Cross-section nano-Auger analysis to reveal bulk chemical/morphological information in composites for energy storage

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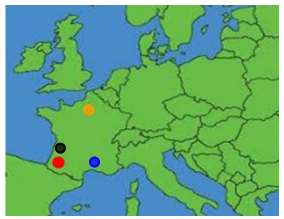


In collaboration with:

2 Chimie Paris

3 icmcb

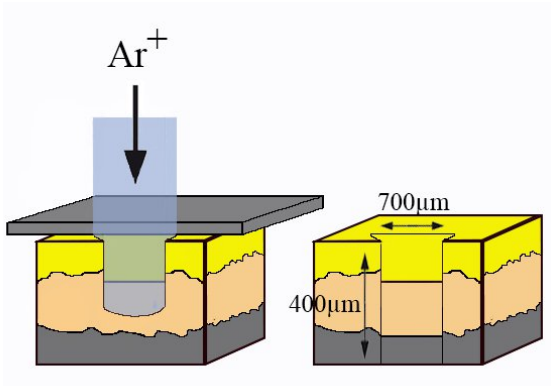
4 ICG Montpellier

E-MRS, June 1, 2022

How to reveal what is buried inside materials, composites?

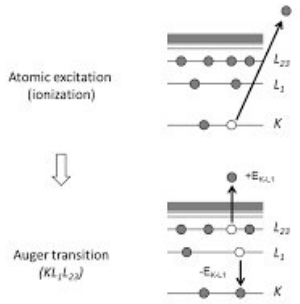
1° Ion-milling preparation

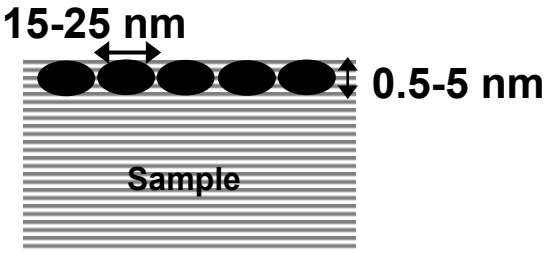
- small area (50-500 µm)
- flat surface
- cryo capability



2° Auger/SEM analysis

- nano resolution
- chemical info
- semi-quantitative





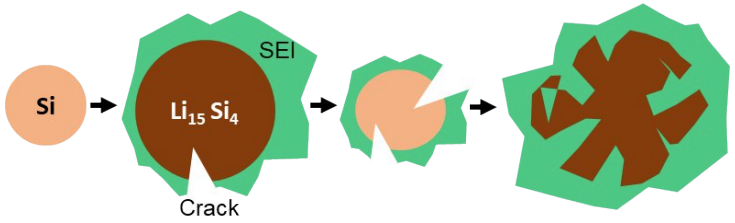
→ nano scale chemical mapping

Conversion material based electrodes for Li-ion

CONTEXT
Energy = Capacity x Cell voltage

Li-ion

Use conversion/alloy materials
+ 20-25 %



BUT
- **High volume expansion (> 200%)**
- **Particles crack = Solid electrolyte interphase formation (SEI)**

Case of a ternary conversion material:
$TiSnSb + 6.5\ Li \leftrightarrow Ti° + Li_3Sb + ½\ Li_7Sn_2$

→ **So far:**
- 1st Lithiation proven by XRD *(J. Mater. Chem.,* **2011**, 21, 10069)
- 1st Delithiation proven by XAS *(Chem. Mater.,* **2017**, 29, 10446)

GOAL

Conversion reaction after long term cycling? Inactive Ti still participating?

Observation of the volume expansion?

Localization of particles crack = solid electrode interphase?

Conversion material based electrodes for Li-ion

Literature approaches

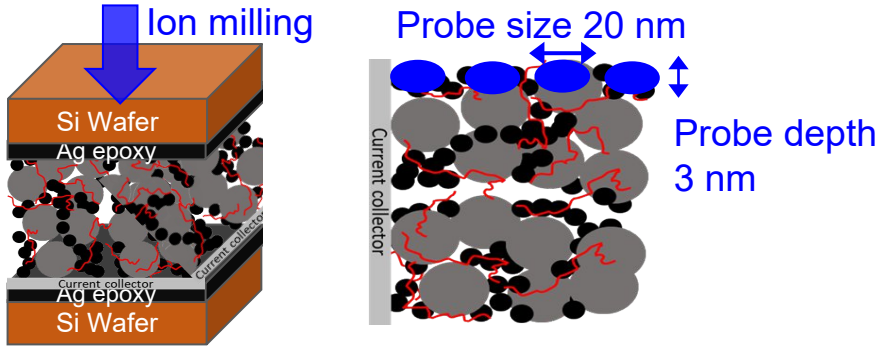
XRD/XAS first cycle only

In situ TEM individual particles

X-ray tomo no chemical info + synchrotron

OUR APPROACH

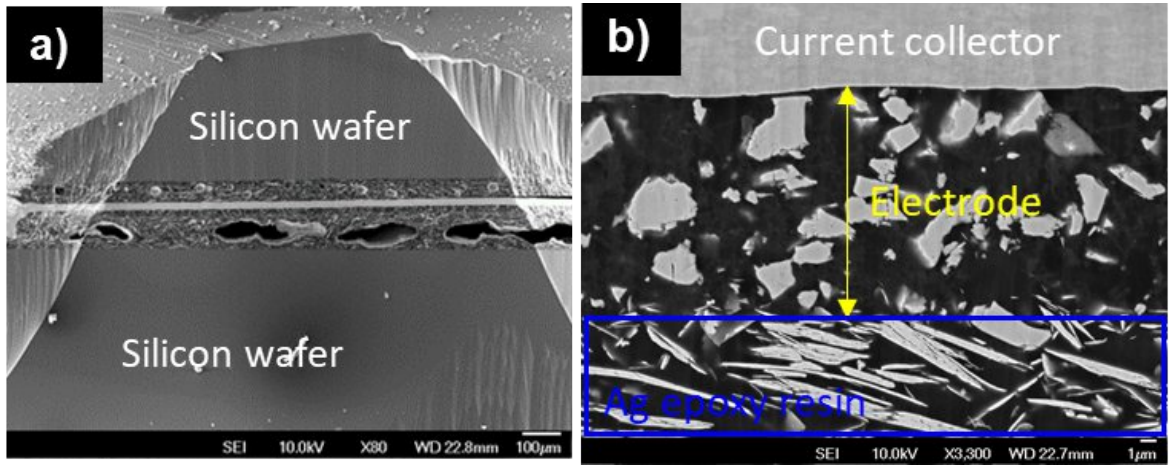
Cross-section + nano Auger



morphology + chemical composition

at electrode / nano scales

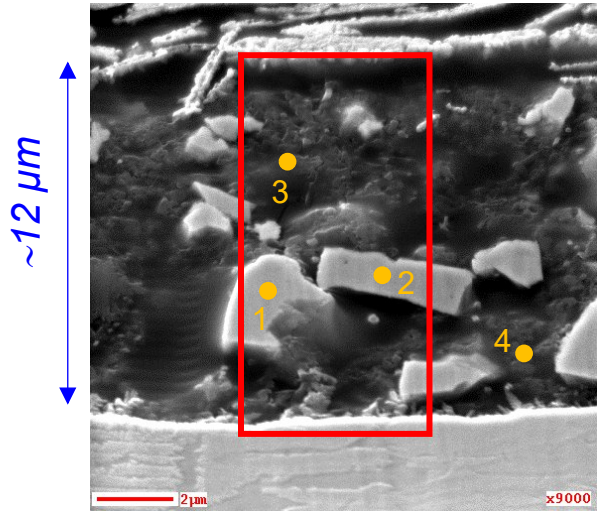
Pristine electrode



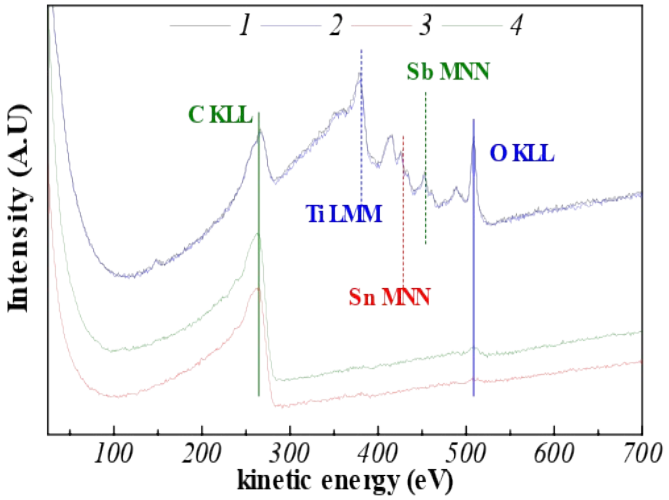
→ Flat surface with no chemical change

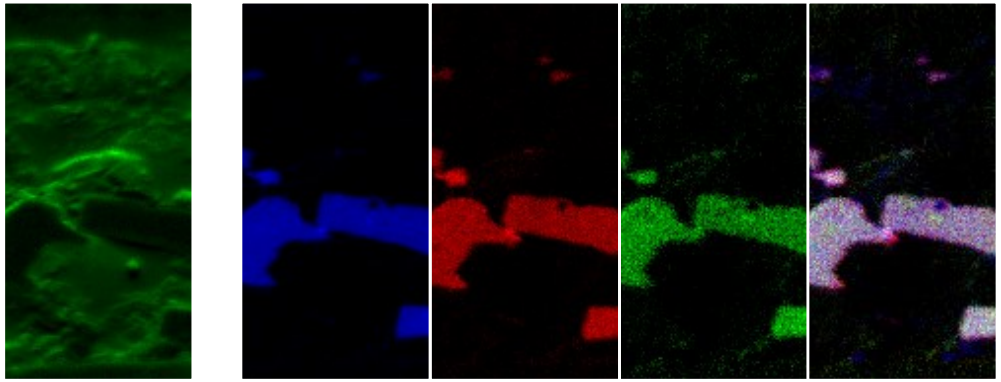
Conversion material based electrodes for Li-ion

Pristine electrode



Remark:
electrode thickness = ~12 µm



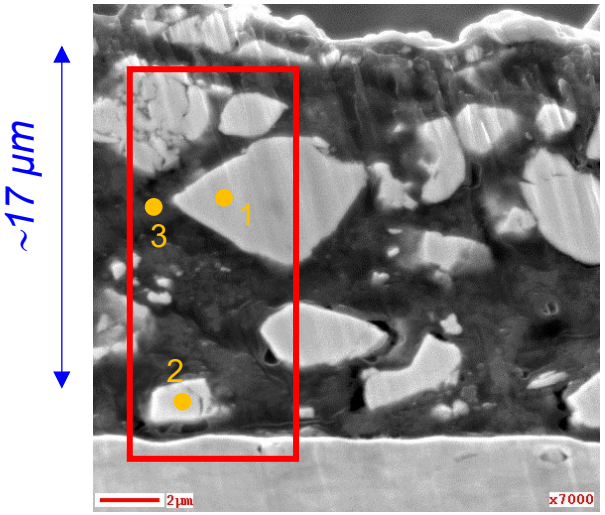


C KLL | Ti LMM | Sn MNN | Sb MNN | Ti/Sn/Sb overlay

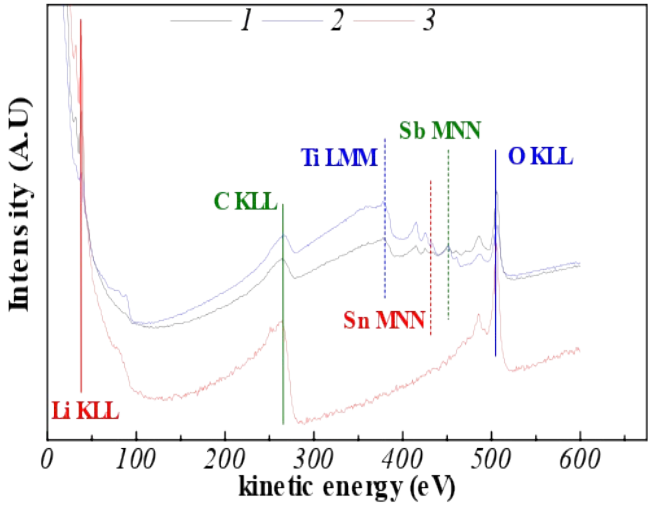
TiSnSb: dense particles (0.5-5 µm) surrounded by the carbon

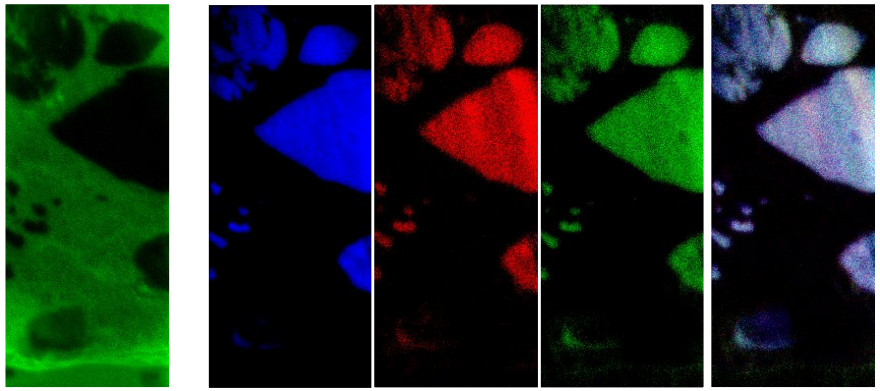
Conversion material based electrodes for Li-ion

Electrode after 1st lithiation

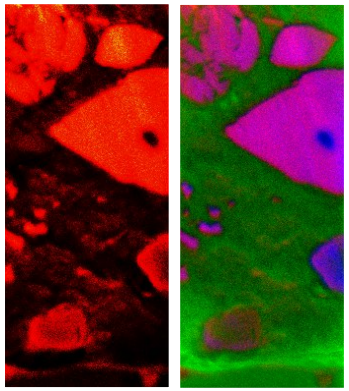


Remark:
electrode porosity buffers the volume expansion





C KLL | Ti LMM | Sn MNN | Sb MNN | Ti/Sn/Sb overlay

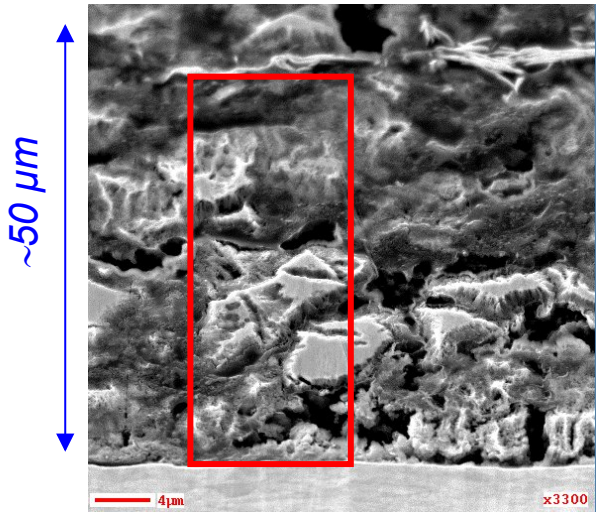


Li KVV | C/Ti/Li overlay

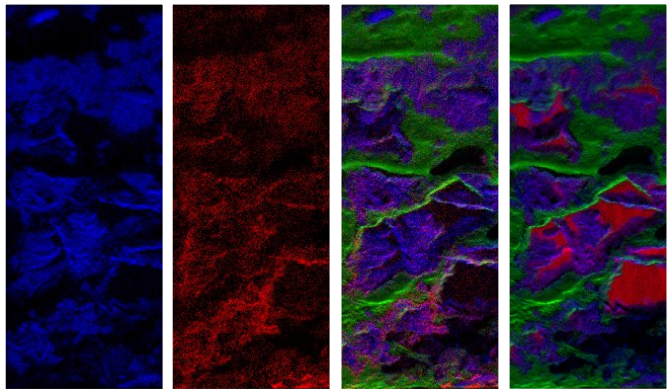
TiSnSb: still dense particles with no crack
Homogeneous lithiation

Conversion material based electrodes for Li-ion

Electrode after 400 cycles at 25°C

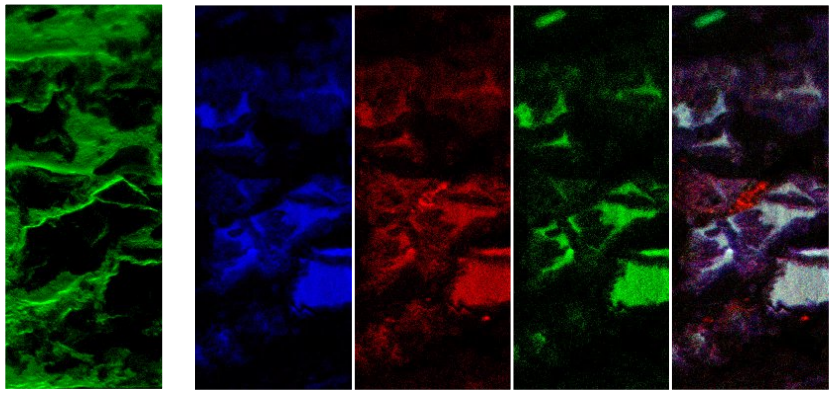


Remark:
large electrode volume expansion



O KLL | F KLL | C/O/F overlay | C/O/Ti overlay

SEI: F and O from electrolyte degradation inside porous shell

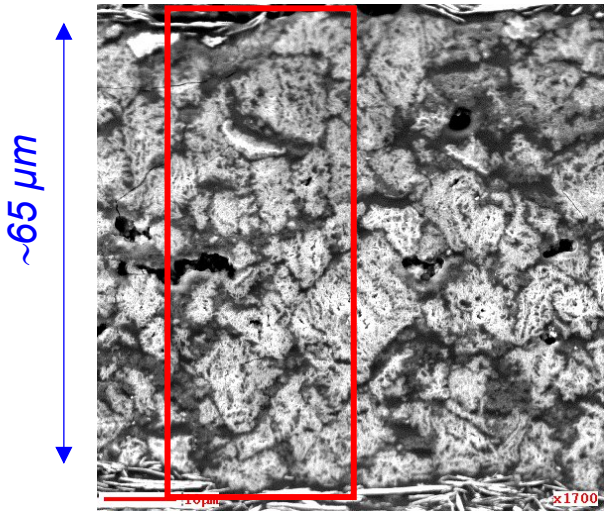


C KLL | Ti LMM | Sn MNN | Sb MNN | Ti/Sn/Sb overlay

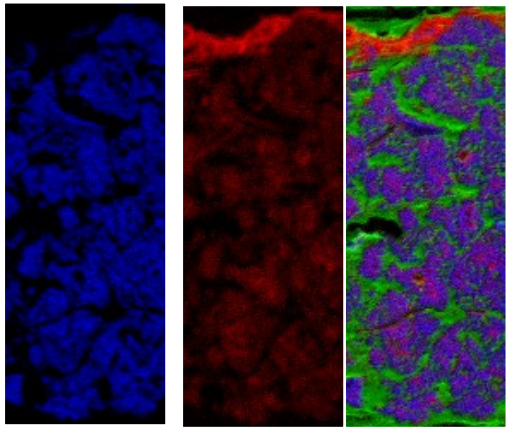
TiSnSb: inhomogeneous dense core / porous shell with µm spreading
➔ **shell to core expansion break up of particles**

Conversion material based electrodes for Li-ion

Electrode after 400 cycles at 60°C



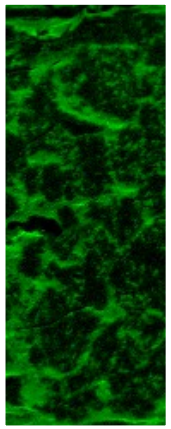
Remark:
larger electrode volume expansion

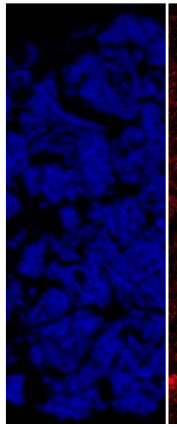

O KLL

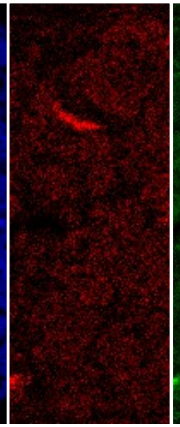
F KLL

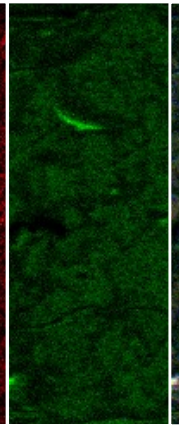
C/O/F overlay

SEI: F and O from electrolyte degradation inside porous particles
➔ **confirms that SEI forms inside particles cracks**


C KLL


Ti LMM


Sn MNN


Sb MNN


Ti/Sn/Sb overlay

TiSnSb: homogeneous porous particles only with µm spreading
➔ **confirms that conversion reaction still occurs with Ti participation**

Pseudocapacitive composite powders for hybrid supercapacitors

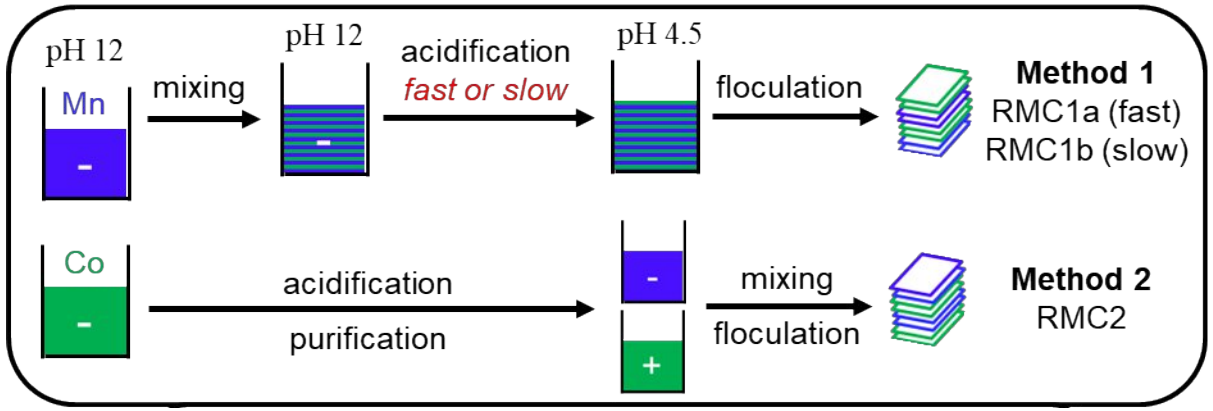
CONTEXT

MnO_2 suffers from low electronic conductivity

Supercap

Use composites made of Mn + Co metal oxide

↗ of electronic conductivity (Co)



→ Composites prepared by exfoliation/restacking of layered Mn and Co metal oxides

GOAL

↳ After restacking, Mn and Co mixed or segregated?

↳ Bulk structure?

↳ Distribution scale/homogeneity?

Pseudocapacitive composite powders for hybrid supercapacitors

Literature approaches

TEM-EDS/EELS individual particles

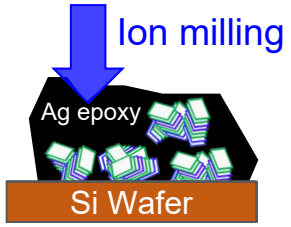
XRD no info on phase organisation

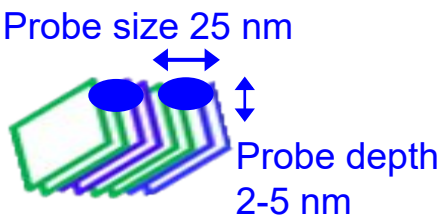
Sample	Size of coherent domain (nm) (001) line of Mn-based phase	Size of coherent domain (nm) (003) line of Co-based phase	Specific BET surface (m^2/g)
H-MnO_2	11	-	85
$\beta 3$-CoOOH	-	5	110
MG	12	3	95
RMC1a	**7**	**3**	**92**
RMC1b	**7**	**6**	**2**
RMC2	**6**	**6**	**100**

Remark: very low BET for RMC1b

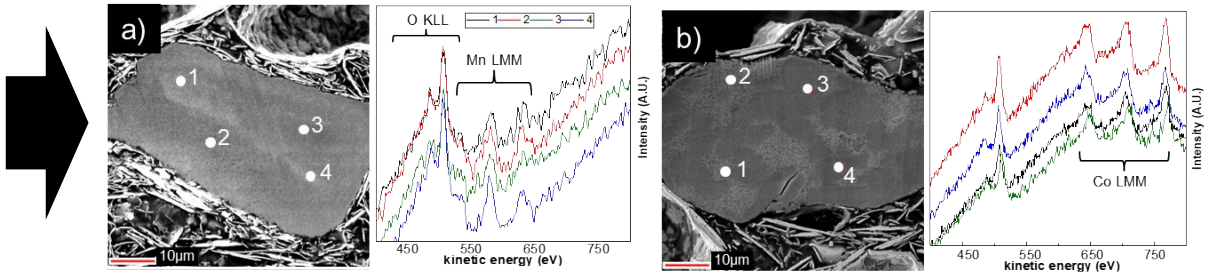
OUR APPROACH

Cross-section + nano Auger

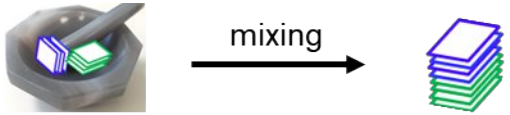




morphology + chemical composition
at agglomerate / nano scales

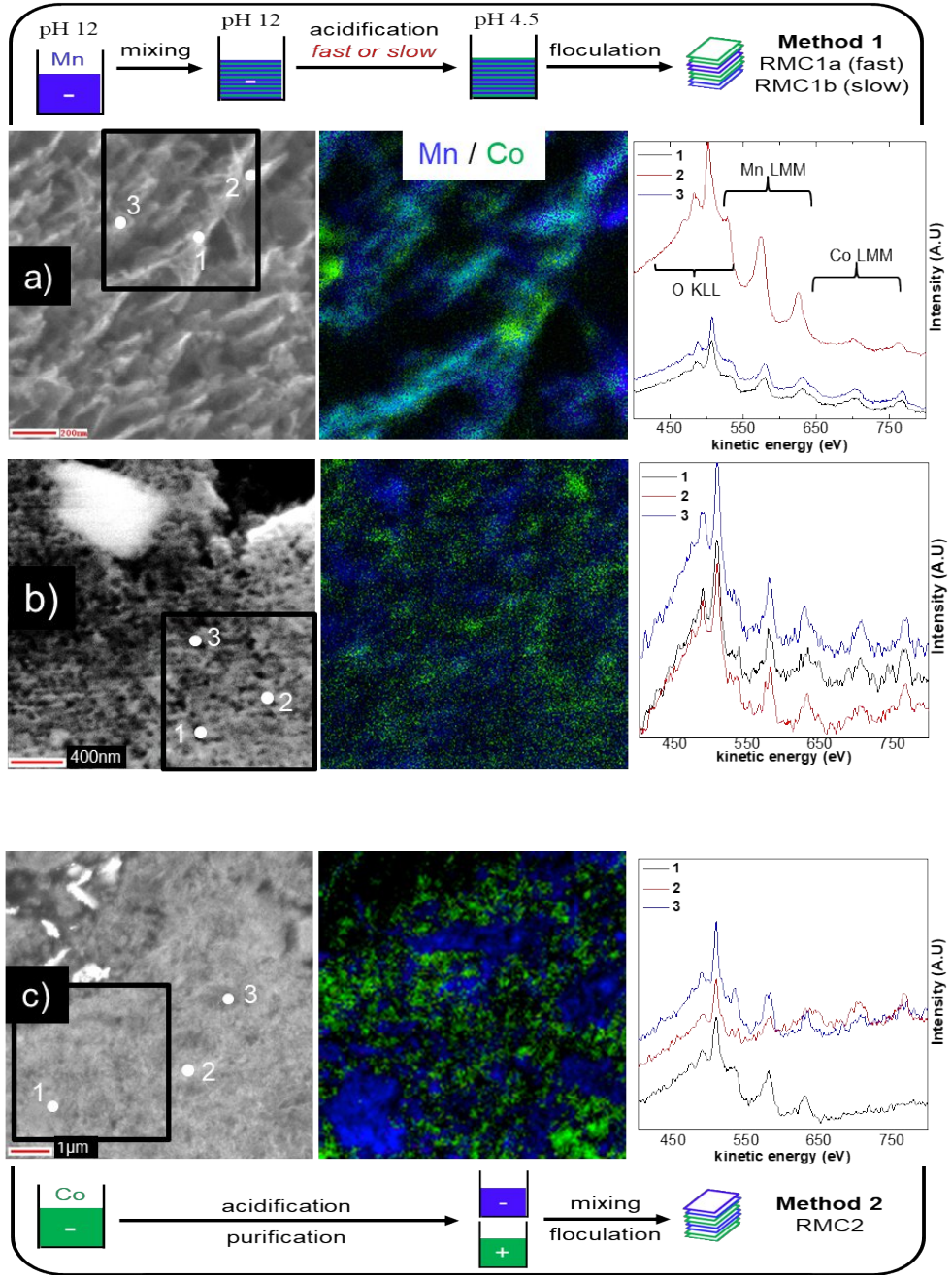


Co and Mn well separated
= µm composite



Mechanically grinded
MG

Pseudocapacitive composite powders for hybrid supercapacitors



Method 1 fast floculation

- Porous structure ⇔ 92 m^2/g
- Mn + Co always

→ **Nanoscale assembly**

Method 1 slow floculation

- Dense structure ⇔ 2 m^2/g
- Mn + Co always

→ **Nanoscale assembly**

Method 2

- Porous structure ⇔ 110 m^2/g
- Mn + Co or only Mn or only Co

→ **Microscale assembly**

Conclusions

How to reveal what is buried inside materials, composites?

Take home

At electrode / nano scales
- Proof of conversion reaction after 400 cycles
- Ti still participates to the reaction
- SEI formation inside particles cracks

L. Madec *et al. J. Power Sources,* **2018**, 391, 51
L. Madec *et al. ACS Applied Energy Mater.,* **2019**, 7, 5300
L. Madec *et al. J. Power Sources,* **2019**, 441, 227213

At agglomerate / nano scales
- Mn and Co distributions scale/homogeneity
- Bulk morphology of restacked composites

C. Tang *et al. Langmuir,* **2018**, 34, 6670
L. Madec *et al. JES,* **2021**, 168, 010508

Perspectives

Transfer methods to reveal buried interfaces in solid state batteries

Thanks

TiSnSb collaboration:

MnCo collaboration:

And thank you for your attention

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