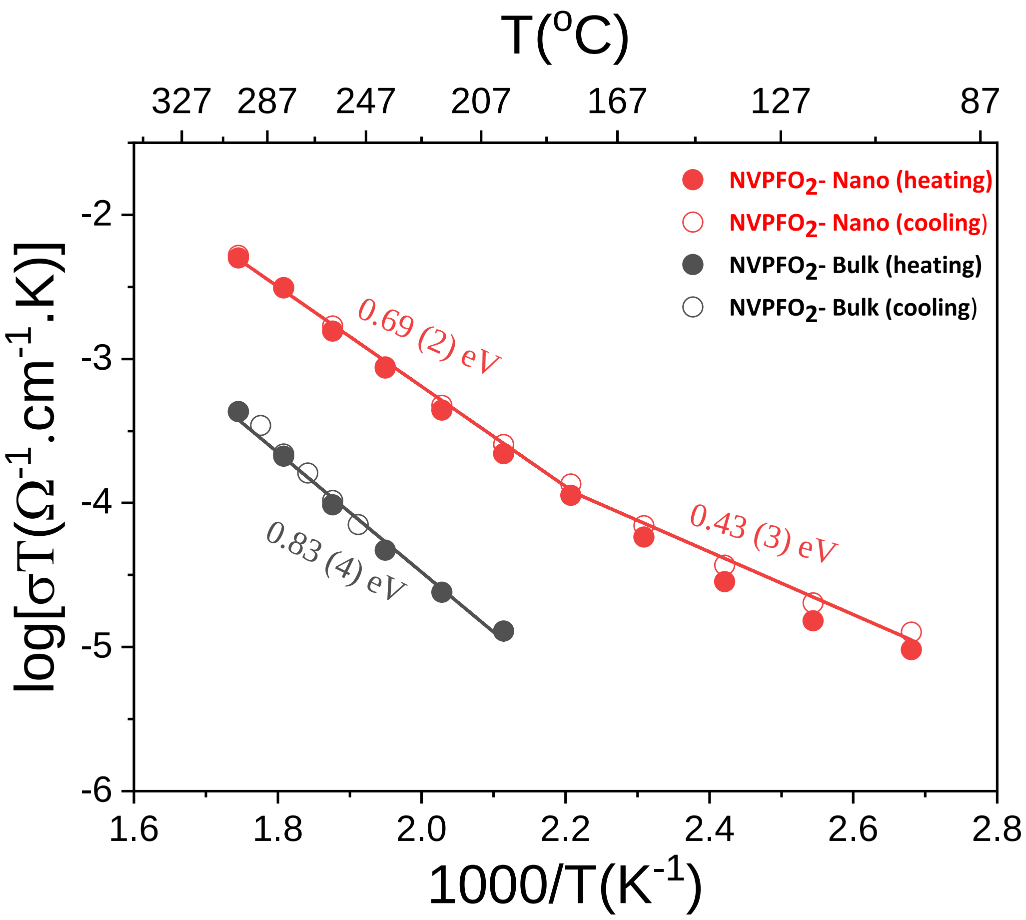
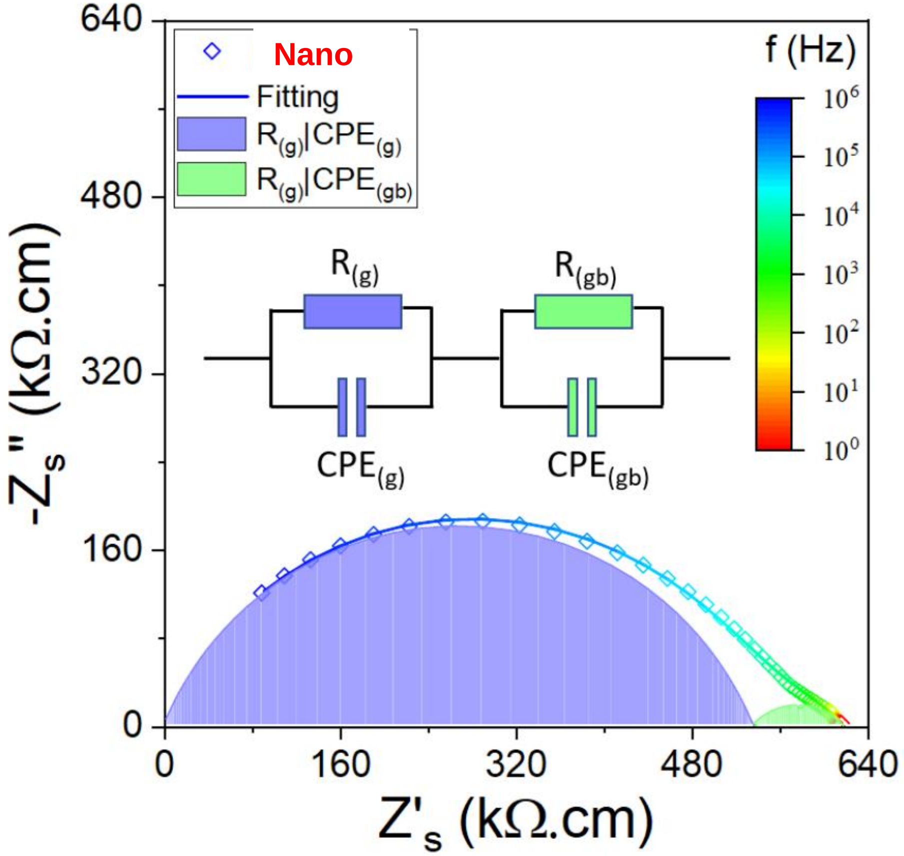
Morphology and cristallinity
Very important influence on electrical conductivity

Olchowka et al. *Nanoscale*, 2022

Particle's nanosizing





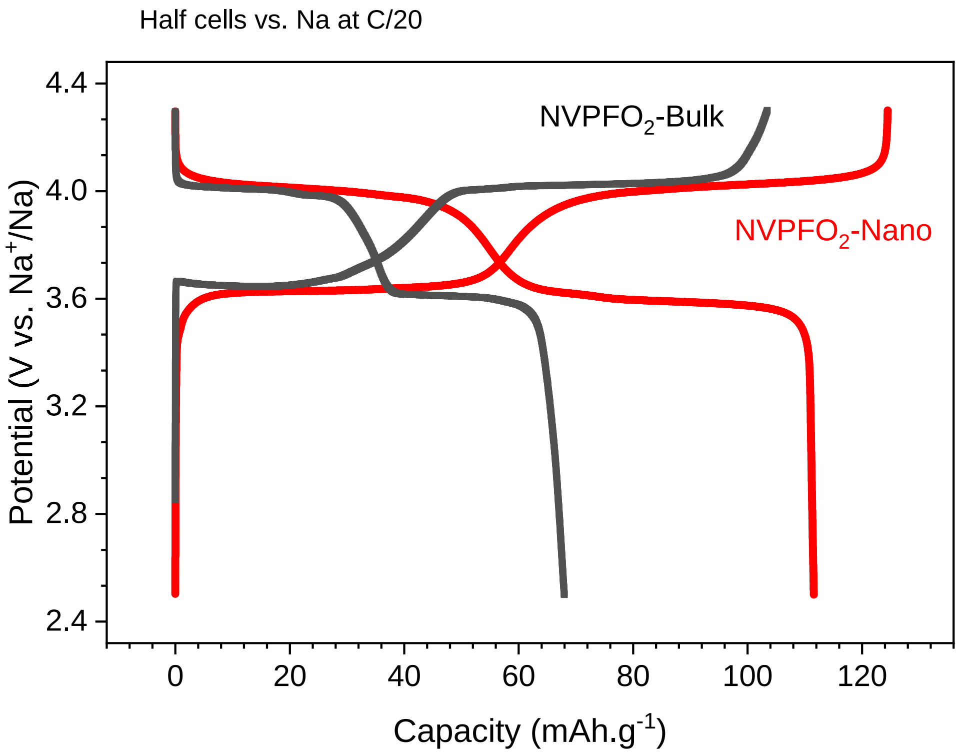
E= OCV
T= 200 °C

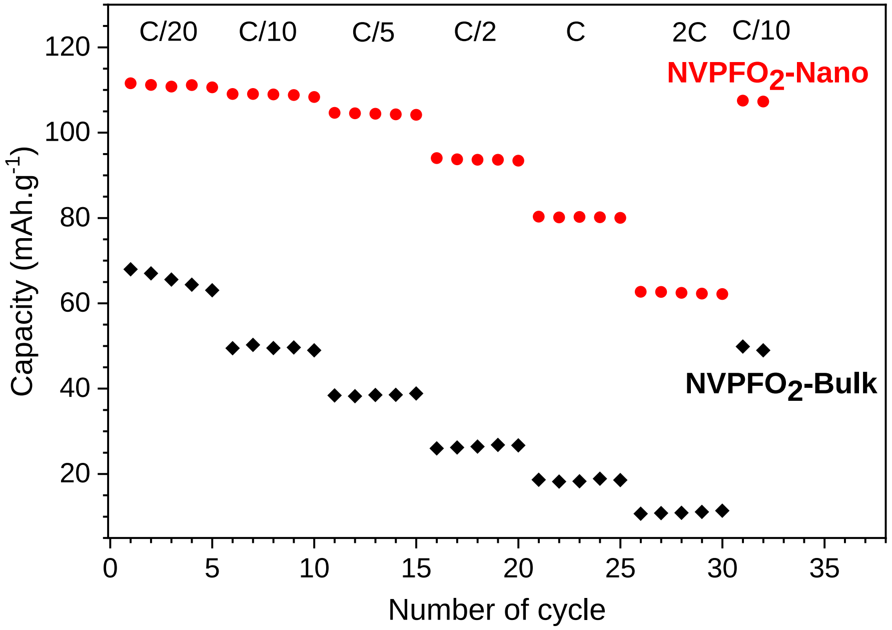
Grain impedance response is about one order of magnitude higher than that of the grain boundaries
→ impedance observed is the impedance of material

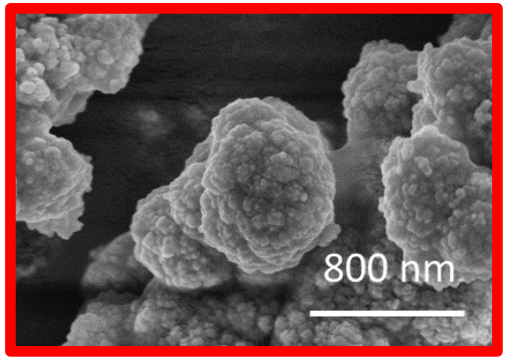
Absence of polarization phenomenon (low f)
→ mostly electronic conductors at this temperature.

Olchowka et al. *ACS Applied Energy Materials*, 2022

Particle’s nanosizing







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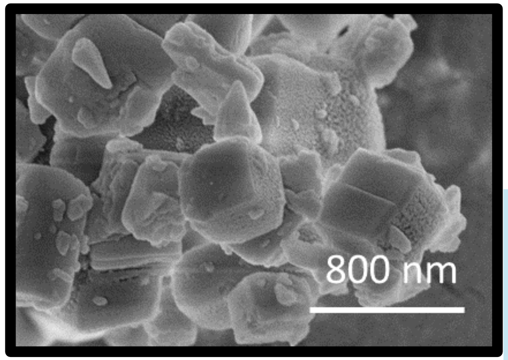


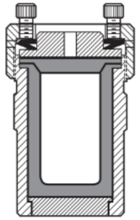
$NVPFO_2$-Bulk
Crystallite size: ~85 nm

Key Message:

Small particle size **decreases electron diffusion parameters**
(benefit: high rate capability; detriment: need for percolation to current collector)
High surface area **allows active material to absorb Na^+ (Li^+) more effectively**
(benefit: higher capacity; detriment: higher reactivity electrode/electrolyte)
Small particle size **may accommodate crystalline expansion of lattice**
(benefit: improved cyclability)

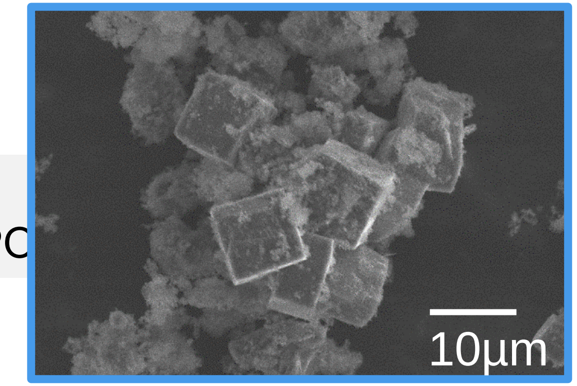
Olchowka et al. *Nanoscale*, 2022

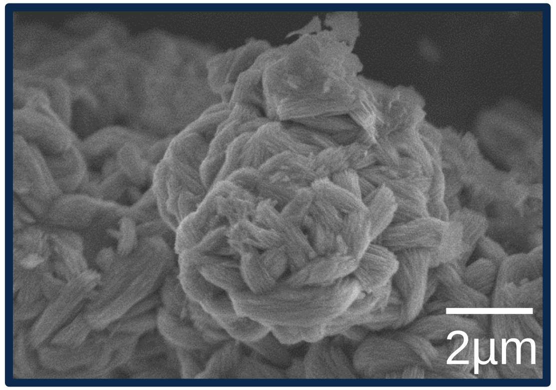
Particles morphology and orientation

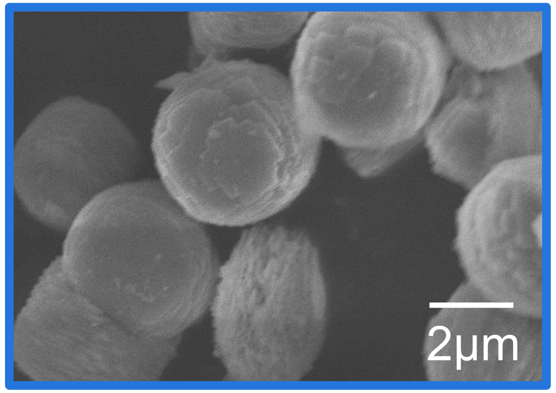


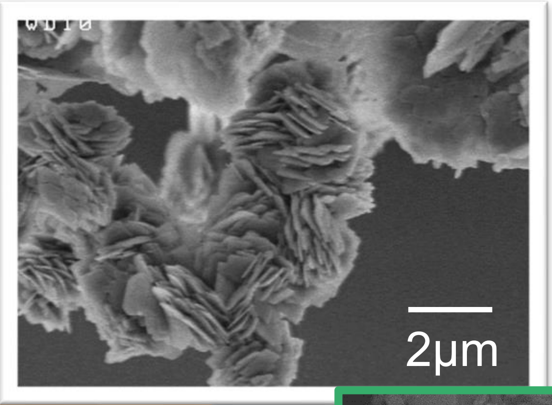
Solvothermal synthesis

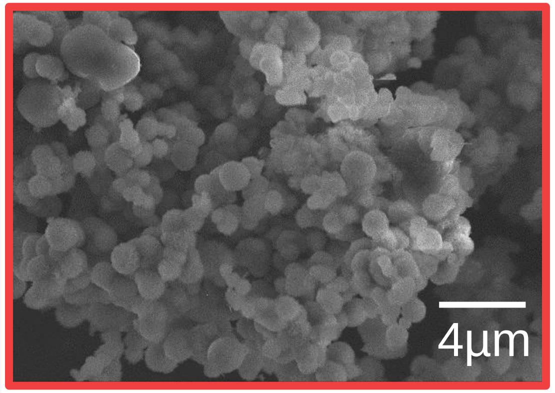
1	**Different precursors:** $xV(C_5H_7O_2)_3/VCl_3/\ldots + yNaF + zH_3PO_4/NaH_2PO$
2	**Different stoichiometries**
3	**Oven:** Standard/microwave oven
4	**Additives:** F127/citric acid etc...
5	**Heating rate:** 1°C / min, 10°C / min etc…
6	**Solvent:** DMF/Ethanol/Water/Acetone/IL/DES

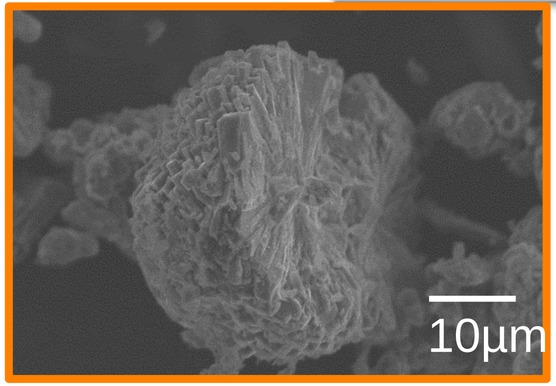


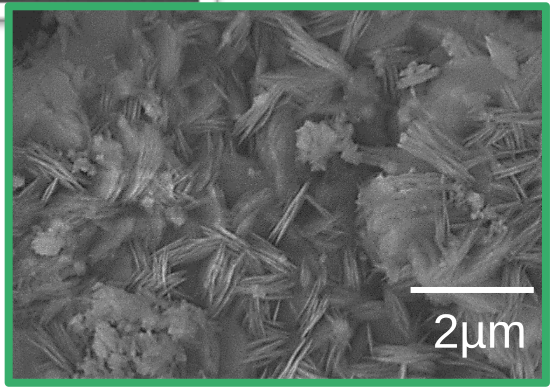








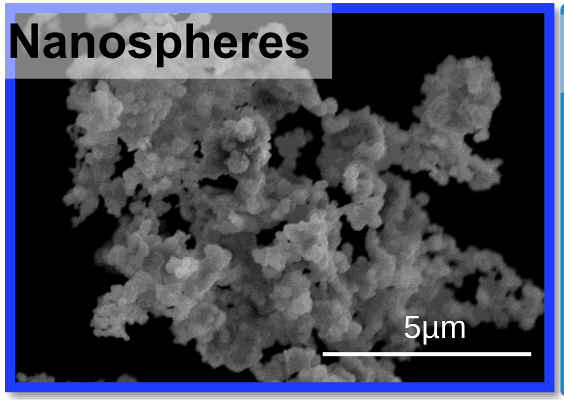




Particles morphology and orientation

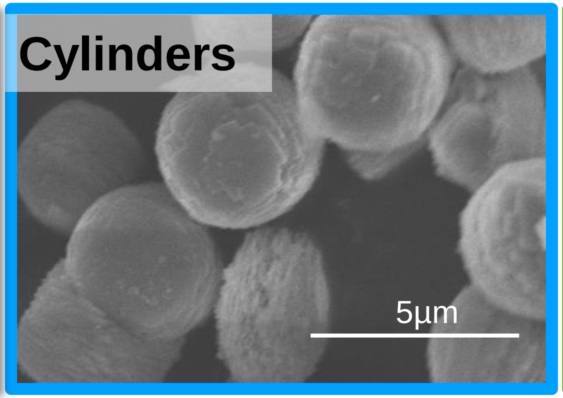
4 samples with homogenous morphologies, good crystallinity and no amorphous part
Reproducible syntheses

∅ ~300-400 nm



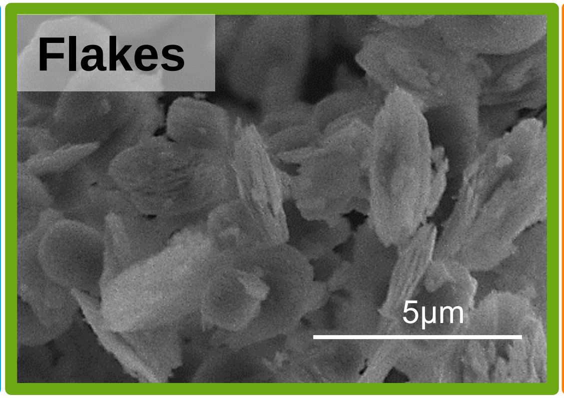
$1V(acac)_3$:**1.5**NaF:**1**H_3PO_4
H_2O:Ethanol=**50%:50%**
10h 180°C autoclave

Length ~3 µm thickness: ~5µm



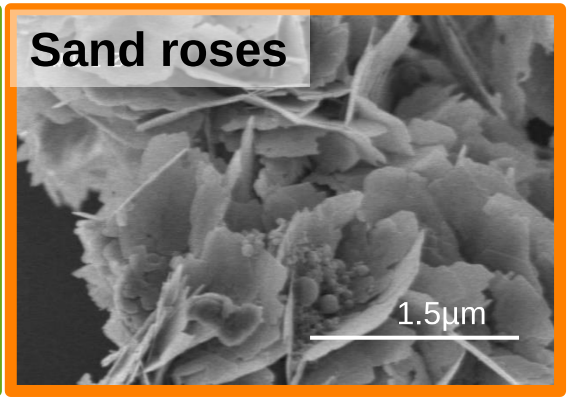
$1V(acac)_3$:**1.5**NaF:**1**H_3PO_4
H_2O:Ethanol=**10%:90%**
Pluronic F127 90mg
10h 180°C autoclave
1°C/min

∅ ~3 µm thickness: nanometric



$1V(acac)_3$:**1.67**NaF:**1.5**H_3PO_4
H_2O:Ethanol=**10%:90%**
10h 180°C autoclave
0.5°C/min

∅ ~1 µm



$1V(acac)_3$:**1.67**NaF:**1.5**H_3PO_4
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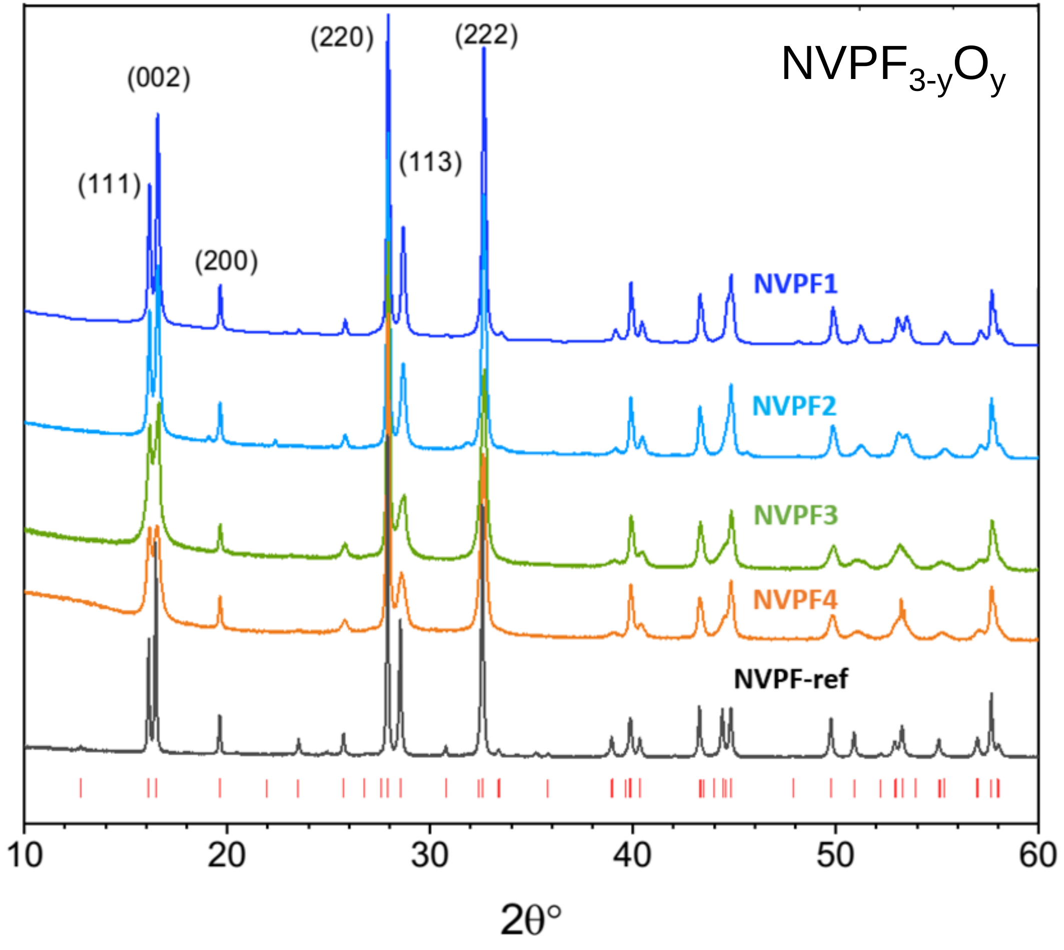
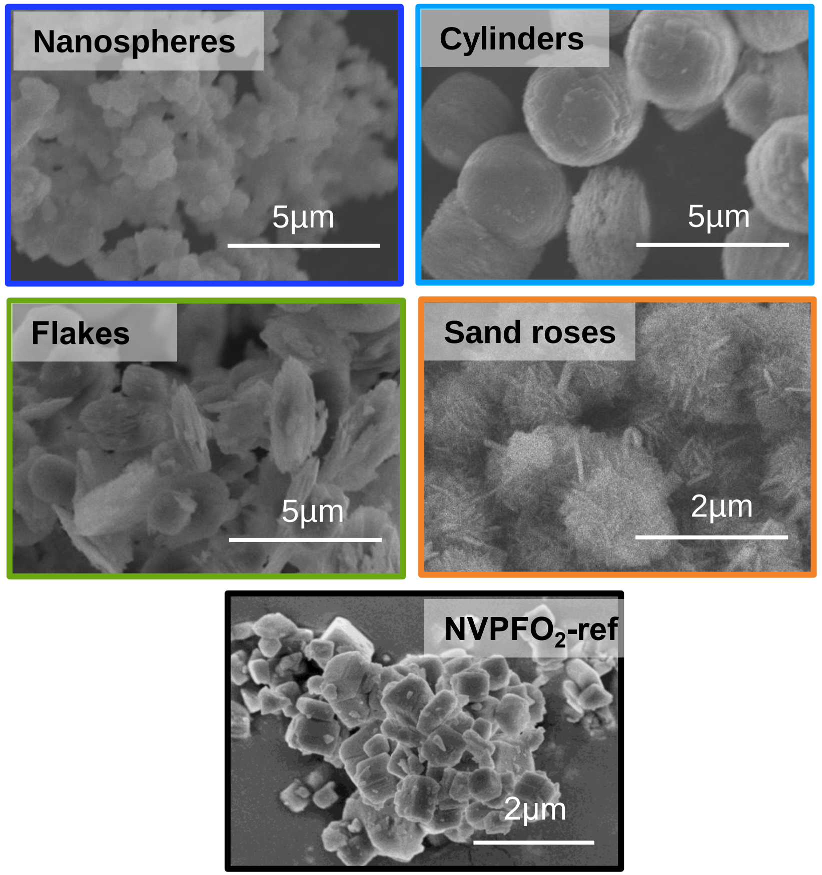
Fang et al., *Batteries and Supercaps.* **2022**, *5*, 1.

Particles morphology and orientation





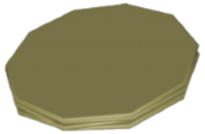
Similar crystallite size ~40-50 nm but different morphology

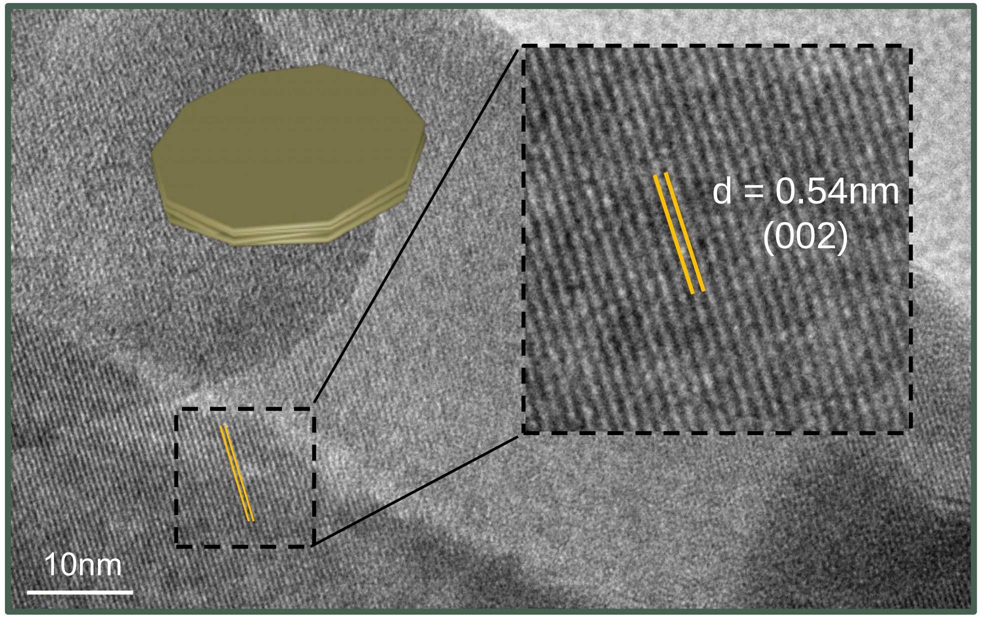
~90 nm for the reference

Fang et al., *Batteries and Supercaps.* **2022**, *5*, 1.

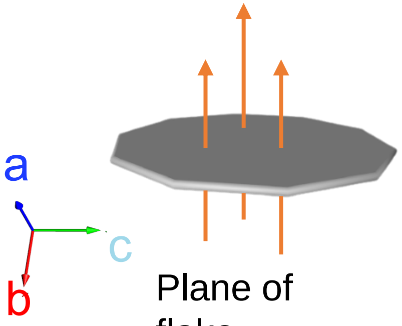
Cylinders, Flakes and Sand roses

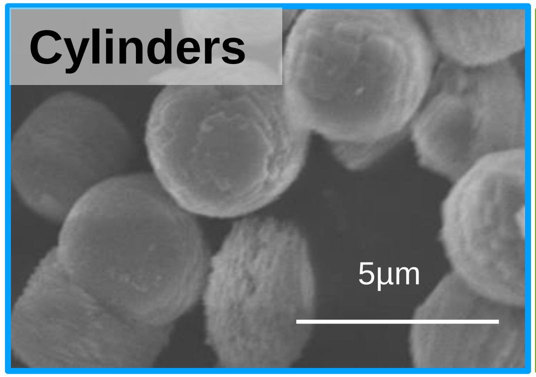
Primary particles exhibit lattice fringes of *(002)* an orientation of the nanoplatelets along c-axis

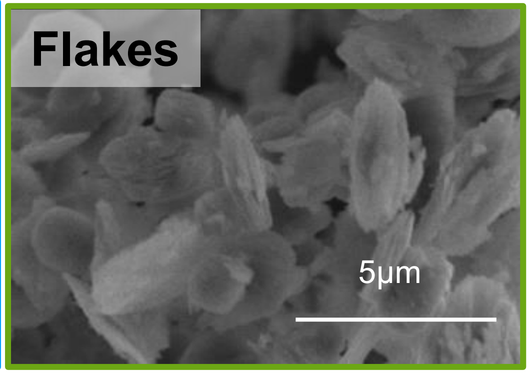




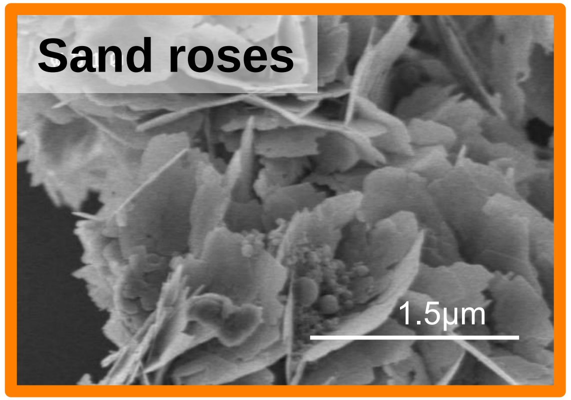
Fang et al., *Batteries and Supercaps*. **2022**, 5, 1.







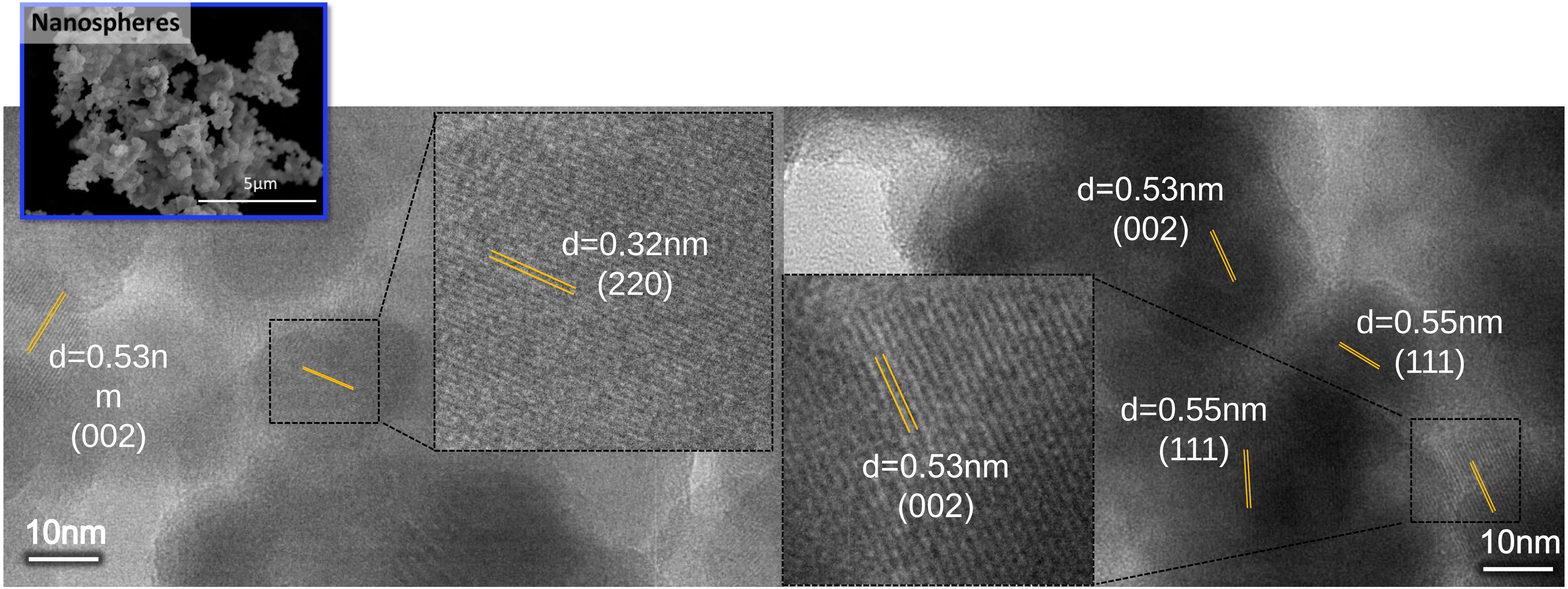
Stacking of nanosheets risks of causing **difficult Na^+ migration**



Easy access to the surface of the nanosheets should **promote Na^+ diffusion**

Fang et al., *Batteries and Supercaps*. **2022**, 5, 1.

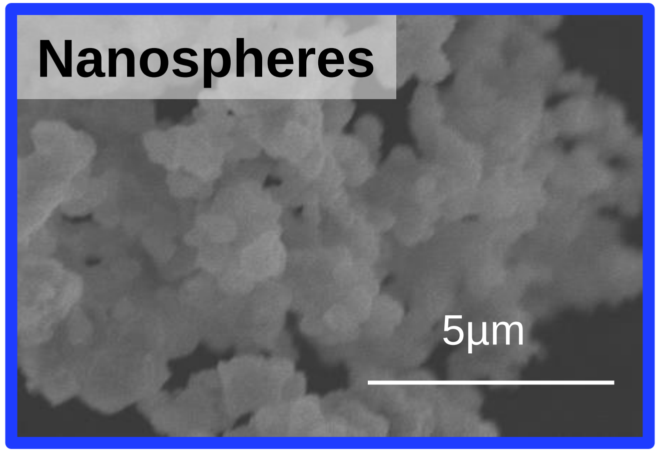
Particles morphology and orientation

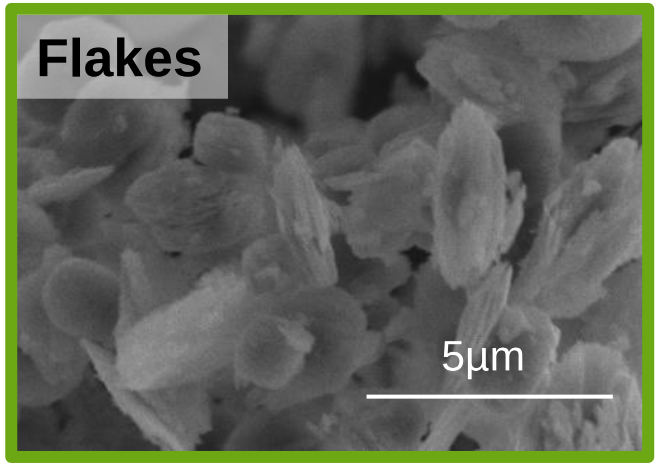


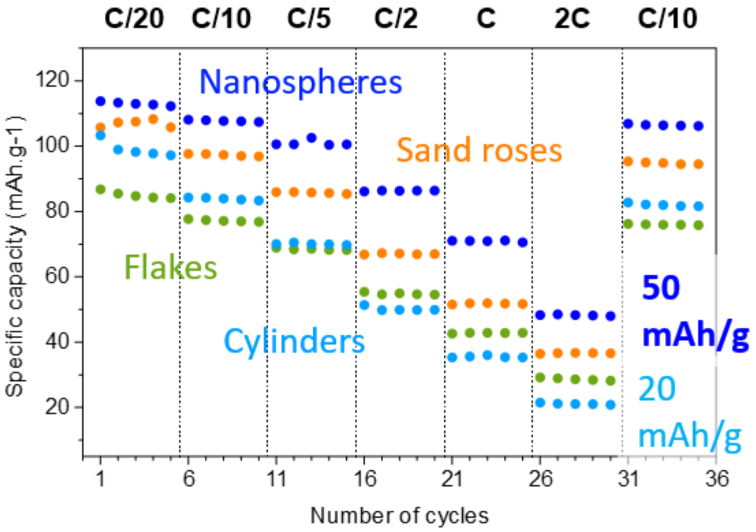
Primary particles exhibit different lattice fringes (220), (002) and (111)
→ tends to confirm spherical morphology which should **promote Na^+ diffusion**

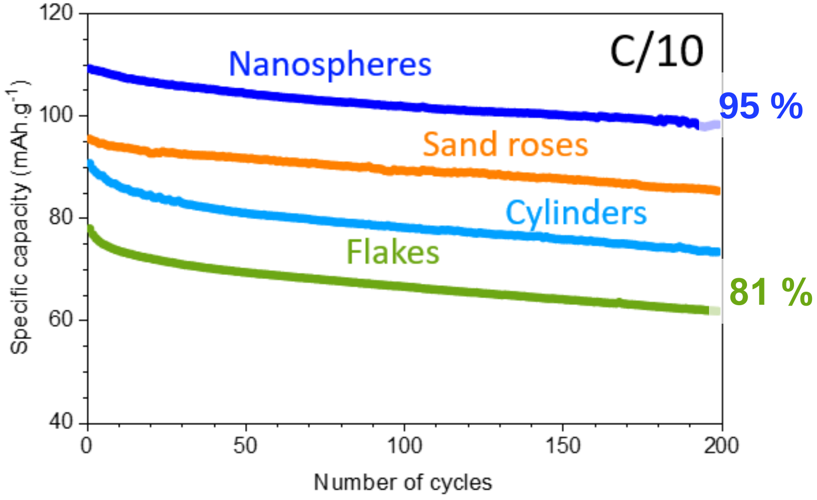
Fang et al., *Batteries and Supercaps*. **2022**, *5*, 1.

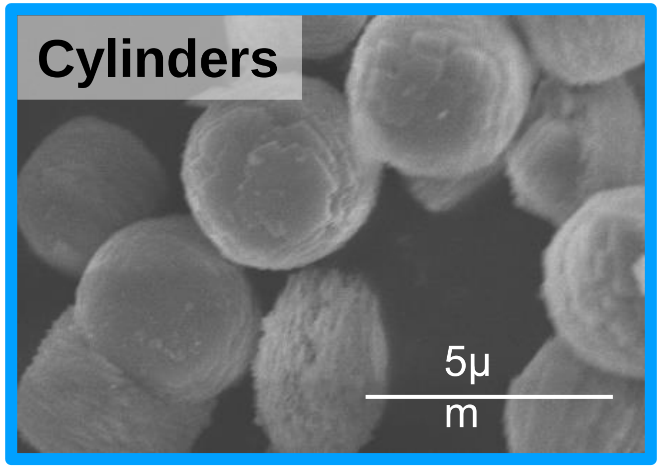
Particles morphology and orientation

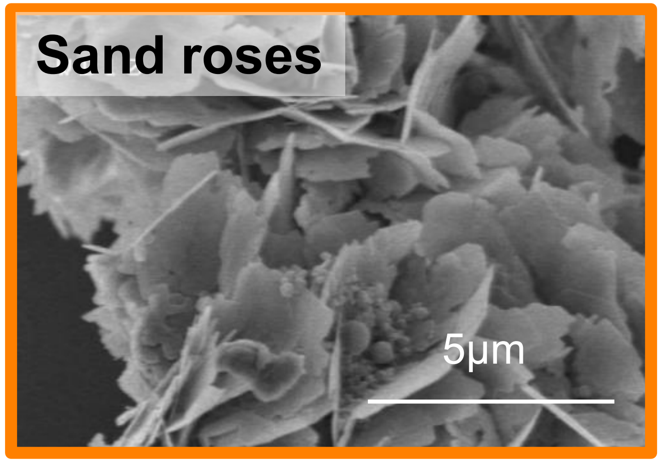








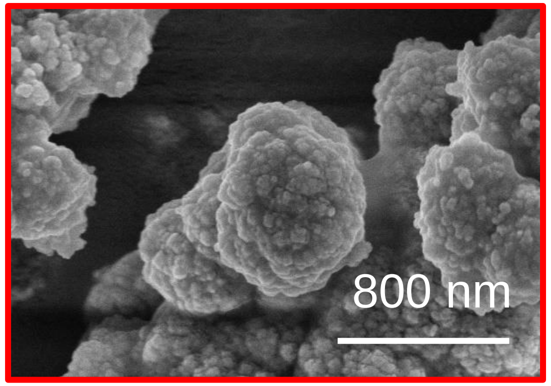




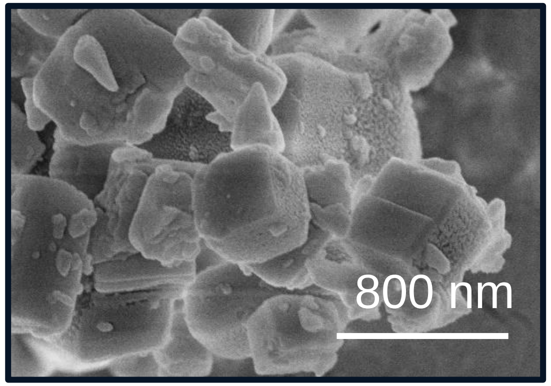
Particles morphology can strongly affected the electrochemical performance
"Nanospheres" deliver the best performance

Fang et al., *Batteries and Supercaps.* **2022**, *5*, 1.

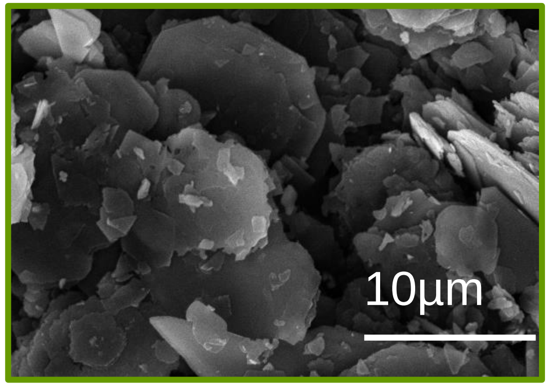
Why commercial cathode material are not « nano »



Solvothermal
Nanospheres

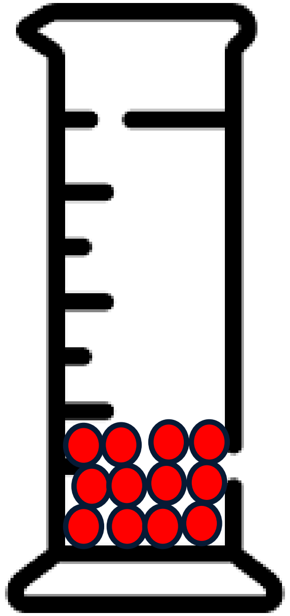


Solid state
Cubes

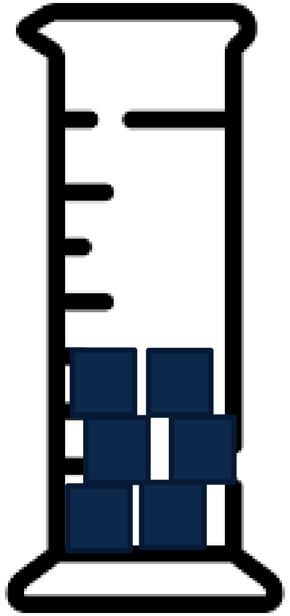


Ionothermal method
Flakes

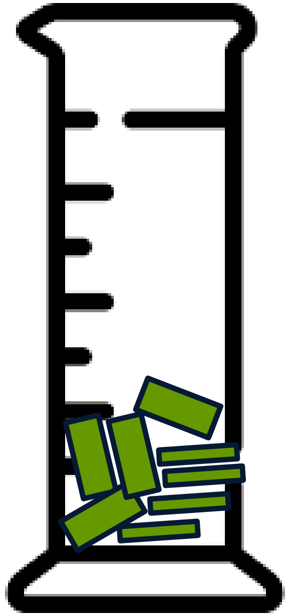
Tapped density



0.85 g/mL



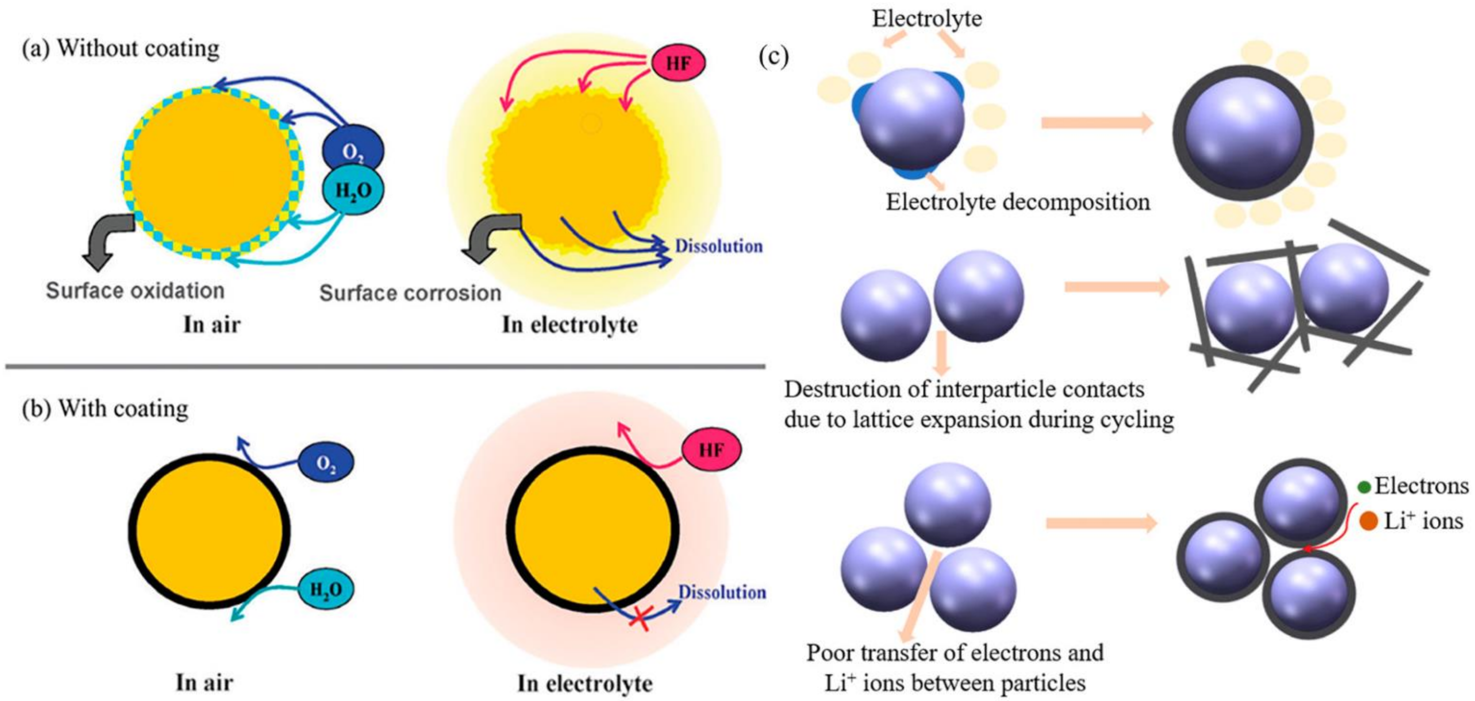
1 g/mL



0.7 g/mL

Synthesis of carbon coated material

Early 20th century Michel Armand ($LiFePO_4$)



Method to apply a Carbon coating

Hydrothermal / Solvothermal

Sol-Gel Method

The Chemical Polymerization Routes

High-Temperature Solid-State Method

Chemical Vapor Deposition

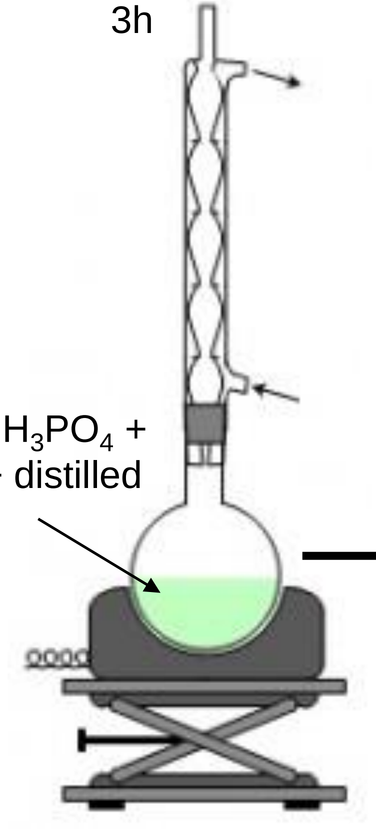
Physical Vapor Deposition

Li, H. et al. Chem. Commun. 2011, 48, 1201–1217

Synthesis of carbon coated material

Reflux, 100°C
3h

$V_2O_5 + H_3PO_4 +$
$HNO_3 +$ distilled
water



→ $VOPO_4.2H_2O$

5°C/min — 250°C, 2h — Under O2 flow — 5°C/min

$VOPO_4$

+ carbon source
(e.g. sucrose)

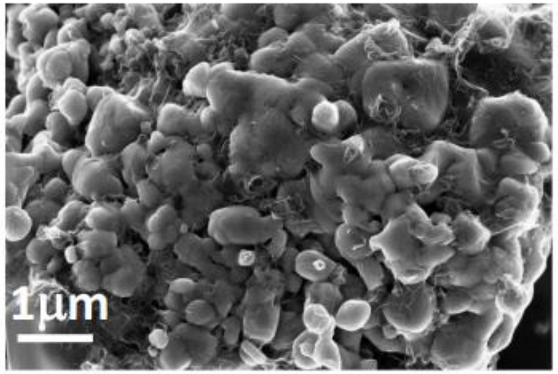
5°C/min — 890°C, 2h — Under Ar/H_2 flow — 5°C/min

VPO_4

700°C / Ar flow
+ 1.5 NaF
+ Carbon source

→ $Na_3V_2(PO_4)_2F_3@C$

$C\text{-}VPO_4$ + 1.5 NaF → $Na_3V_2(PO_4)_2F_3@C$

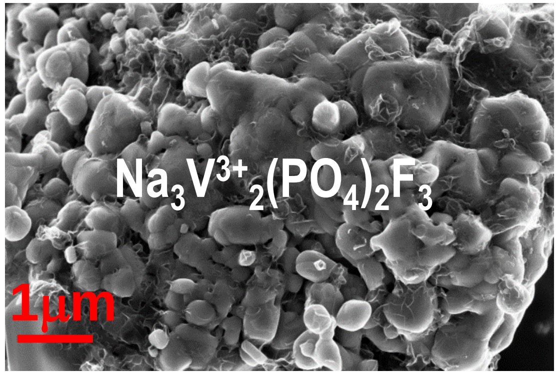


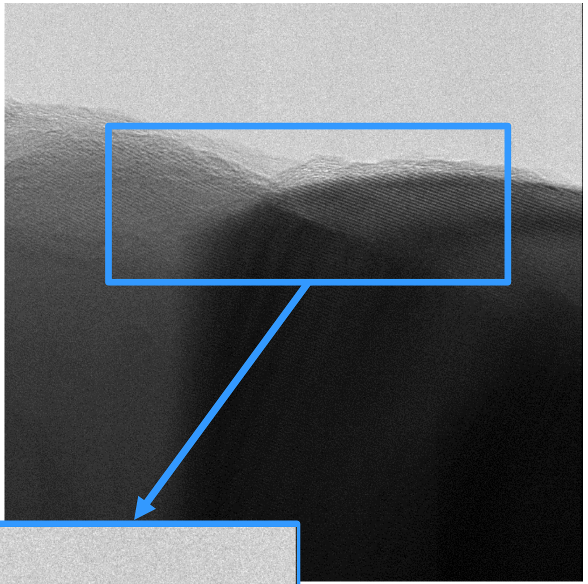
Broux, Fauth, Hall, Chatillon, Bianchini, Bamine, Leriche, Suard, Carlier, Reynier, Simonin, Masquelier, Croguennec - Small Methods 2019

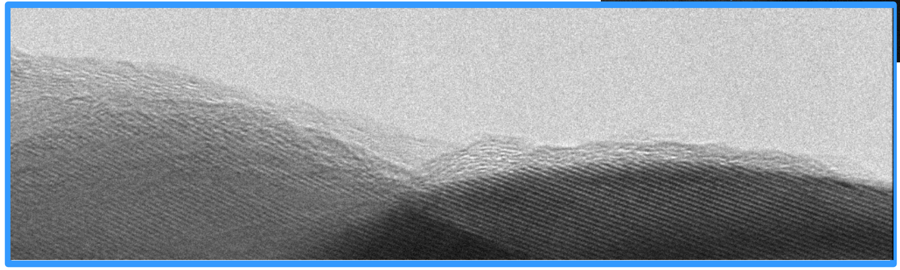
Synthesis of carbon coated material

An homogenous **coating** at the material surface

Prepared from cellulose decomposition

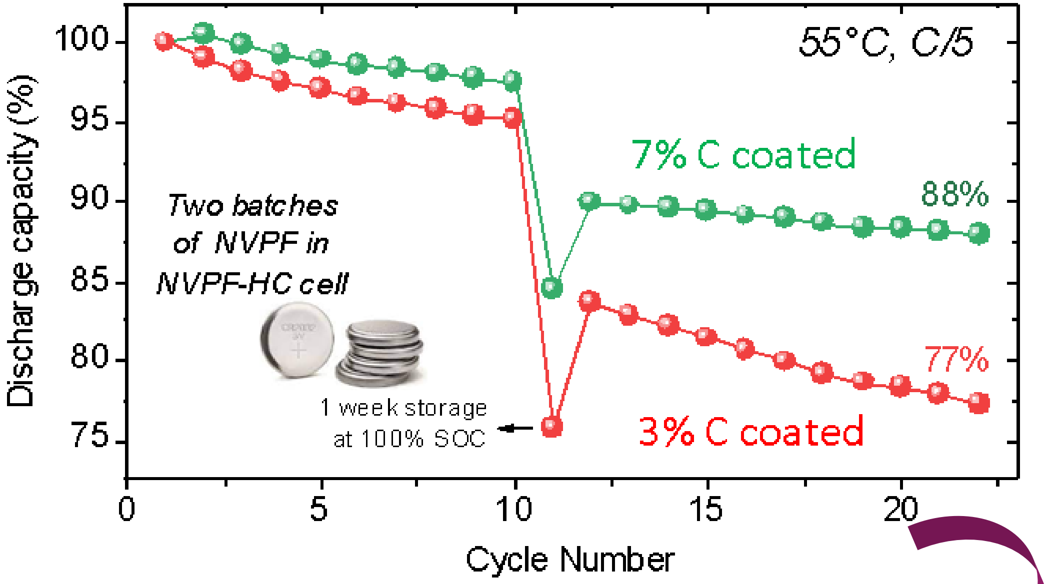




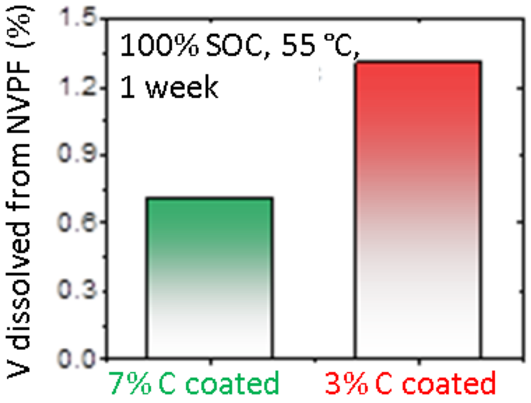


Increase electronic conductivity
Stabilize the material / avoid V dissolution

Broux et al. - Small Methods 2019



$Na_3V_2(PO_4)_2F_3$ // 1M $NaPF_6$ in EC-DMC // Hard carbon

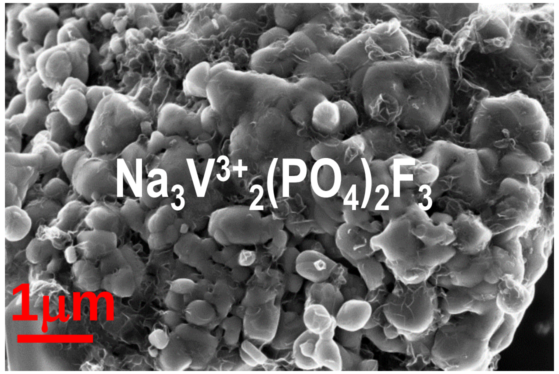


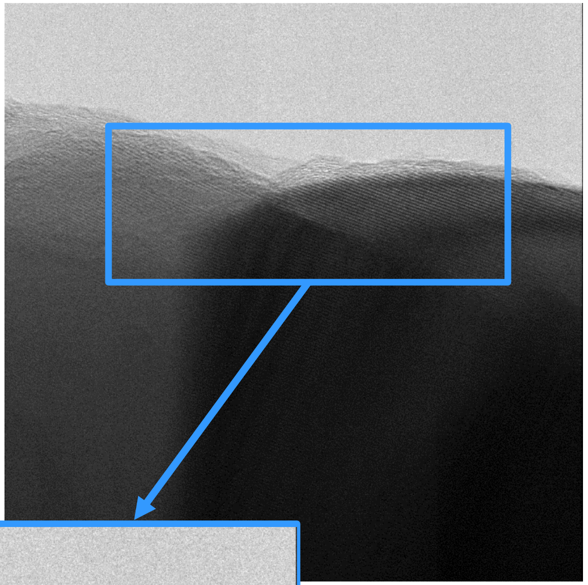
Desaii et al., Energy Storage Materials, 2023

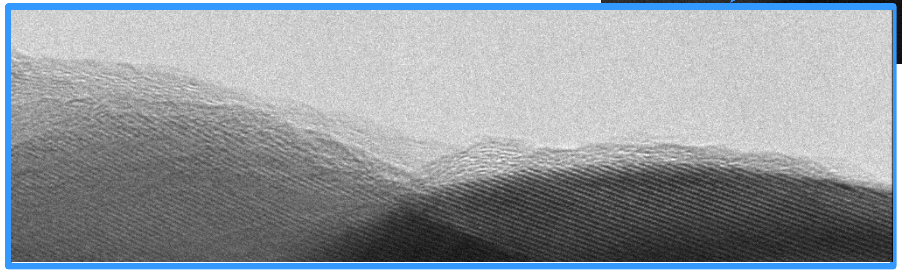
Synthesis of carbon coated material

An homogenous **coating** at the material surface

Obtained from cellulose decomposition

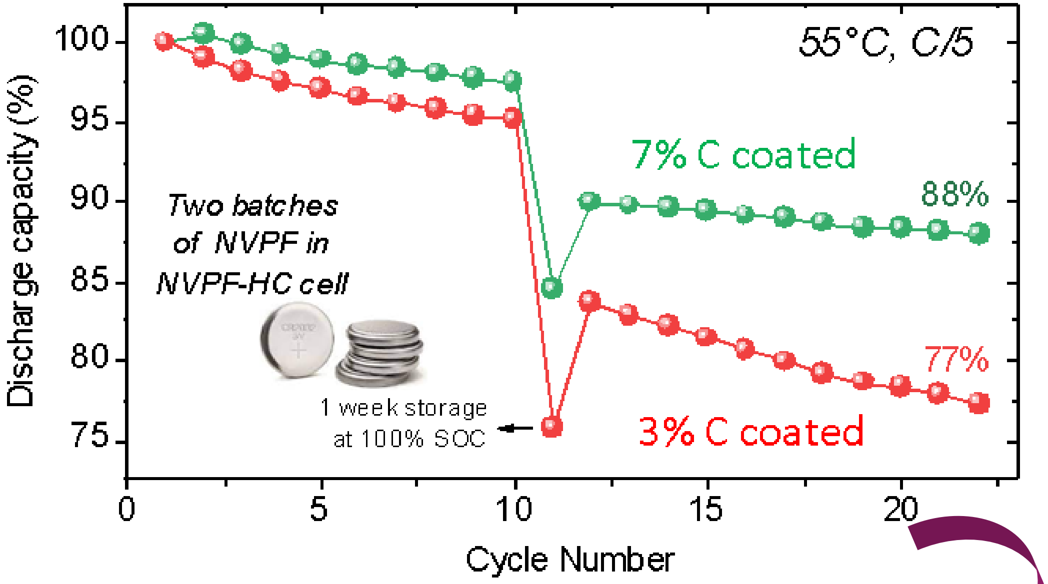




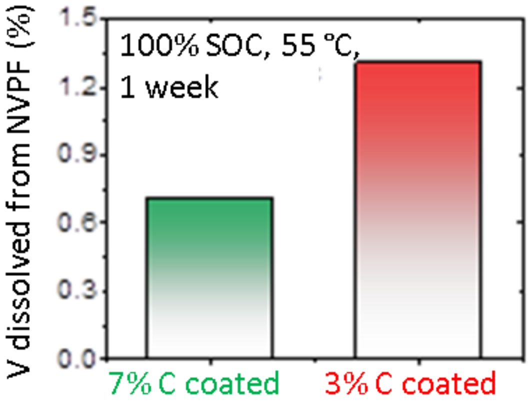


Increase electronic conductivity
Stabilize the material / avoid V dissolution

Broux et al., Small Methods, 2019

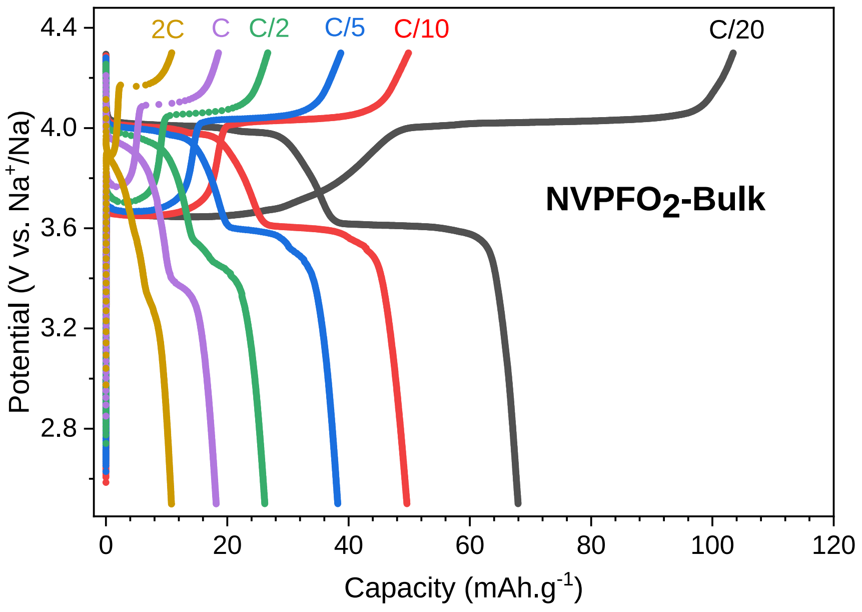


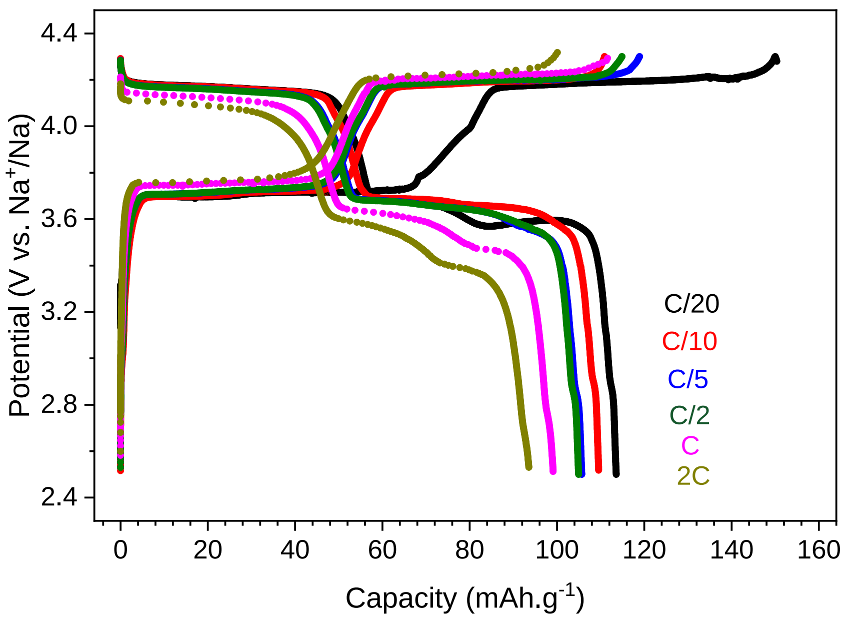
$Na_3V_2(PO_4)_2F_3$ // 1M $NaPF_6$ in EC-DMC // Hard carbon



Desai et al., Energy Storage Materials, 2023,

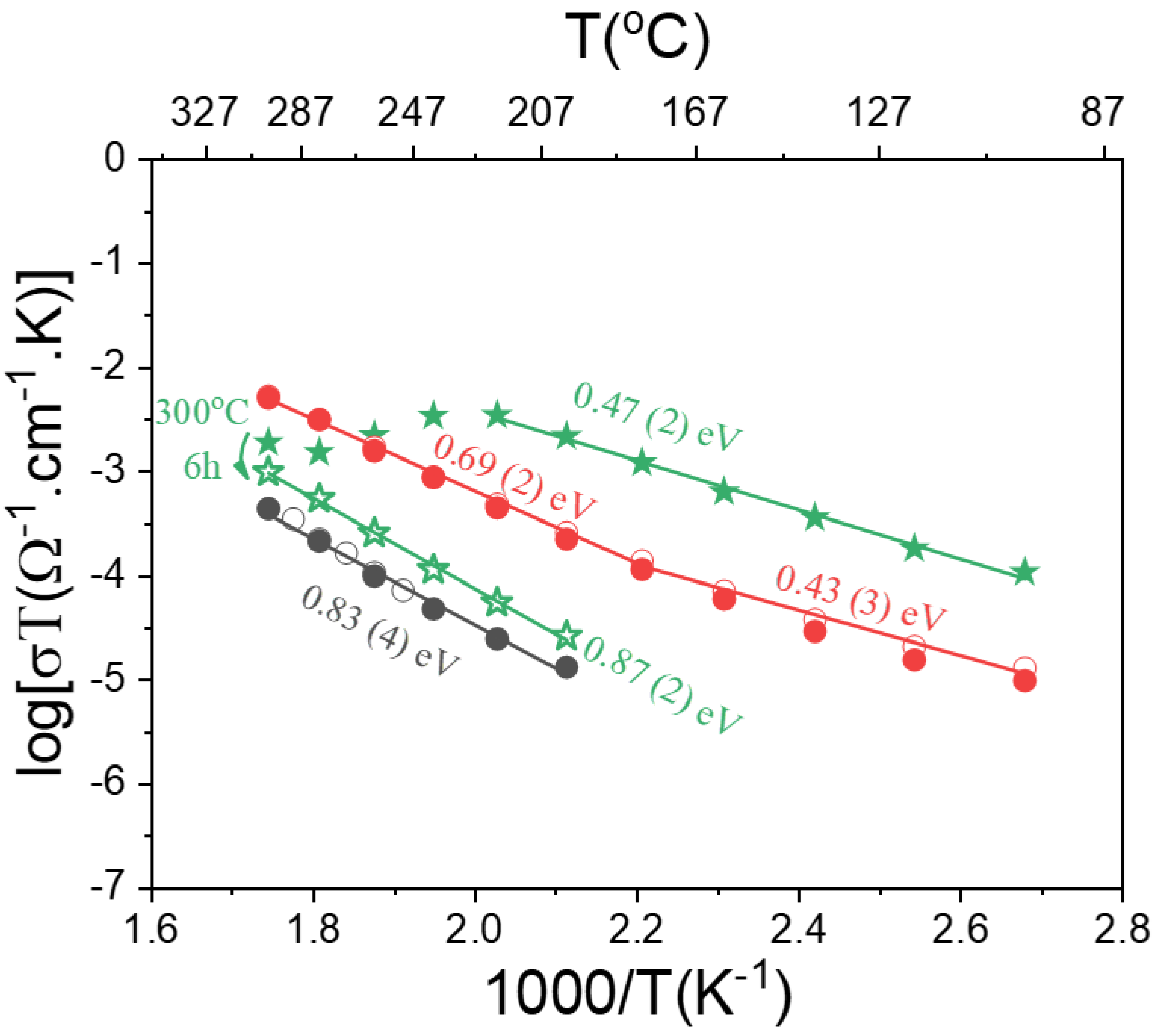
Synthesis of carbon coated material



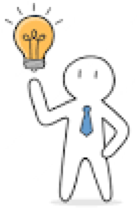


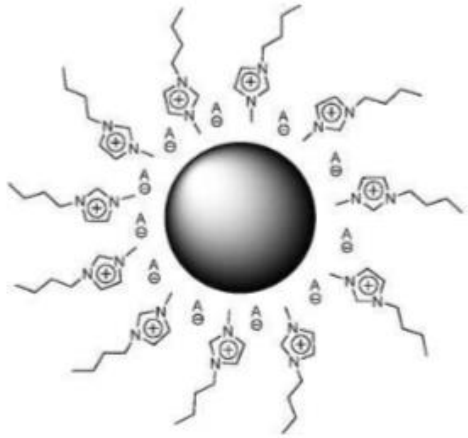
Better performance especially for fast charging

Arrhenius-like plots electric conductivity



Coating by an Ionic Liquid
to enhance ionic conductivity





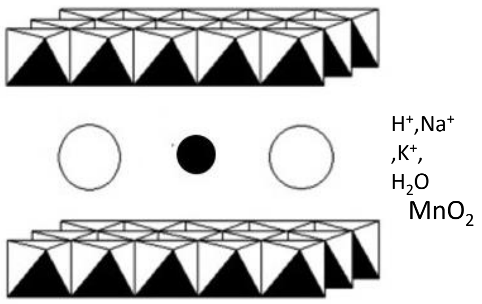
At 200 °C the conductivity:
$NVPFO_2$-Iono(h)≈$10^{-2.5}$ >
$NVPFO_2$-Nano≈$10^{-3.5}$ >
$NVPFO_2$-Bulk≈10^{-5}
≈**$NVPFO_2$-Iono**(c)

IL enhances significantly the ionic conductivity, especially at grain boundary
But do not really improves energy storage performance ☹

Olchowka et al. *Nanoscale*, 2022

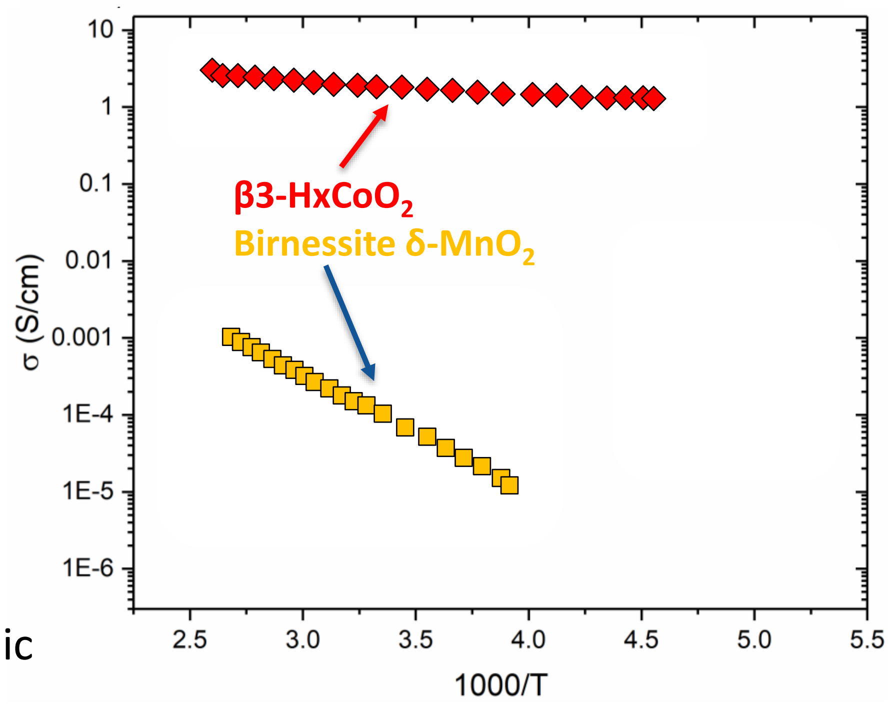
Towards composite materials

Birnessite δ-MnO_2

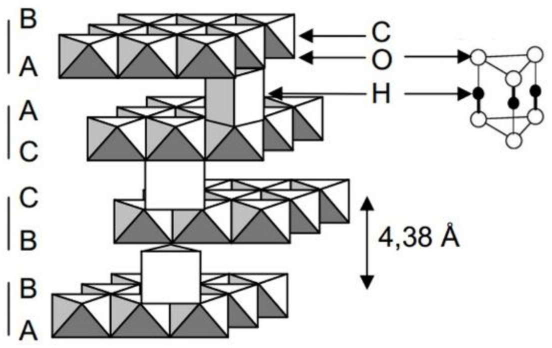


- Abundance
- Low cost
- Layered structure => favored the ionic diffusion
- High theoritical capacity : 300 mAh/g

Conductivity



β3-H_xCoO_2



- Good faradic properties
- High conductivity

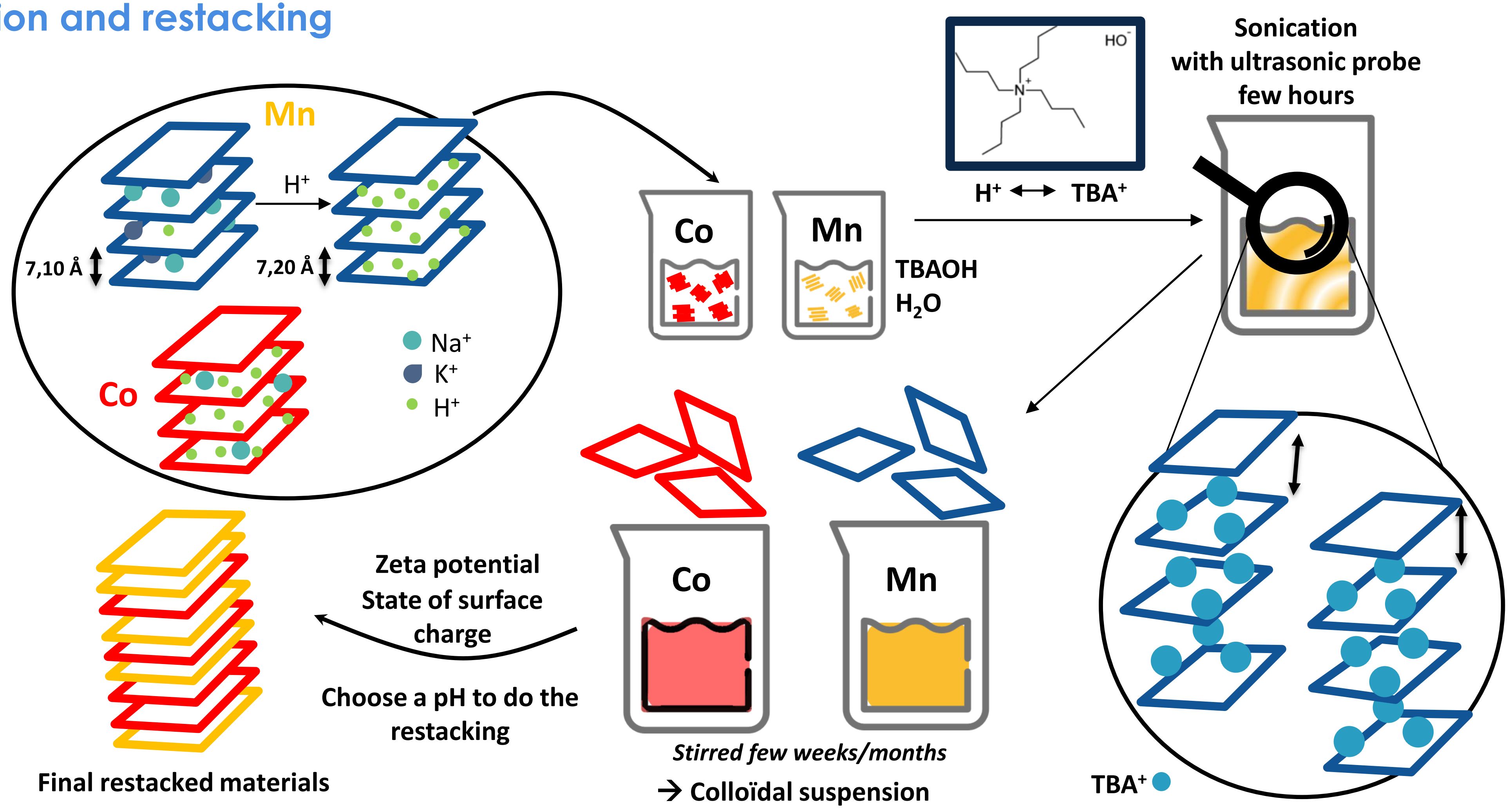
=> Combine the two materials for a synergy effect

=> Play on the morphology of the initial precursors

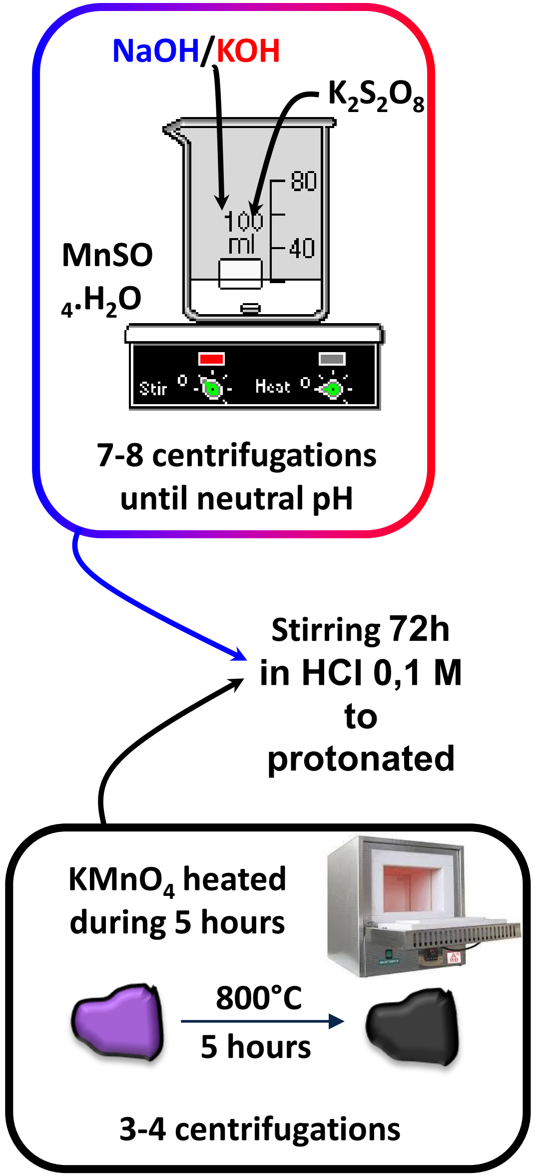
Invernizzi et al. Nanoscale advances, 2023

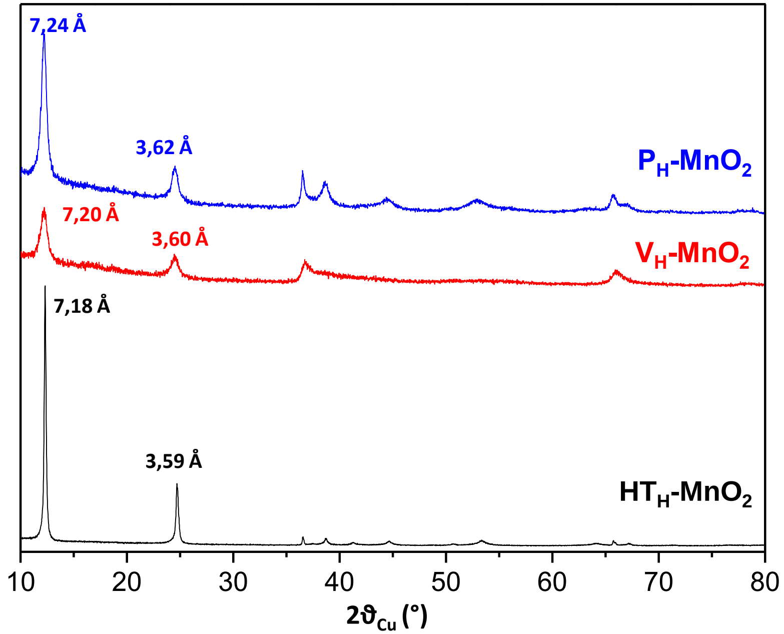
Towards composite materials

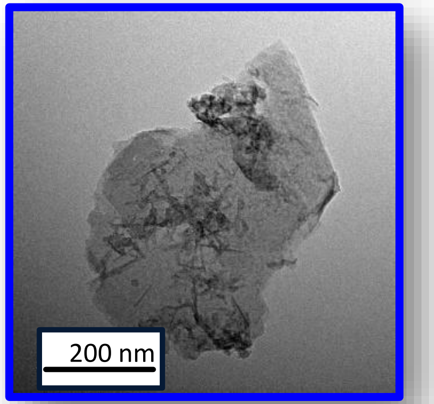
Exfoliation and restacking

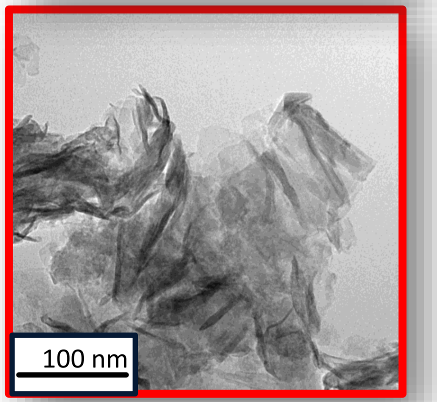


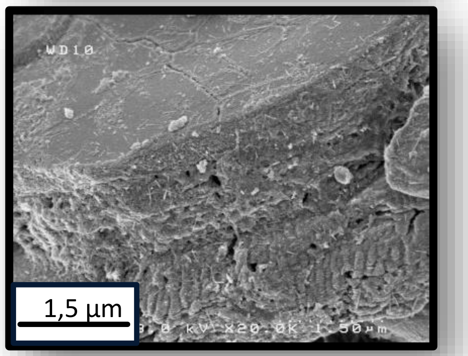
Towards composite materials











3 different morphologies for the birnessite

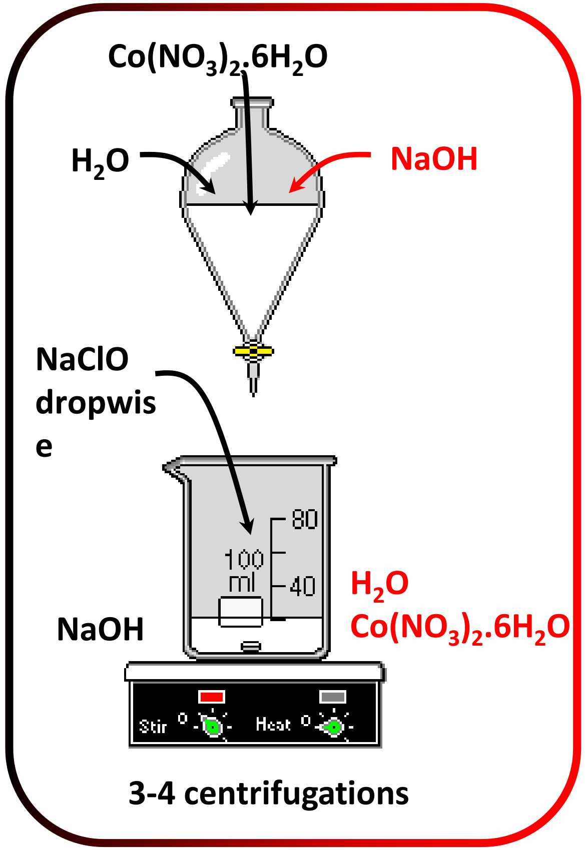
$Na_{(prec)}$ birnessite : small platelets (nm) P_H-MnO_2

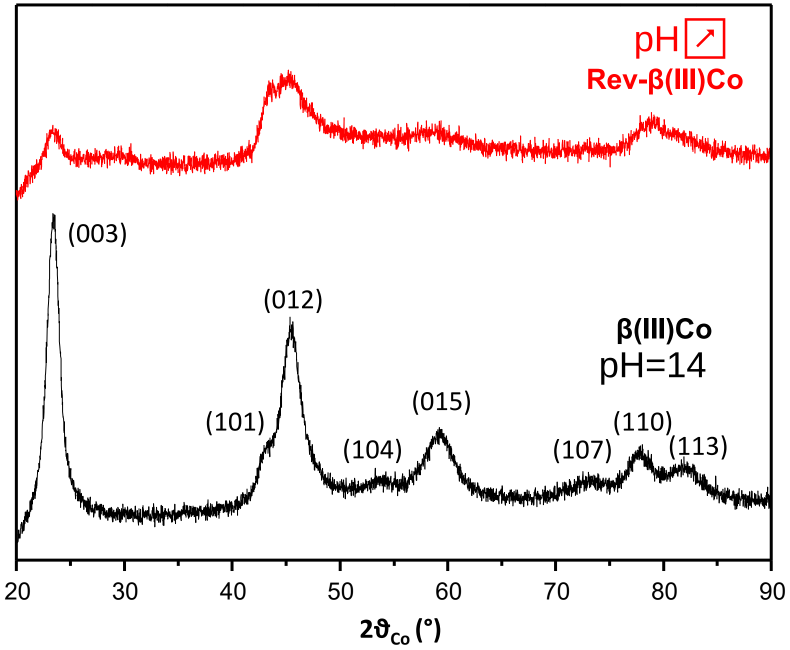
$K_{(prec)}$ birnessite : veals V_H-MnO_2

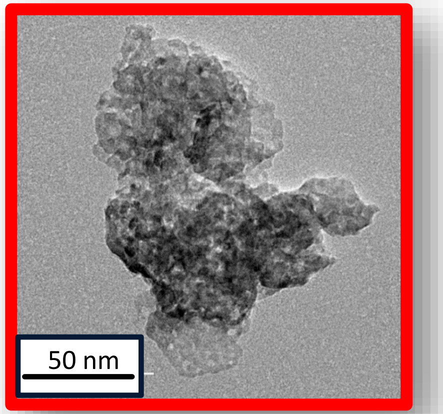
$K_{(solid)}$ birnessite : large platelets (µm) HT_H-MnO_2

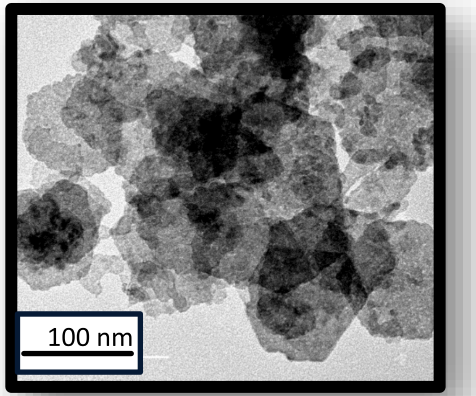
Invernizzi et al. Nanoscale advances, 2023

Towards composite materials









2 different morphologies for the β(III)Co :

β(III)Co => platelets (~80-100 nm)

Rev-β(III)Co => small platelets (~30 nm)

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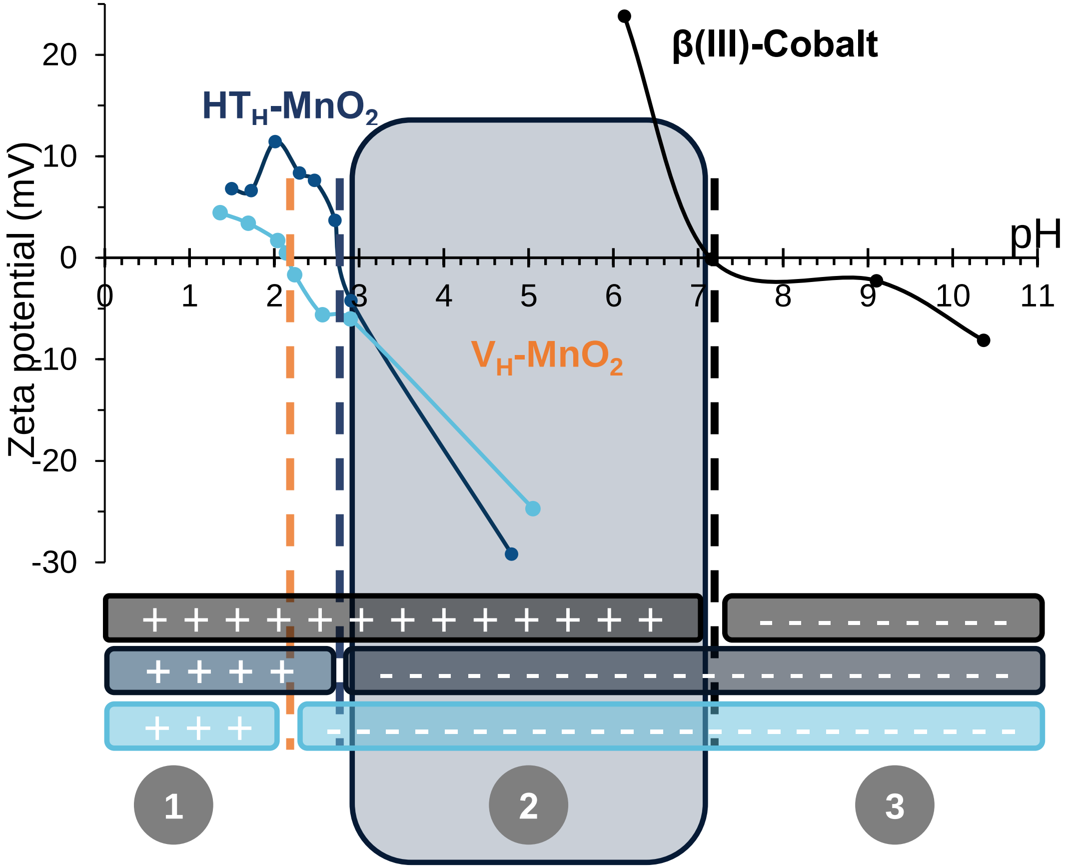
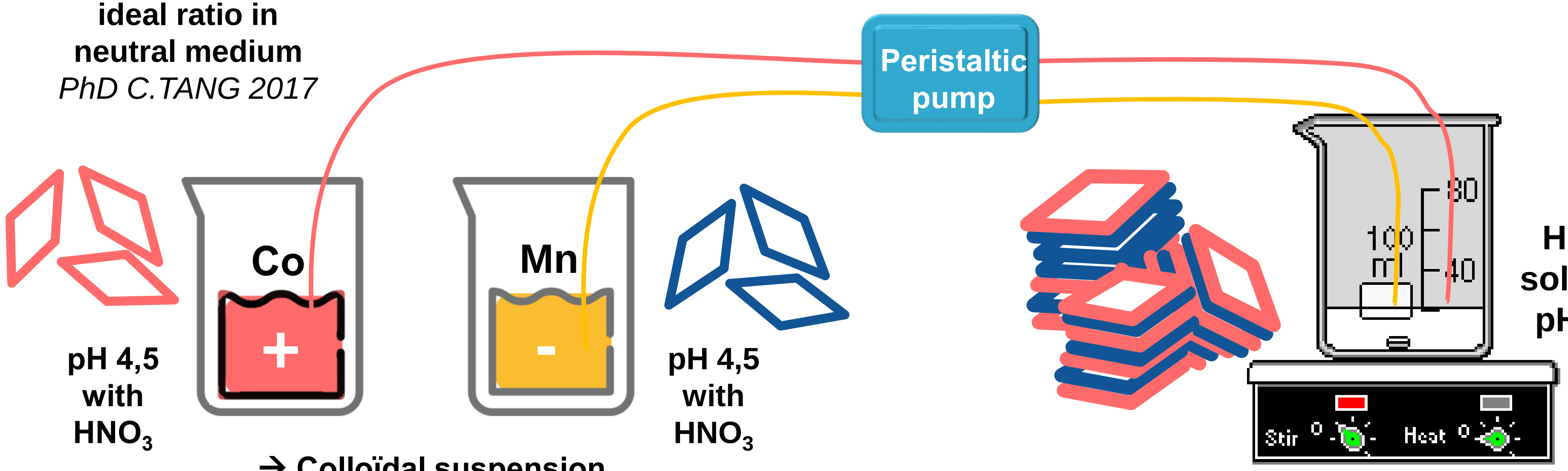


	Mn	Co
1	+	+
2	-	+
3	-	-

Large pH range to make the restacking : between 3 and 7 => 4.5

Towards composite materials

Molar Ratio
choose Mn/Co = 3 :
ideal ratio in
neutral medium
PhD C.TANG 2017



pH 4,5 with HNO_3

pH 4,5 with HNO_3

→ Colloïdal suspension

HNO_3 solution pH 4,5

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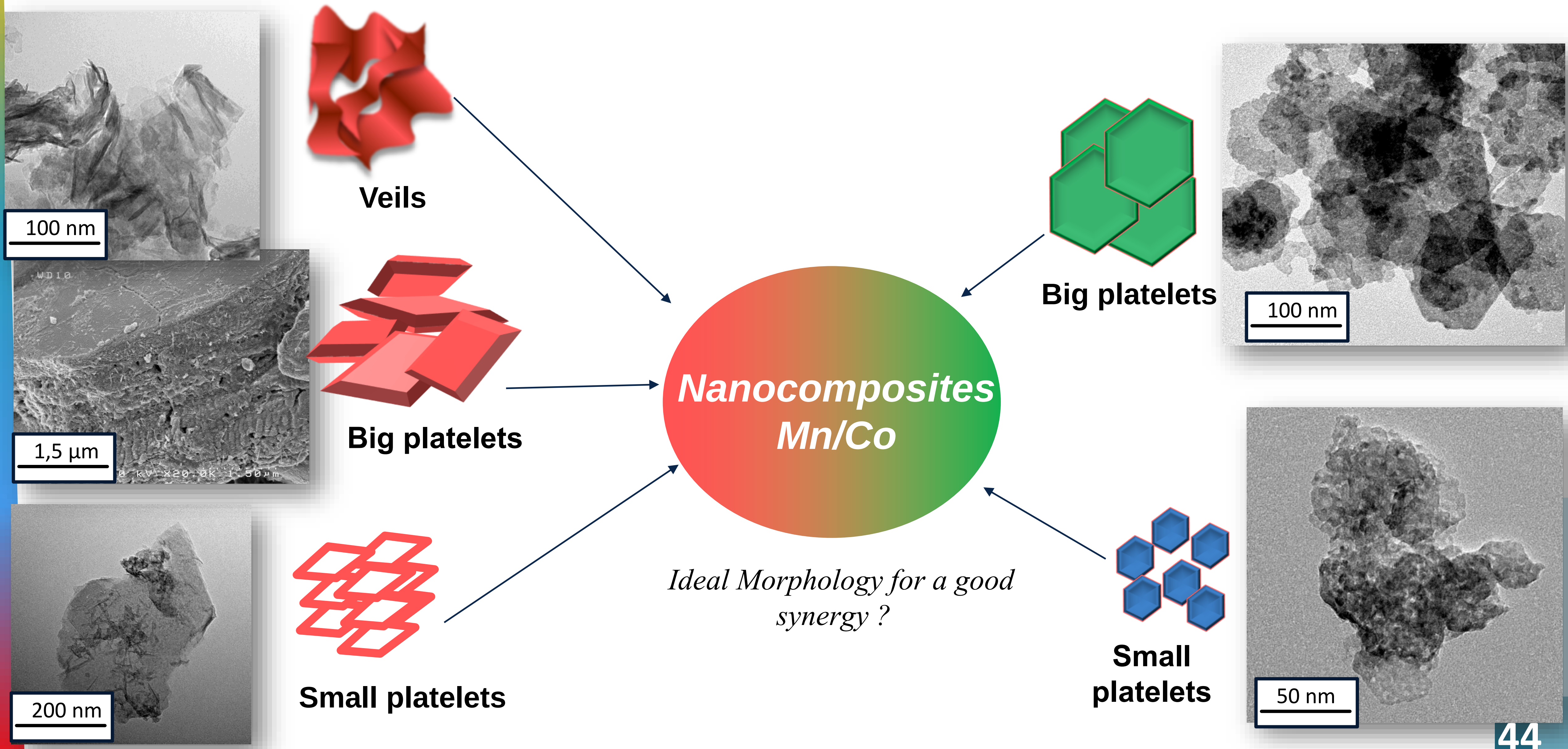
Towards composite materials



Ideal Morphology for a good synergy ?

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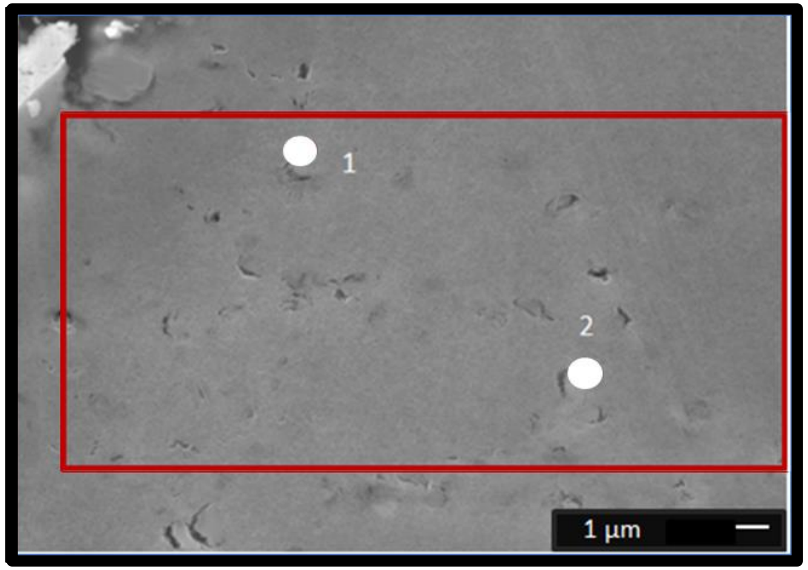
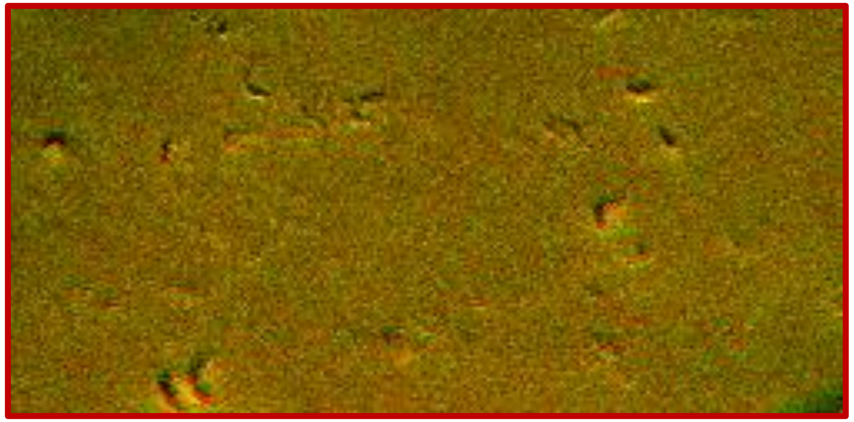
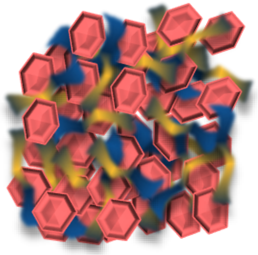


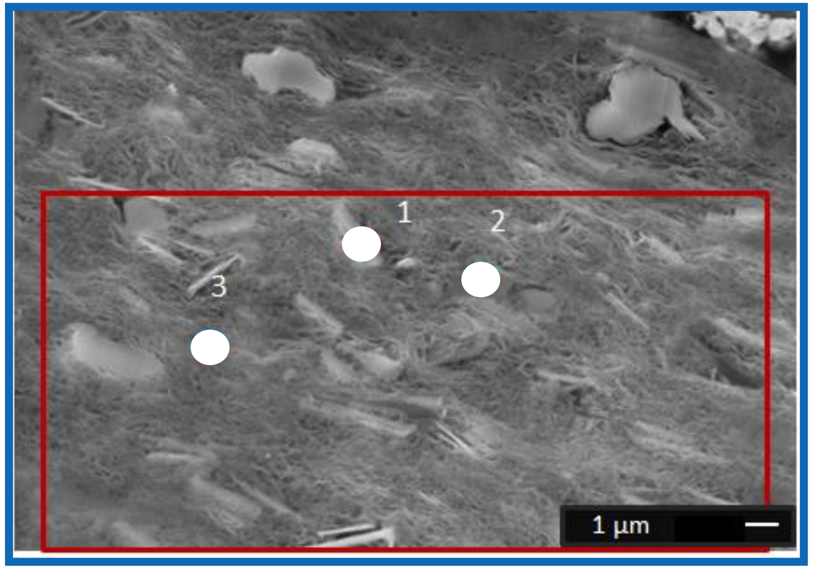
Mn Veils + Co Nano platelets



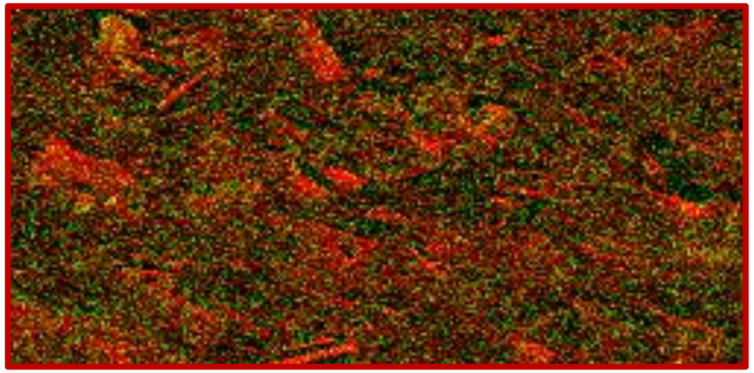
Homogeneous distribution between Mn and Co objects



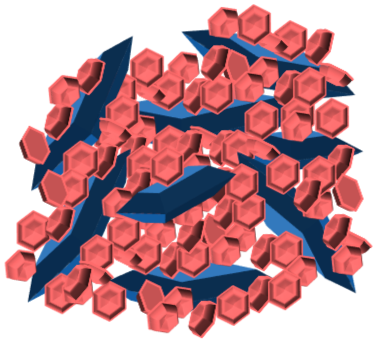
NanoAuger mapping



Mn platelets + Co Nano platelets



Partial homogeneity between Mn and Co objects



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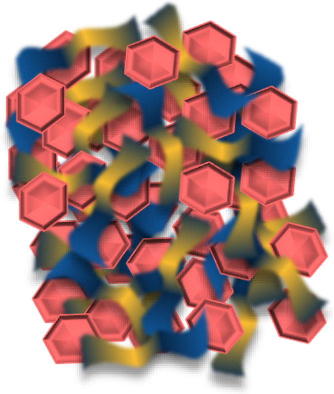

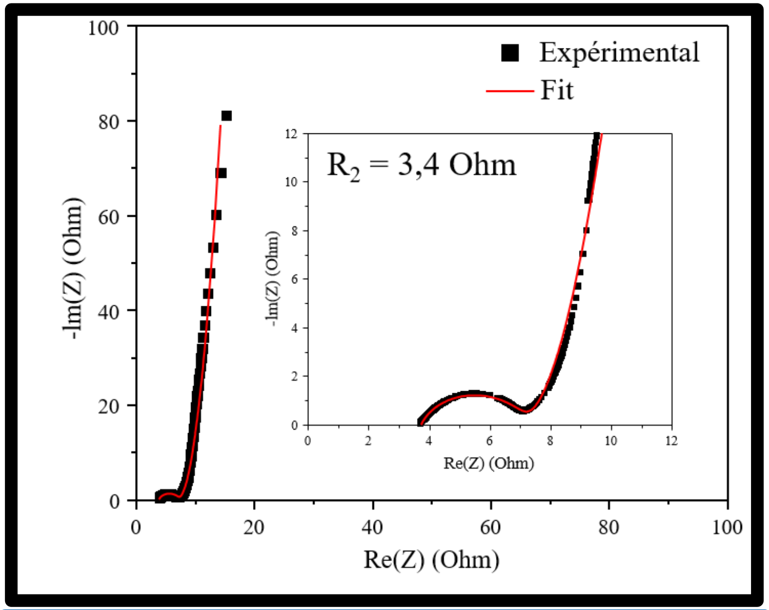

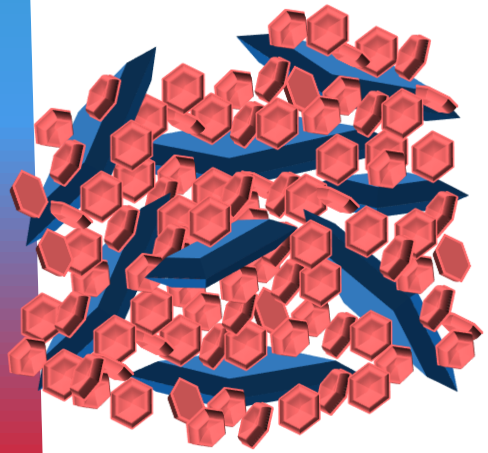

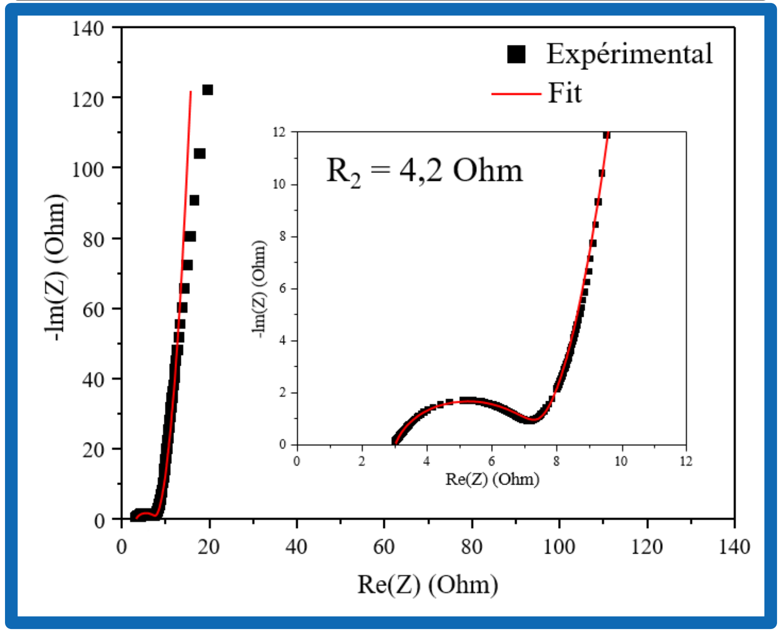

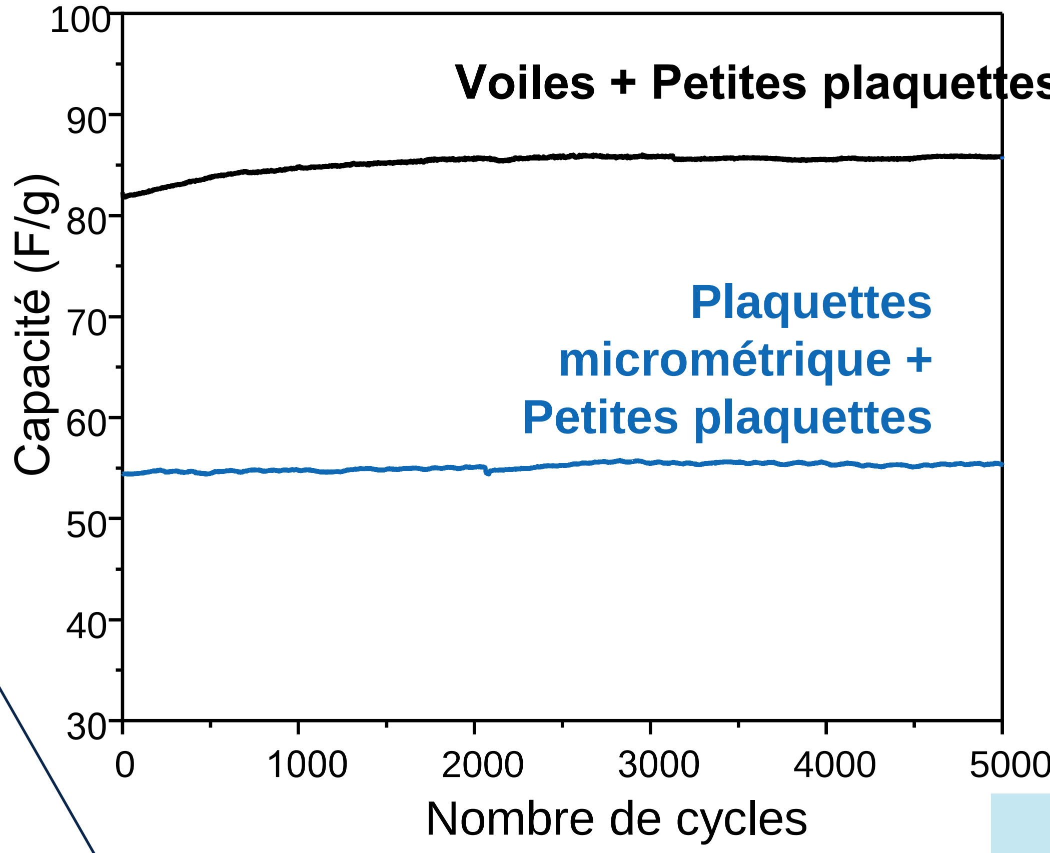

Lower resistance,
Higher capacity

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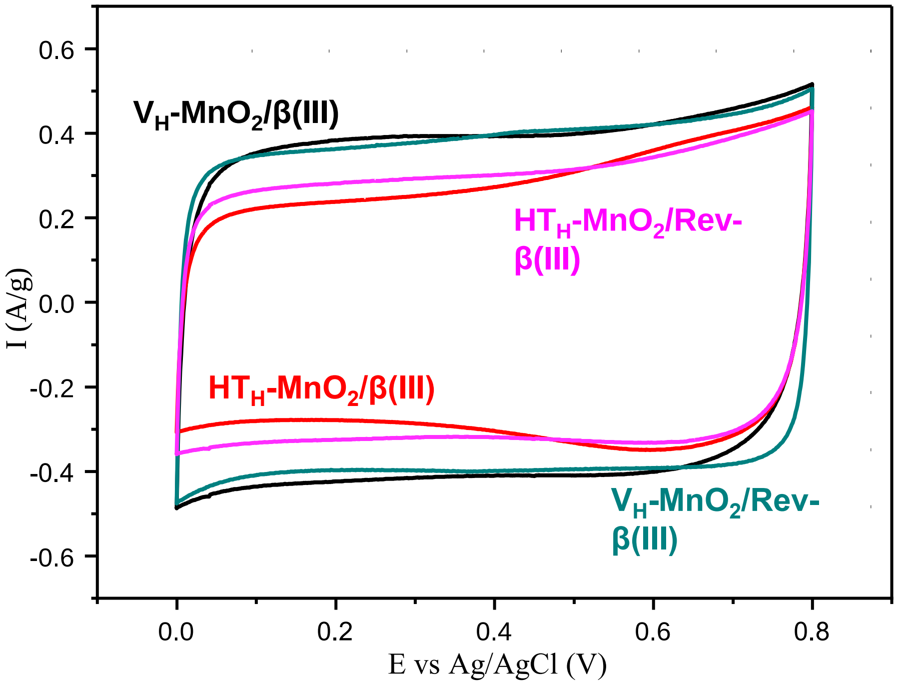
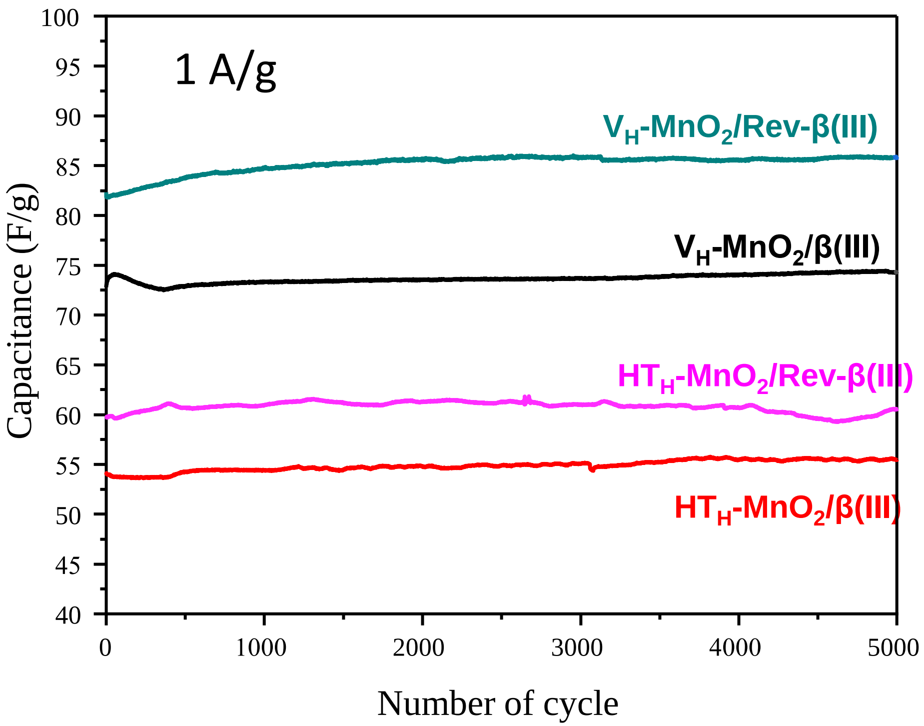
Towards composite materials

Mass loading : 7 mg/cm²
Scan rate and Current density : 5mV/s and 1 A/g
Electrolyte : K_2SO_4 0.5 M
Potential window : 0-0.8 vs Ag/AgCl
Current collector : stainless steel grid





Same composition but different performance
Synergy between the different phases in a composite is extremely important

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Take home message

Battery is a challenging and interesting field of research ☺

Batteries performance strongly depend on the positive electrode material (cathode)

Several approaches to optimized a material:

- Nanostructuration and adapt particle’s morphology according to its structure

- *Apply a coating to stabilize the material (and make it more conductive (carbon coating))*
- *Synthesize composite materials to take advantage of the synergetic effect*

However, a good approach at the lab scale is not always good for industrial partners

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Thank you all for listening

ENERGIE RS2E

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