UMR 5518 CNRS / Grenoble INP - UGA

Characterization of Lithium-ion battery negatives by scanning electron microscopy

SEMPA
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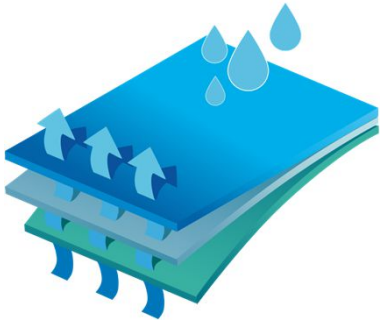
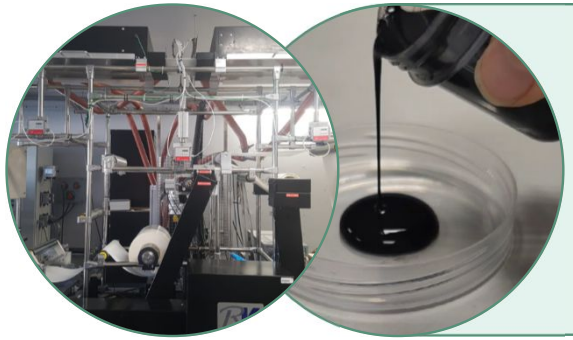
Julie Luneau, Raphaël Passas, Céline Martin, Karine Janel
julie.luneau@grenoble-inp.fr
Laboratory of process engineering for biorefinery, bio-based materials and functional printing

1. LGP²



Paper manufacturing and functionalization laboratory



Expertise in ink formulation and coating techniques.

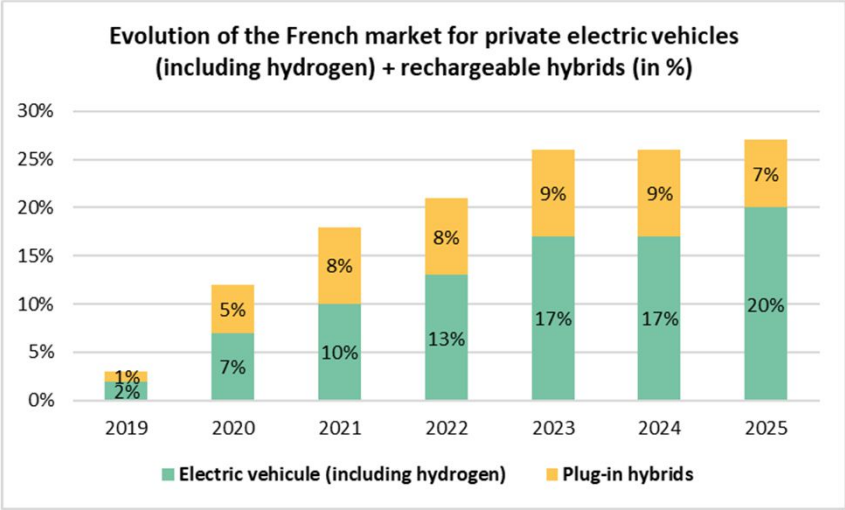
Objective:
Transferring papermaking expertise to lithium-ion battery manufacturing

2. About batteries

	BLA	BSi	BLi
Specific energy *Wh/kg*	30-40	75~156	125-180
Lifetime cycles	300-500	4000	1200

Comparison between:

- Lead-Acid batteries (BLA)[1]
- Sodium ion batteries(BSi)[2]
- Lithium-ion batteries (BLi)[1]



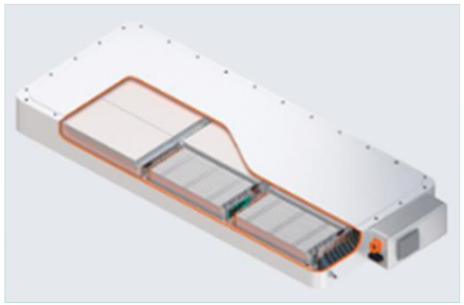
PFA 2025[3]

Improving batteries and their manufacturing: a key challenge for the industry

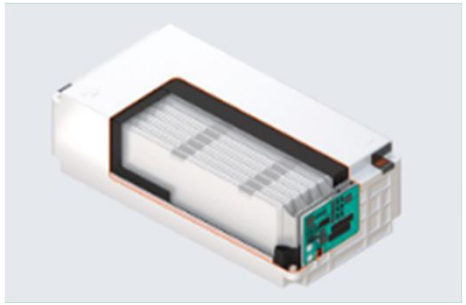
3. Russian Doll Structure

Batterie

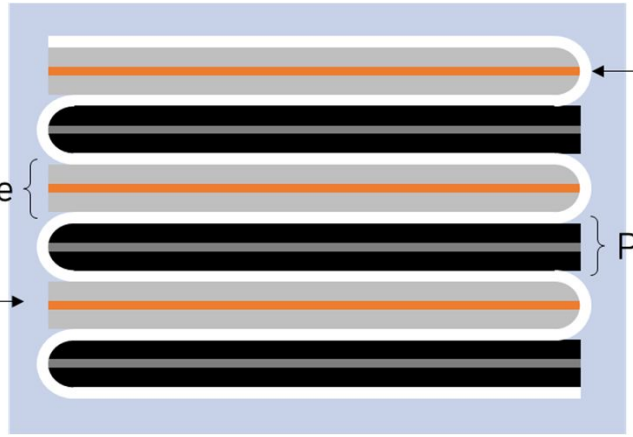
Packs



Module



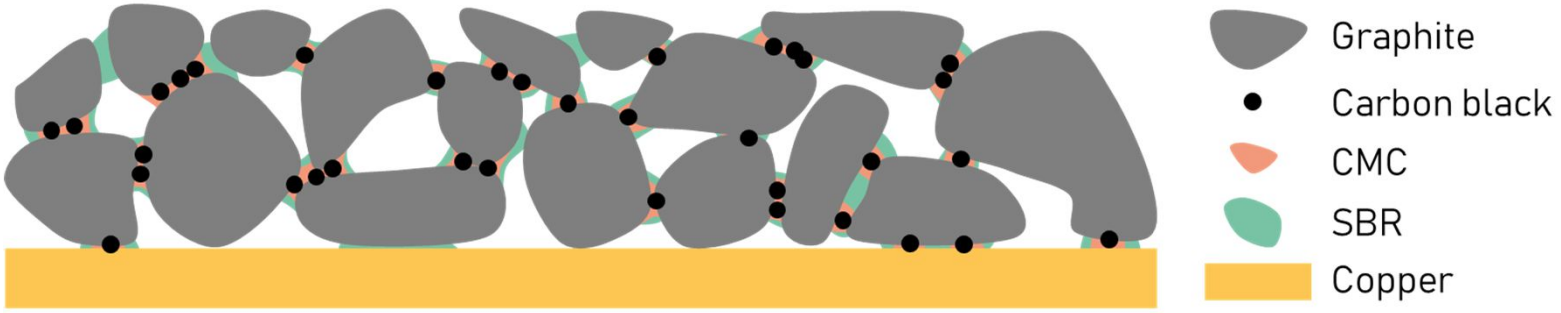
Pouch cell



60 electrodes

We will focus on the negative graphite electrode

2. Negative electrode structure



	Negative electrode
Current collector	Copper film
Active material	Graphite
Conductive additive	Carbon black
Binder	SBR, CMC

→ Mechanical support & conducts electrons

→ Li^+ intercalation

→ Electrical contact[4]

→ CMC: Binder, stabilizer, dispersant[5]
SBR: Binder, flexibility enhancer, reinforcing agent[5]

Observe the distribution of components within the thickness of the electrode using SEM

5. Summary

1. Negative electrode: Lab manufacturing
2. Components repartition
3. Determination of the internal cohesion
4. Conclusions and perspectives

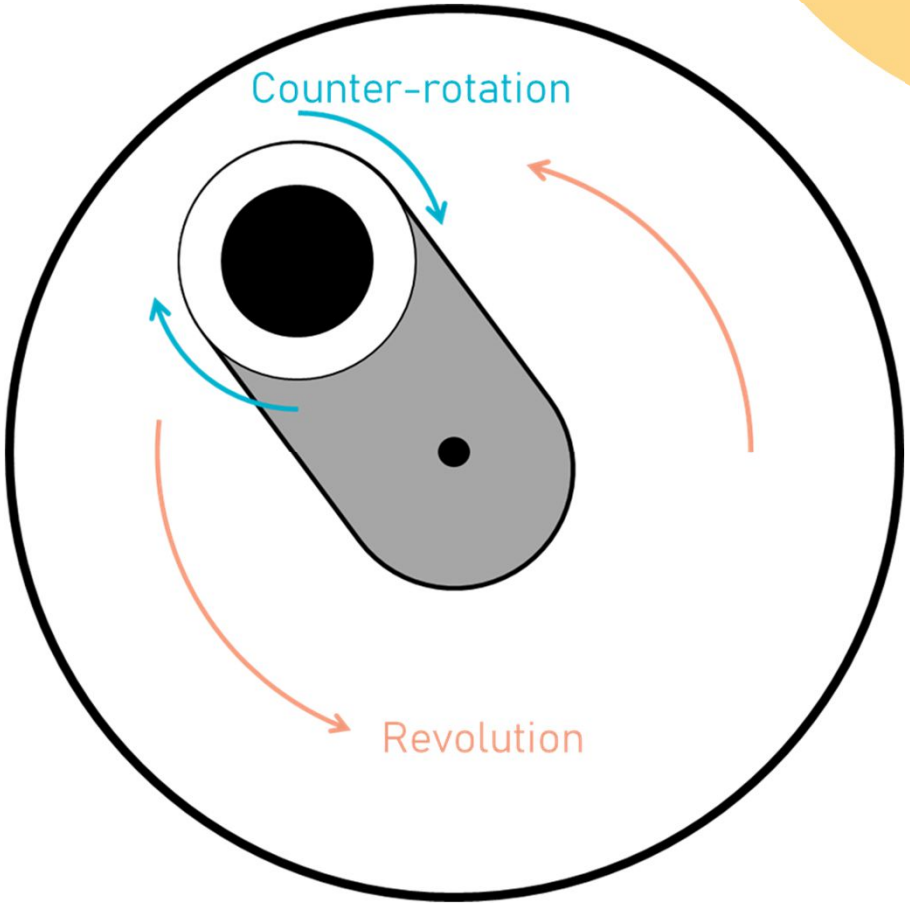
1. Negative electrode: Lab manufacturing

1. Slurry formulation

1) Dissolution of the CMC into water [6,7,8]
2) Adding carbon black and graphite[7,8]:
   - Time = 8 minutes
   - Revolution speed = 2 000 rpm[9]
   - Counter-rotation speed = 250 rpm[9]
3) Adding SBR :
   - Time : 2 minutes
   - Revolution speed = 1 000 rpm[9]
   - Counter-rotation speed = 125 rpm[9]

✓ Slurries composition :

	Wet	Dry
Graphite %	53,6	96,4
Carbon black %	0,8	1,4
CMC %	0,6	1,1
SBR %	0,6	1,1
Water %	44,4	0

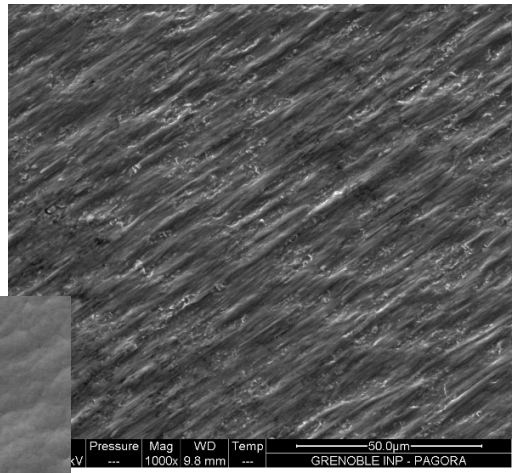


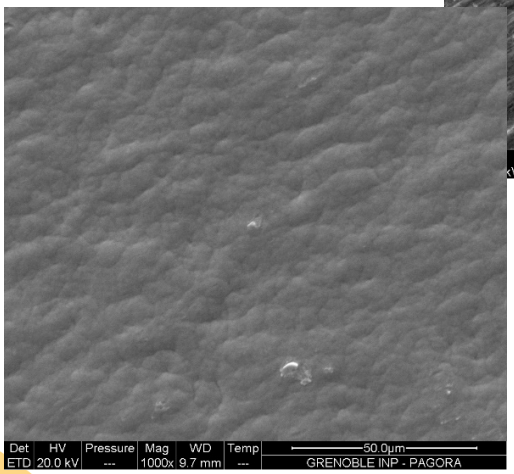
Schema of a speed mixer

2. Copper strip

- Weight : $G = 71{,}93\ g.m^{-2} \pm 1{,}20\ g.m^{-2}$
- Thickness : $e = 8\ \mu m\ \pm 1\ \mu m$

Mat side of the copper





Shiny side of the copper

✓ Surface free energy measured by contact angle

	Shiny side of copper	Mate side of copper
Polar *mN.m^{-1}*	51,17	24,87
Dispersive *mN.m^{-1}*	0,14	4,09
Surface energy *mN.m^{-1}*	51,31	28,96

✓ Bekk roughness

	Shiny side of copper	Mate side of copper
Time *s*	8013	6315

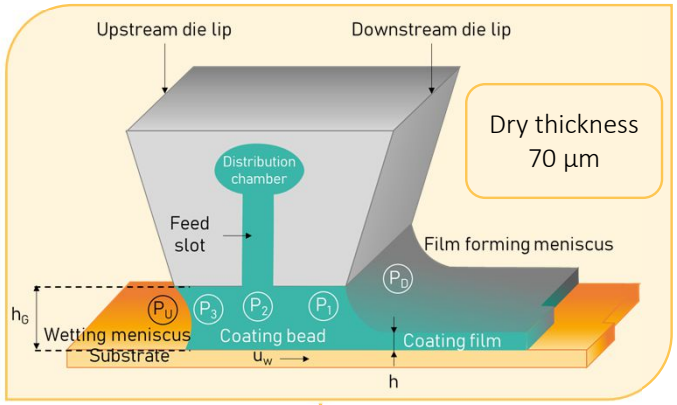
➡ Mate side is rougher than the glossy side

➡ Differences in roughness and surface energy of the copper can lead to :

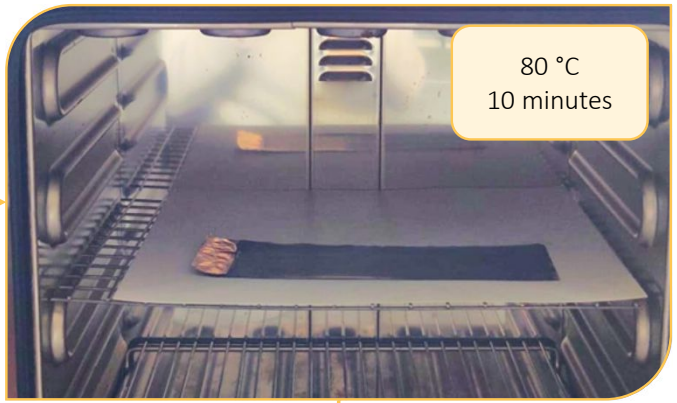
- differences in slurry adhesion
- differences in electrochemical performances between the two sides

3. Lab manufacturing

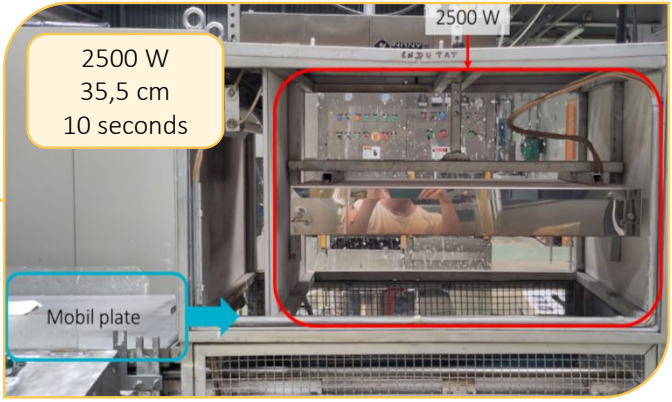
Slot die coating[10]



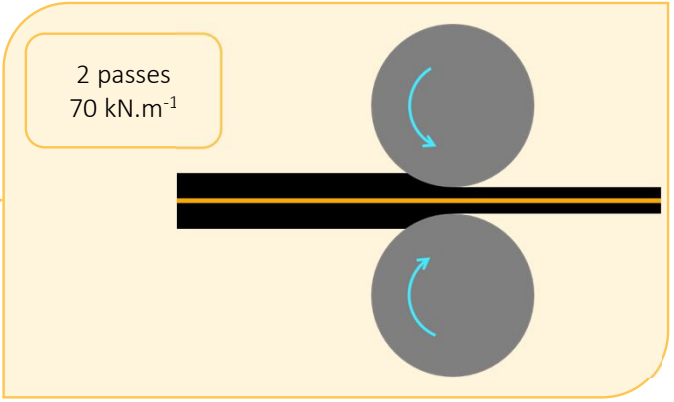
Oven drying



IR drying



Calendering



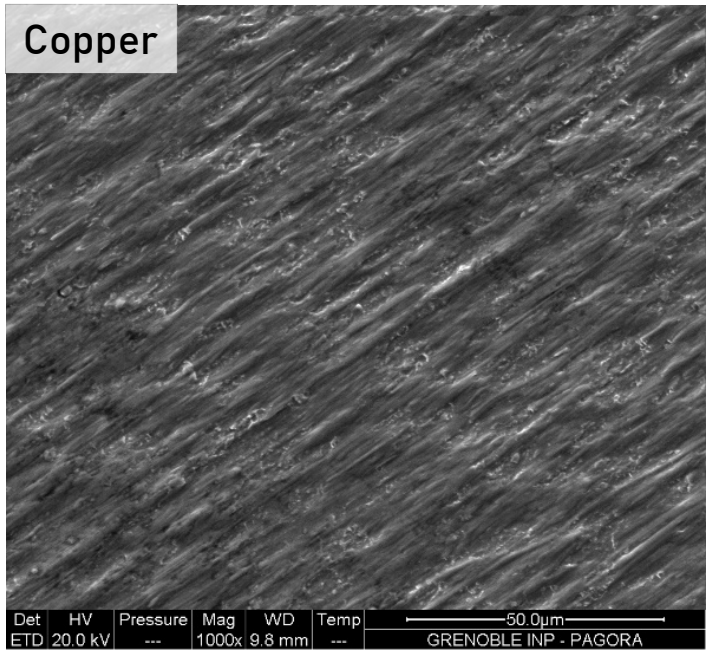
Porosity :
50% ⇒ 30 %

2.Components repartition

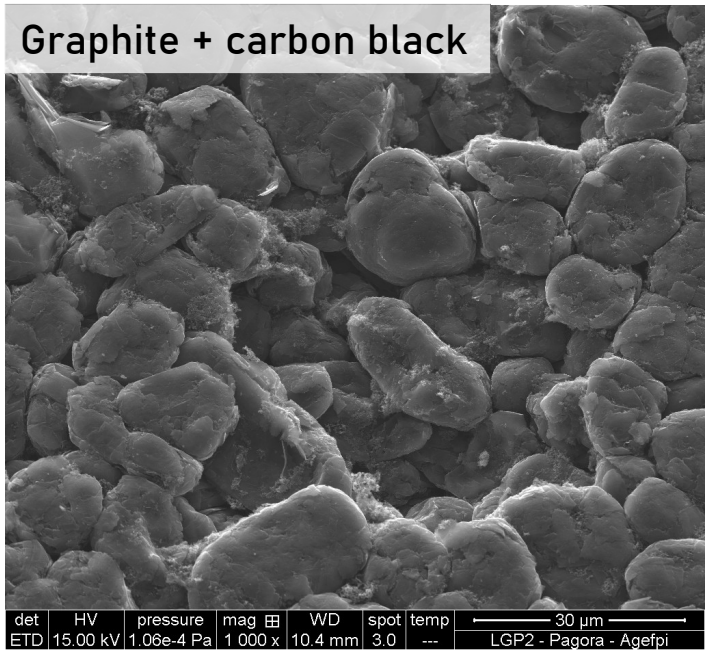
1. Conductive components

Observation on the matte side of the copper

Copper

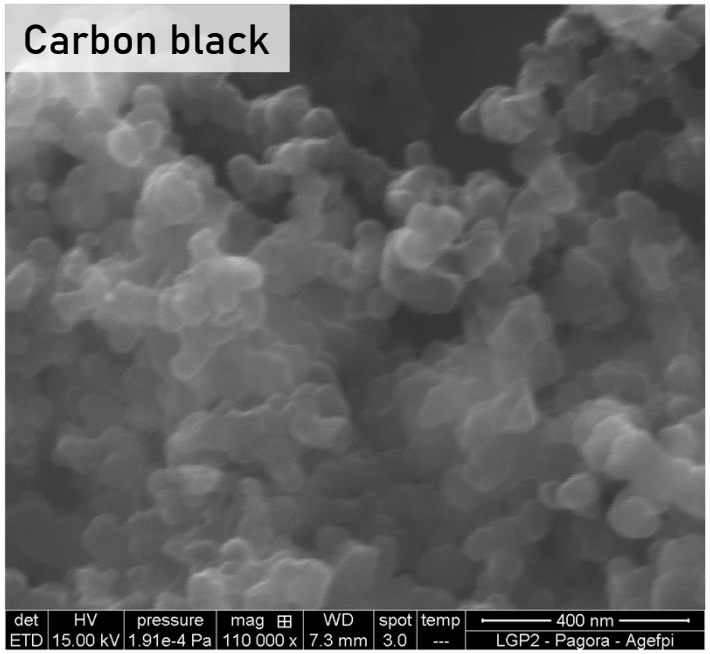


Graphite + carbon black



D50 : 17 µm

Carbon black

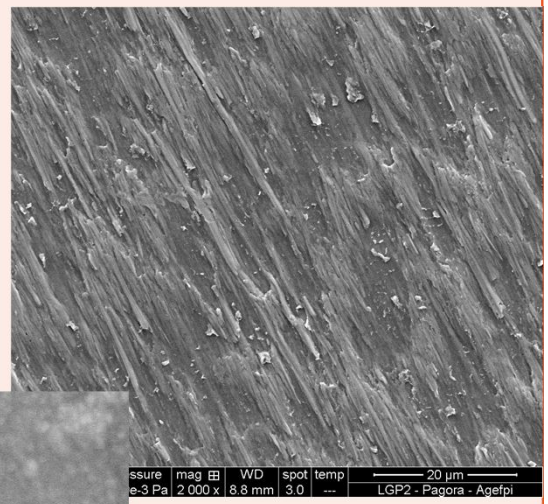


D50 : 7-101 nm

What about polymers ?

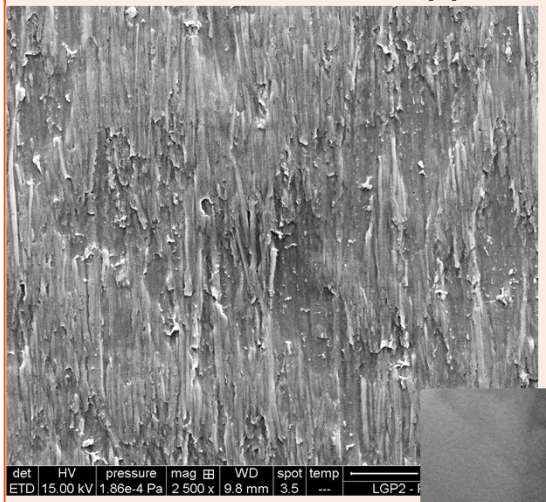
2. CMC observation

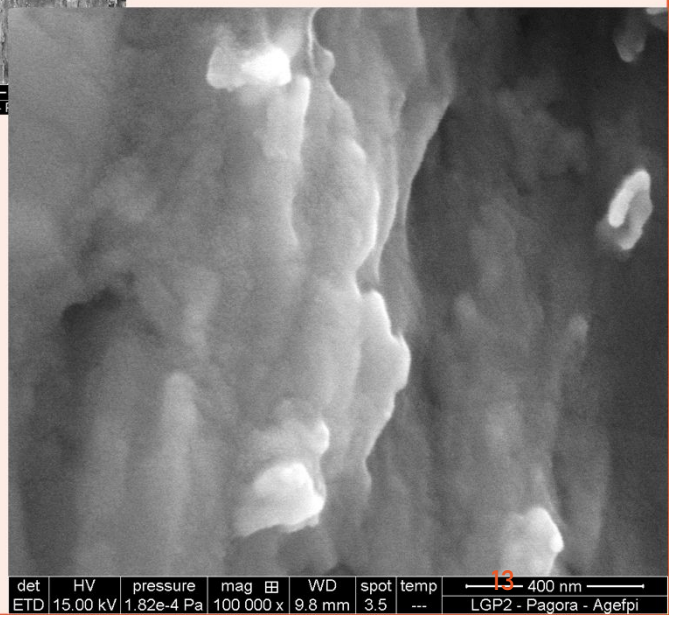
CMC



Speckled on the surface of the copper

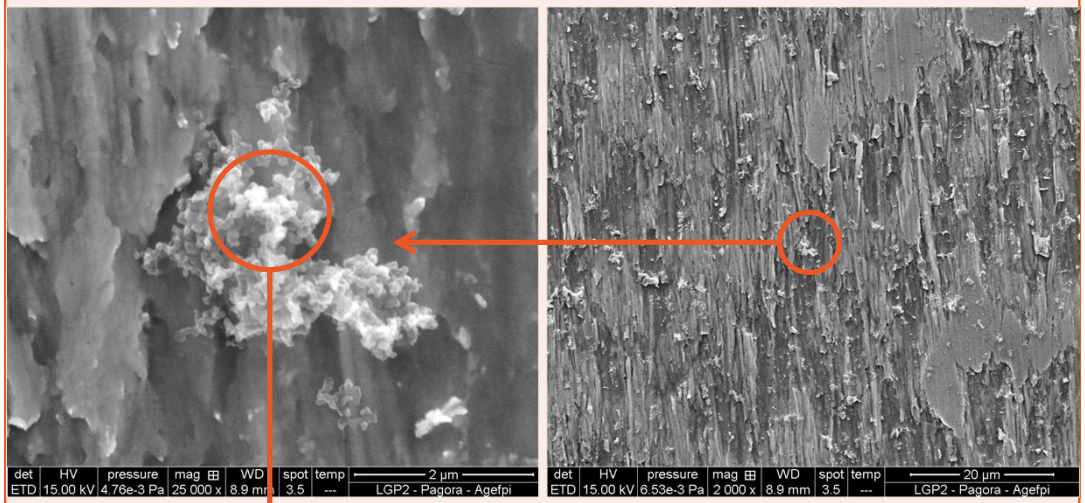
Copper mate side

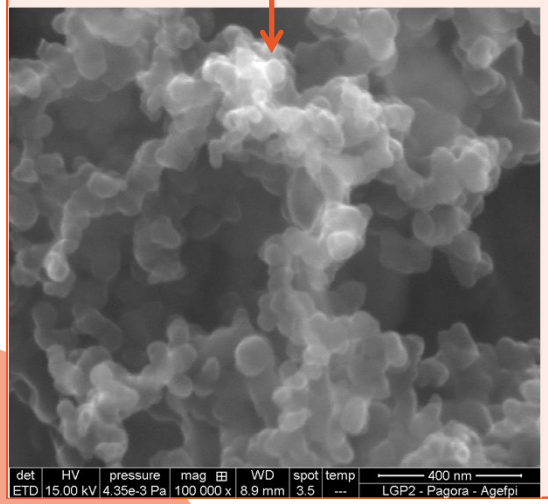




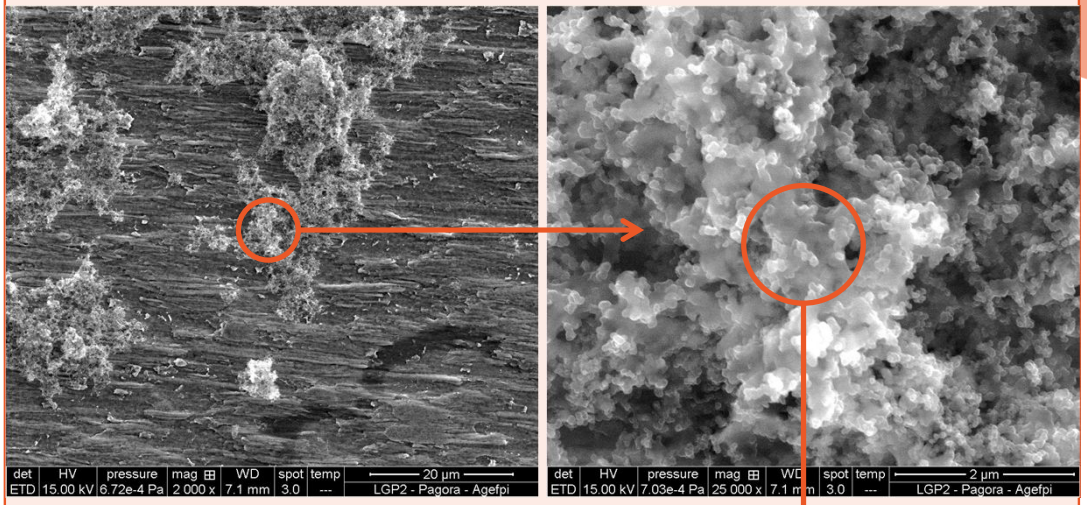
3. SBR observation

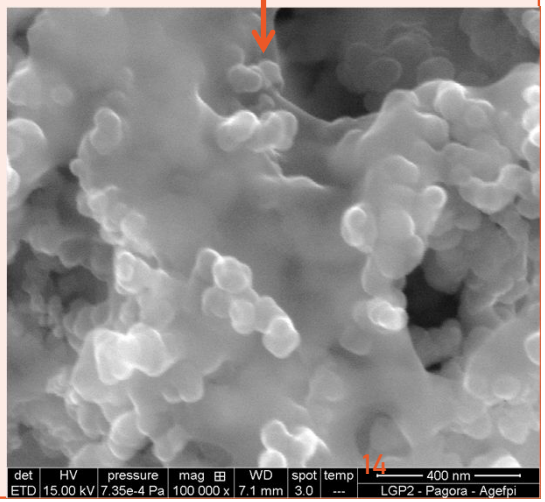
CMC + CB





SBR + CB

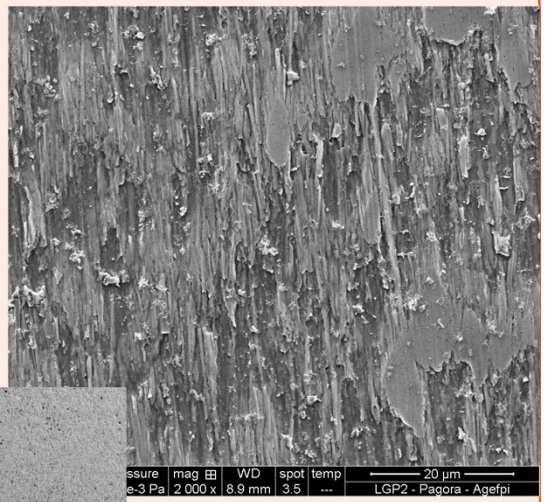


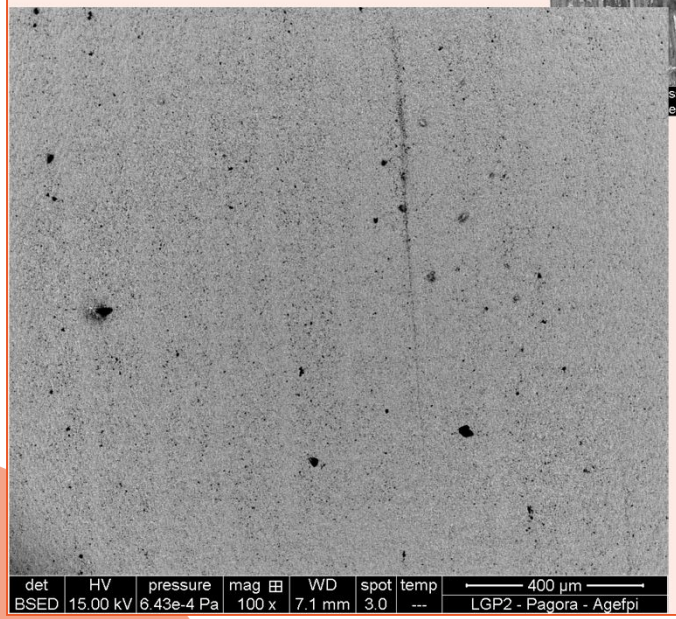


With SBR carbon black particles are embedded

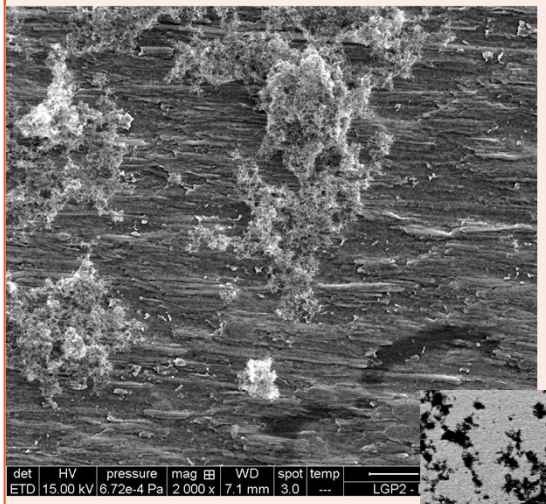
4. Carbon black dispersion

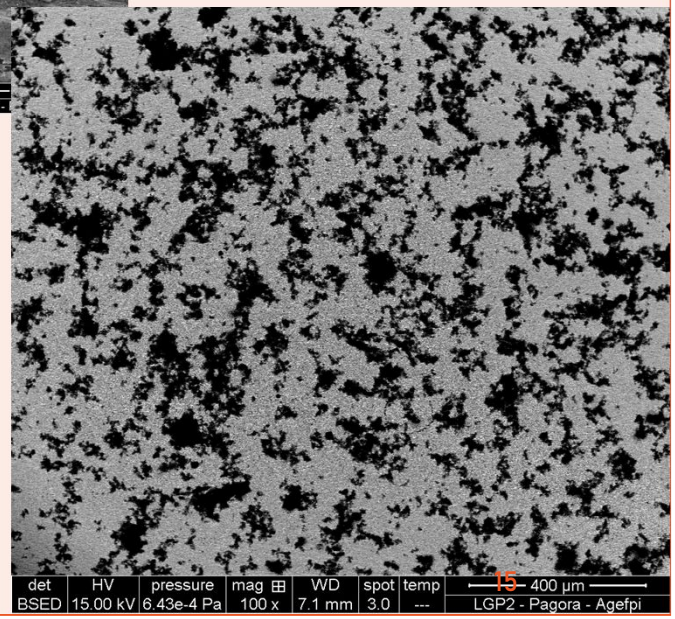
CMC + CB





SBR + CB

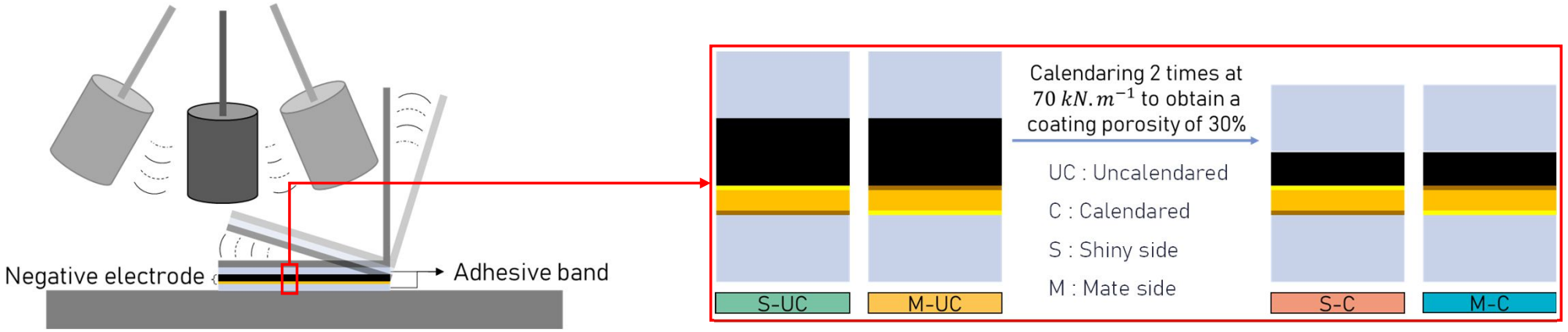


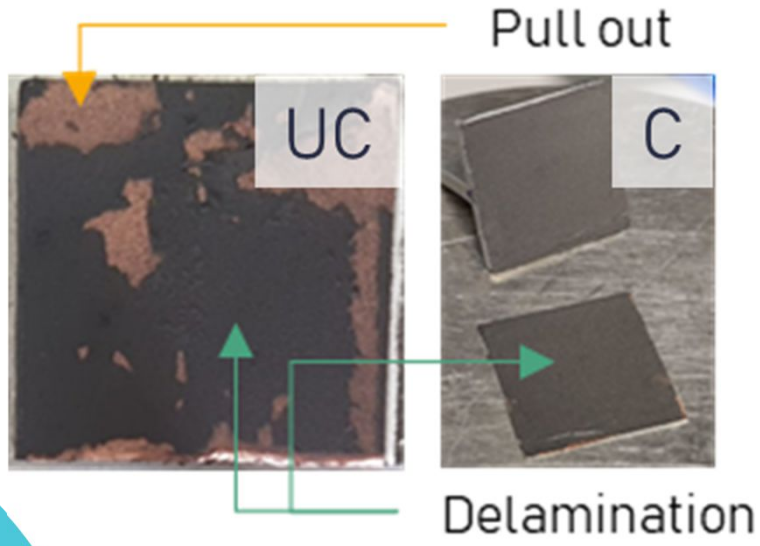


Better dispersion in CMC than SBR

3. Determination of the internal cohesion

1. Adhesion/pull-out: Scott Bond



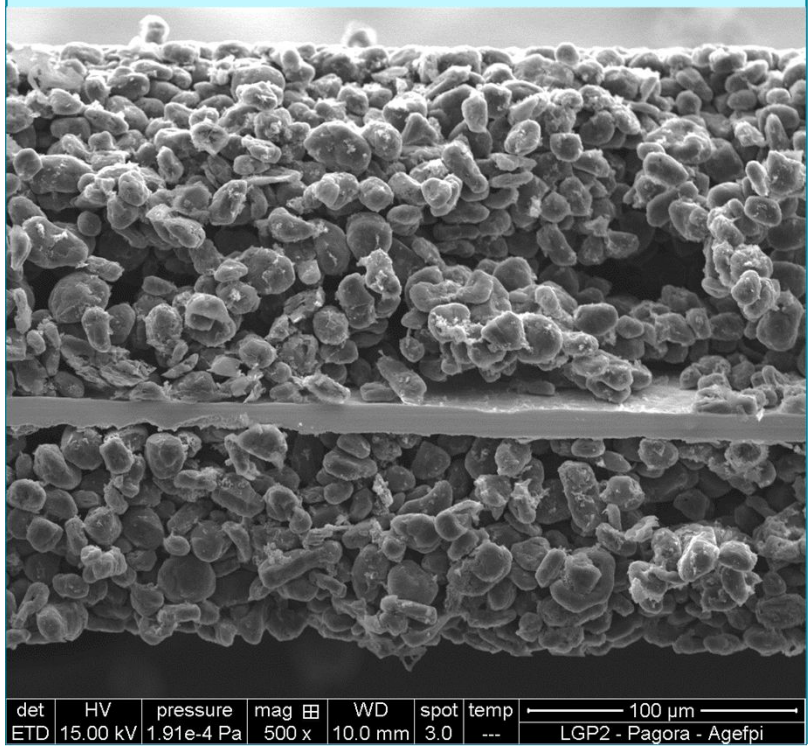


	Pull-out	Delamination
Uncalendared (UC)	→	→
Calendared (C)	X	→

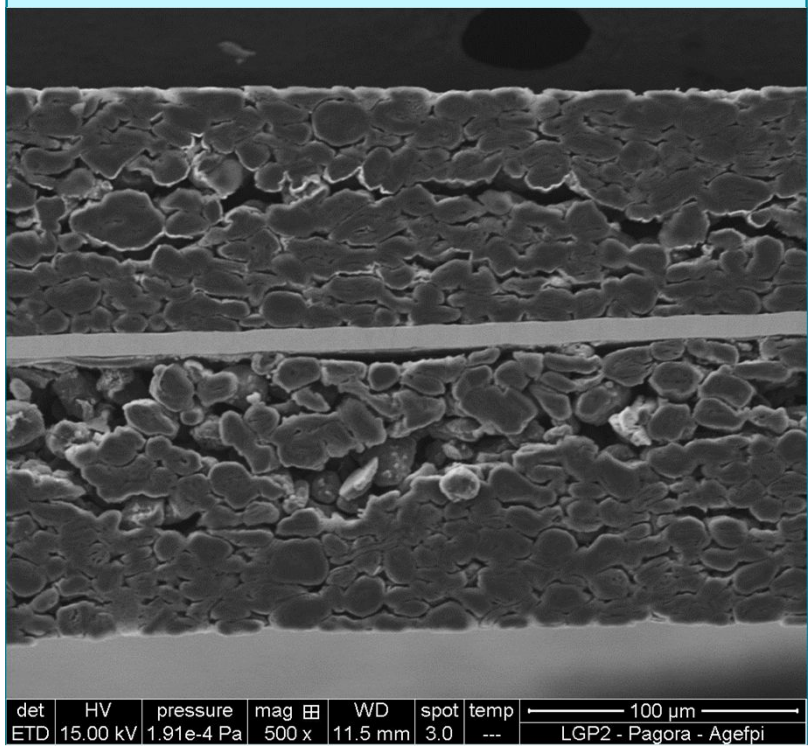
2. Adhesion/pull-out: observation

Cross sectioning performed by cold ion abrasion by IMN Nantes

Uncalendered

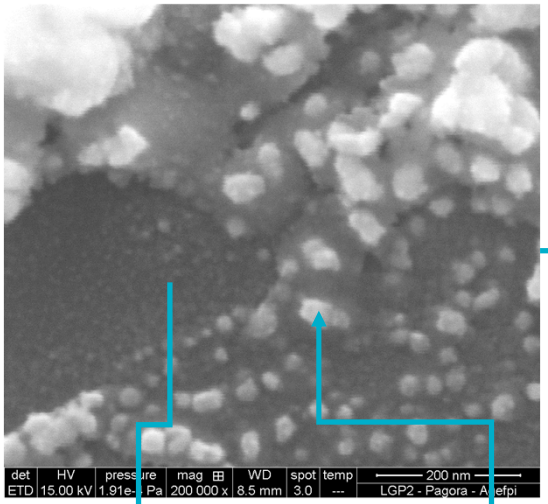


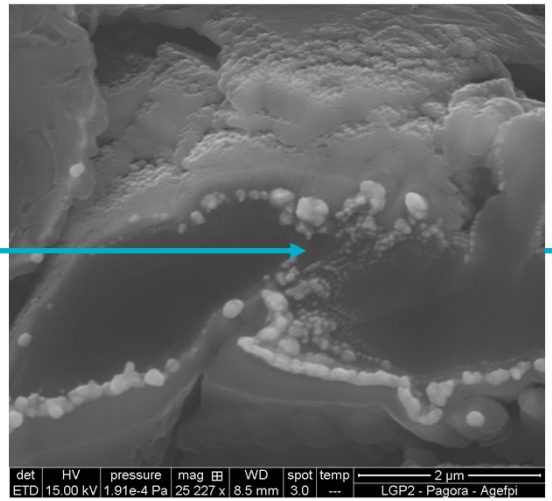
Calendered

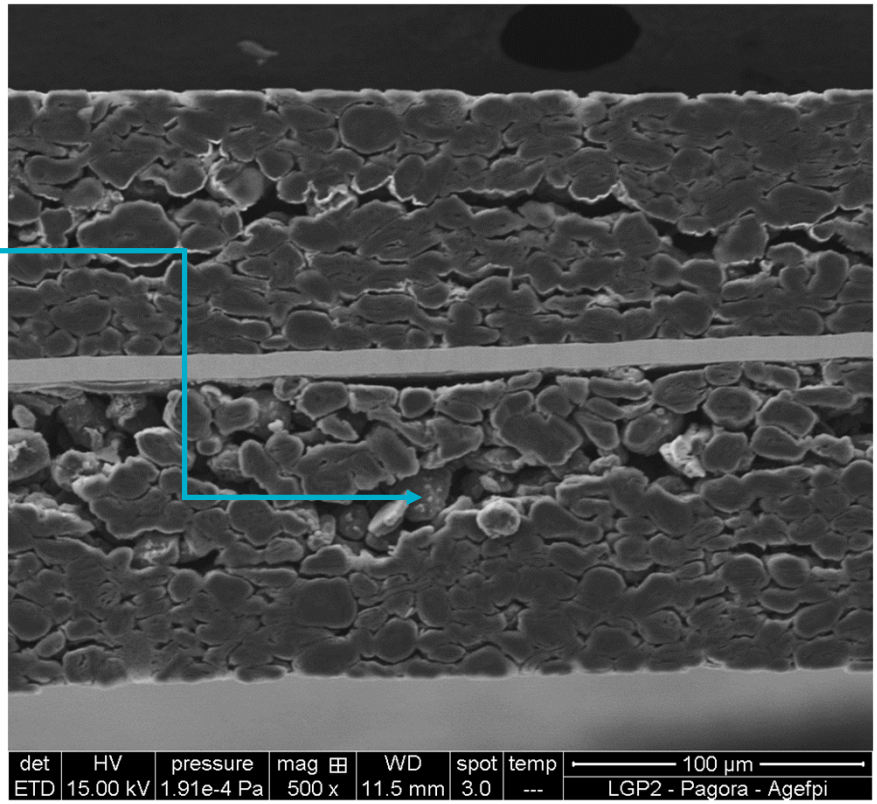


- Improved cohesion during cutting for the calendered electrode
- Delamination during calendaring

3. Delamination zone

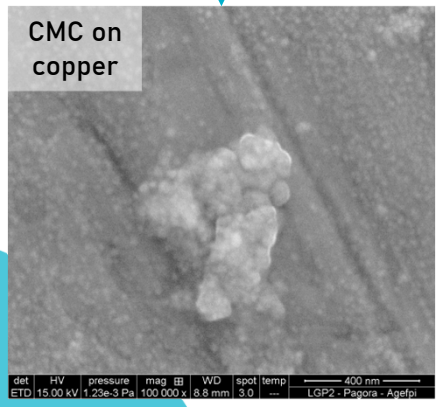






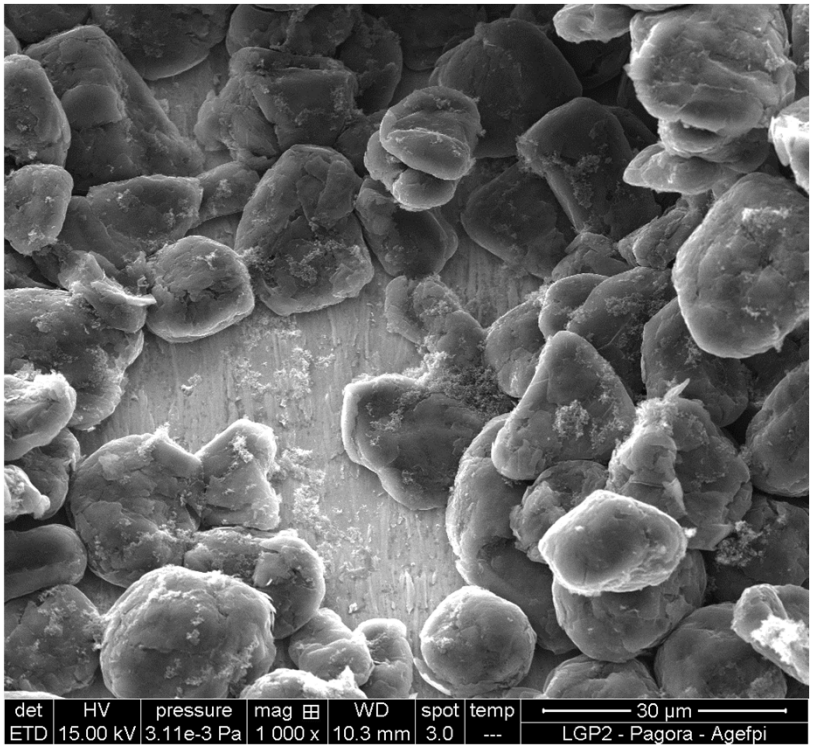
?

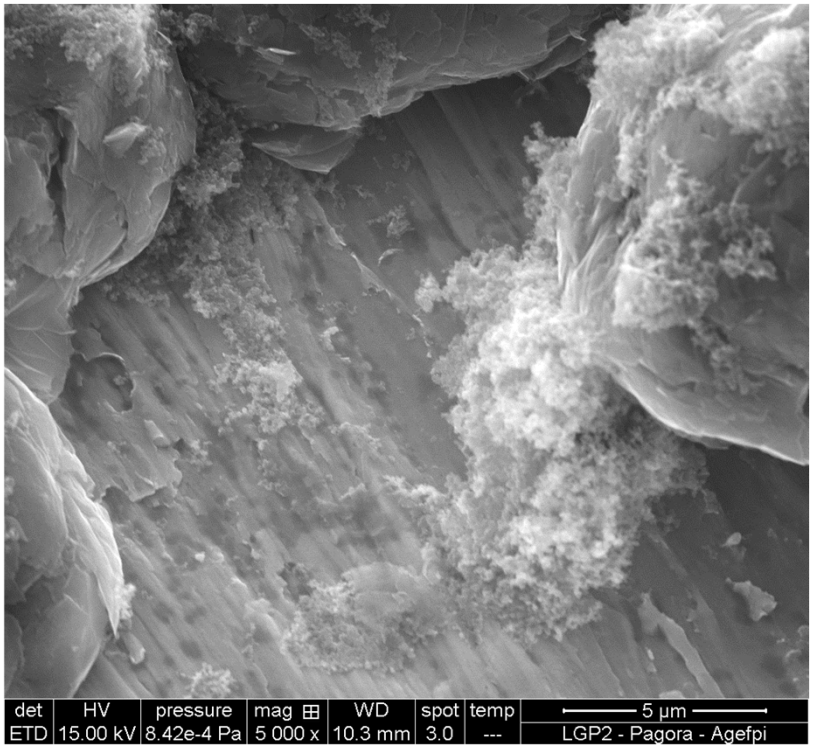
CMC on copper



- Looks like what observed on the copper coated with CMC
- White particles ?

2. Adhesion





Particles seem to exhibit weak adhesion to copper

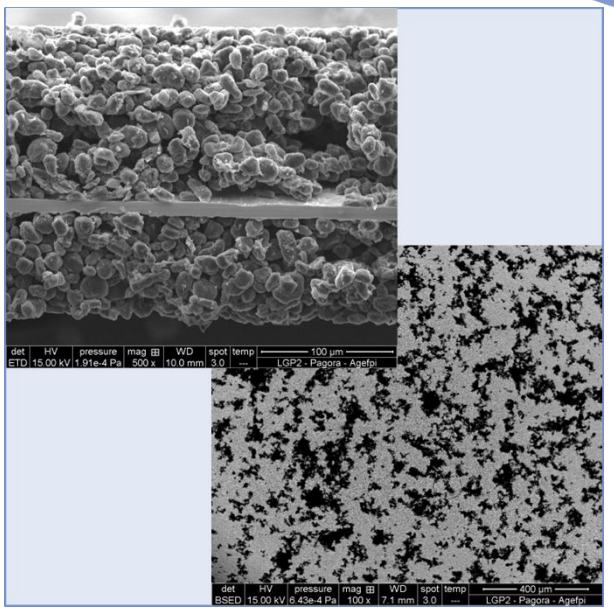
4. Conclusions and perspectives

1. Conclusions and perspectives

1. Identification of the different components in the negative electrode, both at the surface and in cross section

2. Cohesion tests allow the characterization of resistance to peeling and delamination
   - ⇒ Further investigation of the distribution of components is required, particularly for CMC and SBR

3. The previous observation lead to:
   - ⇒ Modification of the slurry composition: increas binders content
   - ⇒ Adjustment of the formulation by first dispersing carbon black in CMC to improve carbon black dispersion around graphite particles.
   - ⇒ To be verified by electrical resistivity measurement and SEM imaging

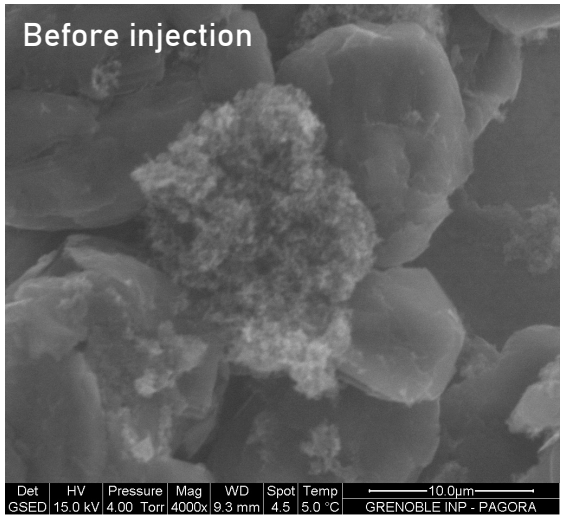


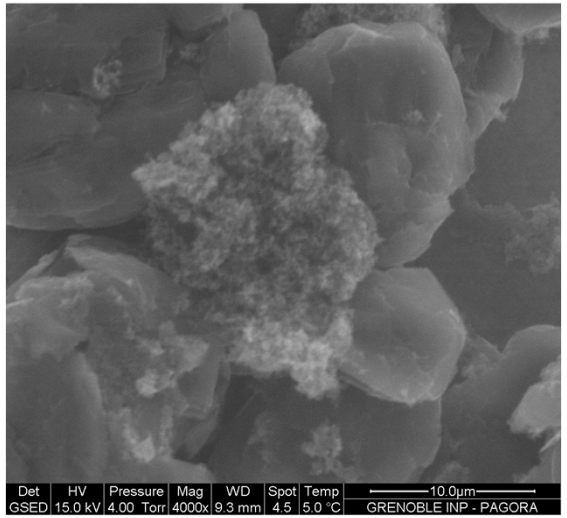
2. Perspectives

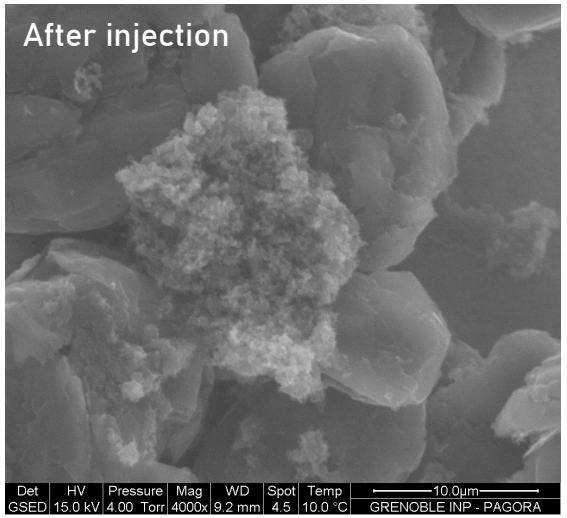
4 Investigation of the electrode surface behaviour in the presence of lithium salt

⇒ Injection of DMSO as a model fluid with rheological properties close to those of the electrolyte

- Environmental mode
- 4 Torr
- Between 5 and 15 °C







5 Electrochemical testing in progress at LEPMI

Thank you for your attention.

Acknowledgements:

- L'Ecole De La Batterie for financial support
- IMN Nantes for electrode cross sectioning – Philippe Moreau
- LEPMI for providing the opportunity to perform electrochemical testing on my electrodes – Renaud Bouchet

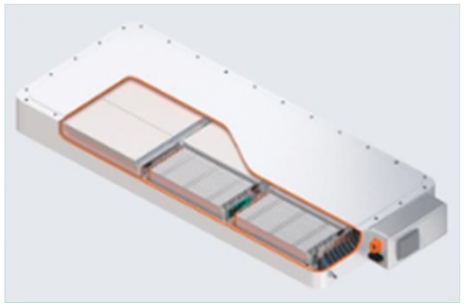
References

1. Dell, R. M., Dell, R., & Rand, D. A. J. (2001). *Understanding batteries*. Royal Society of Chemistry.
2. Abraham, K. M. (2020). How Comparable Are Sodium-Ion Batteries to Lithium-Ion Counterparts ? *ACS Energy Letters*, *5*(11), 3544-3547.
3. PFA (Plateforme Automobile). (2026, janvier). *Dossier de presse – Le marché automobile français (données AAA DATA)* [PDF]. PFA. https://pfa-auto.fr/wp-content/uploads/2026/01/Dossier-de-presse-PFA.pdf
4. Julien, C., & Stoynov, Z. (2012). *Materials for Lithium-Ion Batteries*. Springer Science & Business Media.
5. Lim, S., Kim, S., Ahn, K. H., & Lee, S. J. (2015). The effect of binders on the rheological properties and the microstructure formation of lithium-ion battery anode slurries. *Journal Of Power Sources*, *299*, 221-230.
6. Schmitt, M. (2016). *Slot die coating of lithium-ion battery electrodes*. KIT Scientific Publishing.
7. Bitsch, B., Dittmann, J., Schmitt, M., Scharfer, P., Schabel, W., & Willenbacher, N. (2014). A novel slurry concept for the fabrication of lithium-ion battery electrodes with beneficial properties. *Journal Of Power Sources*, *265*, 81-90.
8. Makino, S., Akimoto, Y., Ishii, M., & Nakamura, H. (2024). Impact of slurry preparation method on the rheological behaviour of dense anode slurries for lithium-ion batteries. *Rheologica Acta*, *63*(4), 319-331.
9. Kitamura, K., Tanaka, M., & Mori, T. (2022). Effects of the mixing sequence on the graphite dispersion and resistance of lithium-ion battery anodes. *Journal Of Colloid And Interface Science*, *625*, 136-144.
10. Kistler, S. F., & Schweizer, P. M. (1997). *Liquid film coating : Scientific Principles and Their Technological Implications*. Kluwer Academic Pub.

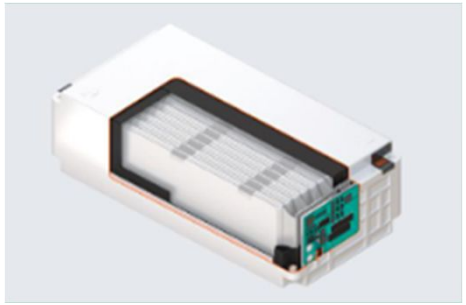
Russian Doll Structure

Batterie

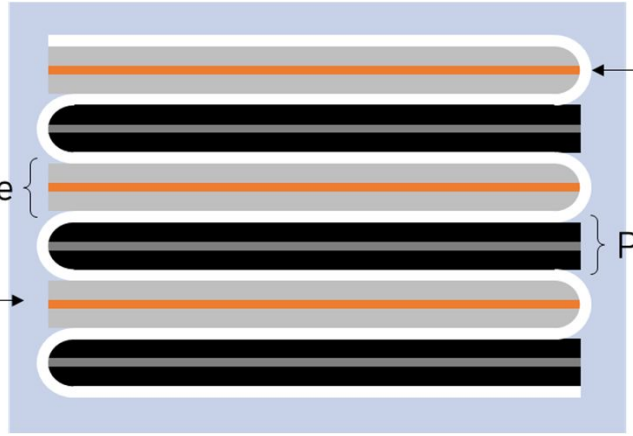
Packs



Module



Pouch cell



60 electrodes

We will focus on the negative graphite electrode

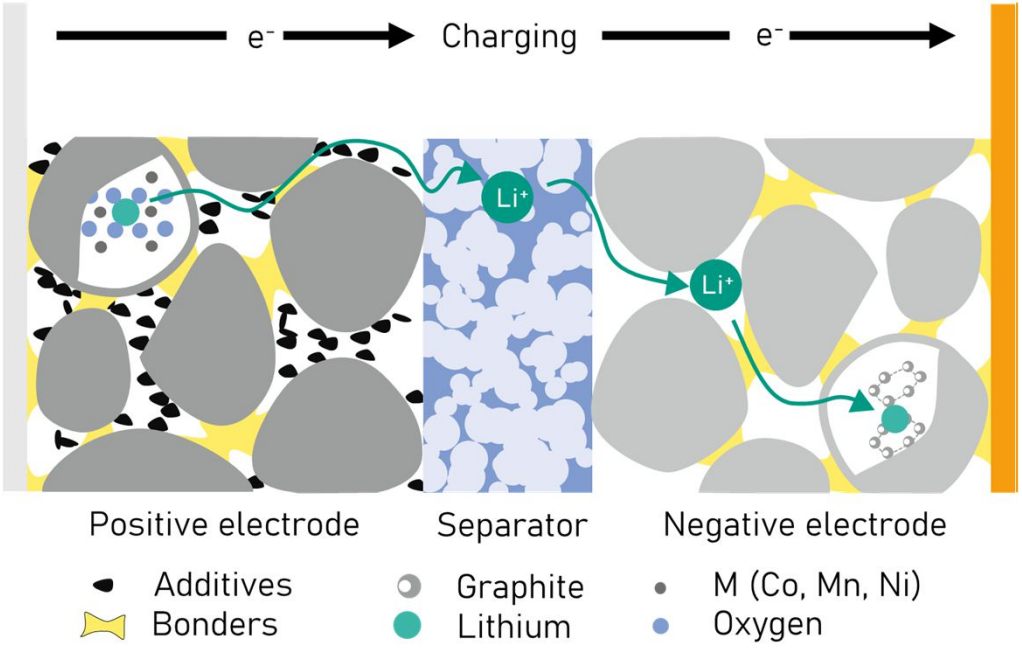
NMC – lithium ion batterie

	Negative electrode	Positive electrode
Current collector	Copper film	Aluminium film

	Negative electrode	Positive electrode
Active material *Mass percentage*	Graphite 50 %	LNMC811 70 %
Conductive additive *Mass percentage*	Carbon black 1 %	NMC 1 %
Binder *Mass percentage*	SBR, CMC 1 %	PVDF 1 %
Solvent *Mass percentage*	Water 48 %	NMP 28 %

Electrolyte	LiClO4, LiAsF6, LiPF6, Li(CF3SO3), Li[N(CF3SO2)2]

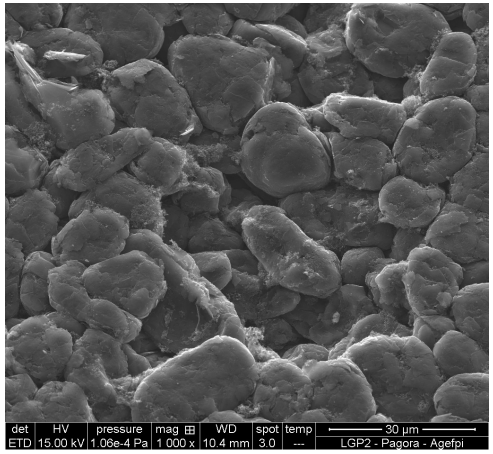
Separator	Polyethylene or polypropylene

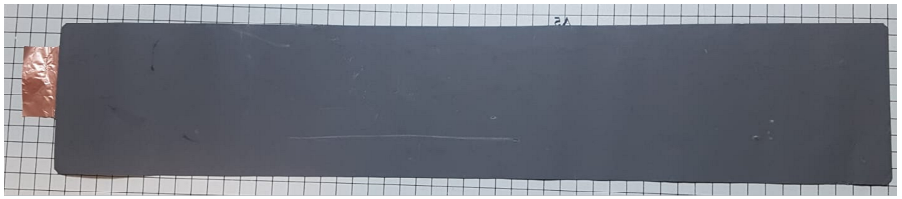


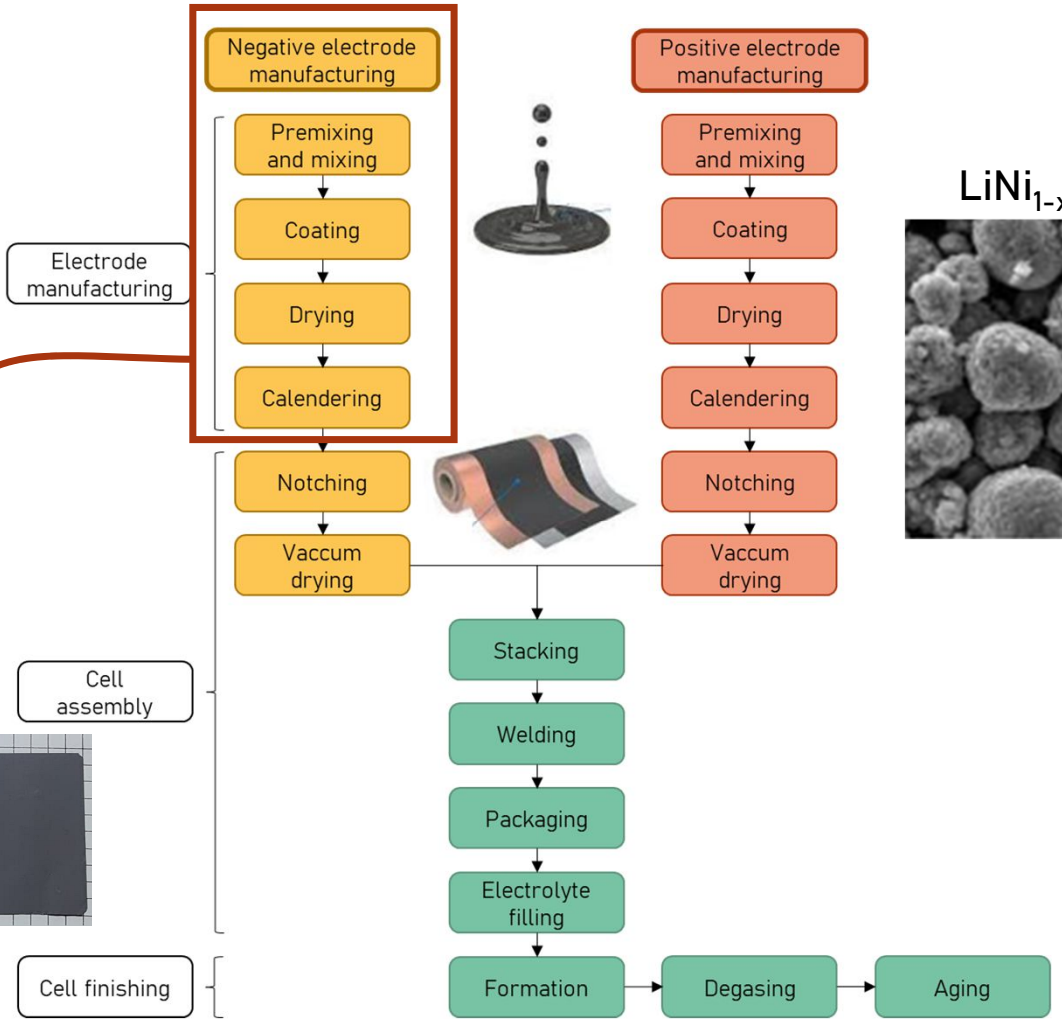
Lithium-ion battery operating diagram M. Schmitt, 2015[6]

BLi manufacturing

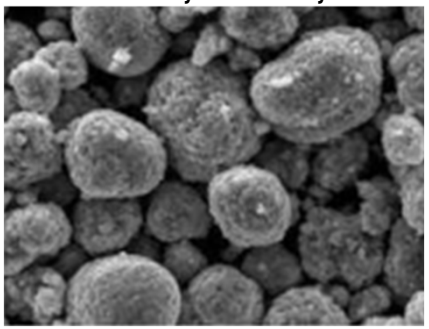
Graphite





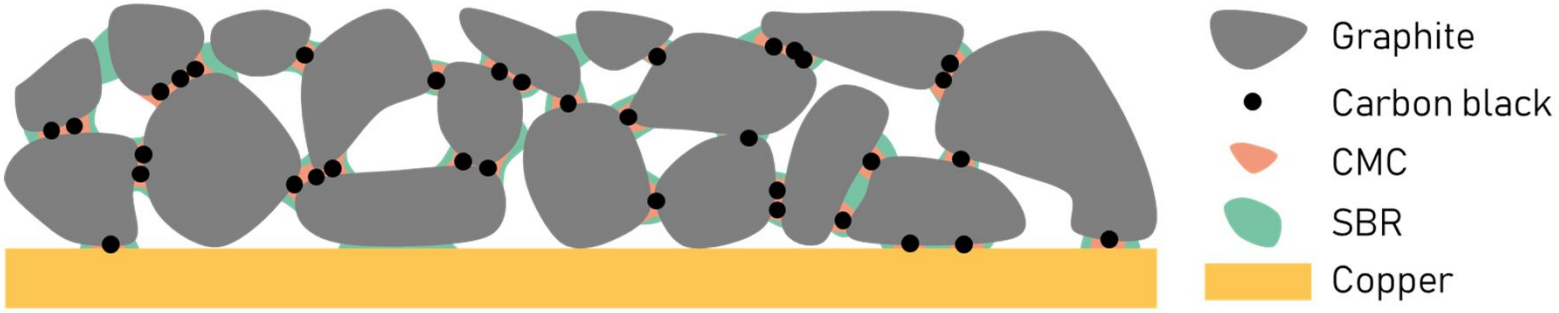


$LiNi_{1-x-y}Co_xMn_yO_2$



Lithium-ion batterie manufacturing process

Negative electrode structure



	Negative electrode
Current collector	Copper film
Active material	Graphite
Conductive additive	Carbon black
Binder	SBR, CMC

→ Mechanical support & conducts electrons

→ Li^+ intercalation

→ Electrical contact[4]

→ CMC: Binder, stabilizer, dispersant[5]
SBR: Binder, flexibility enhancer, reinforcing agent[5]

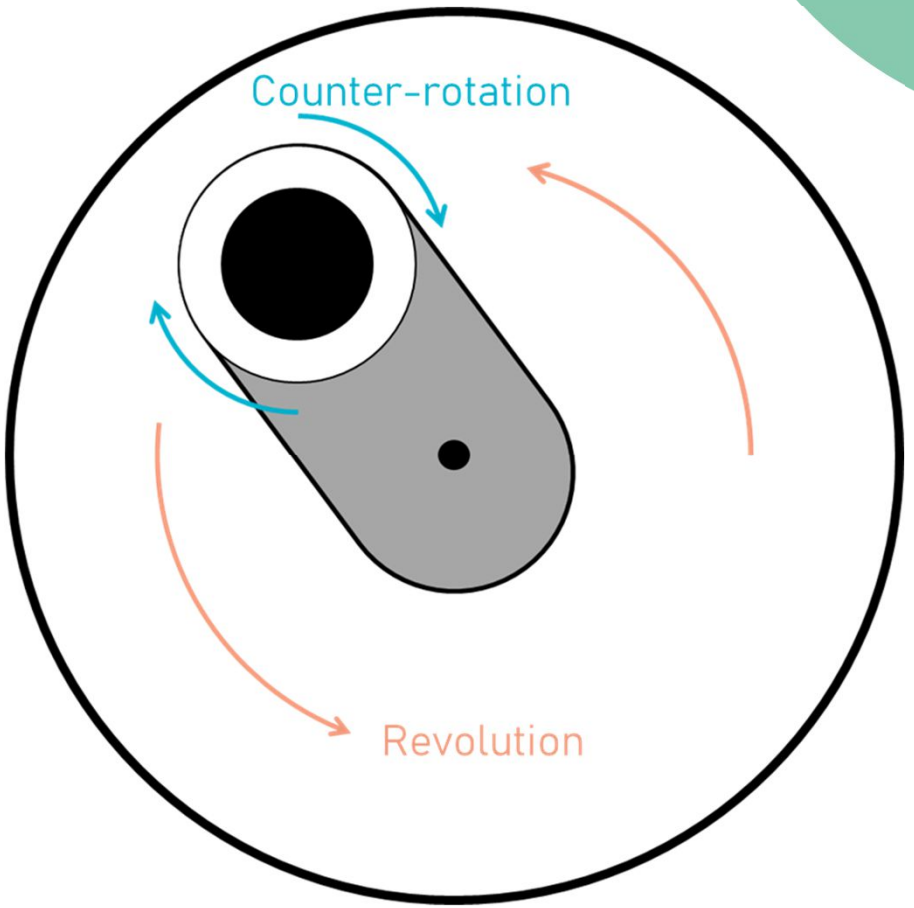
Observe the distribution of components within the thickness of the electrode using SEM

Slurry formulation

1) Dissolution of the CMC into water [6,7,8]
2) Adding carbon black and graphite[7,8]:
   - Time = 8 minutes
   - Revolution speed = 2 000 rpm[9]
   - Counter-rotation speed = 250 rpm[9]
3) Adding SBR :
   - Time : 2 minutes
   - Revolution speed = 1 000 rpm[9]
   - Counter-rotation speed = 125 rpm[9]

✓ Slurries composition :

	Wet	Dry
Graphite %	53,6	96,4
Carbon black %	0,8	1,4
CMC %	0,6	1,1
SBR %	0,6	1,1
Water %	44,4	0

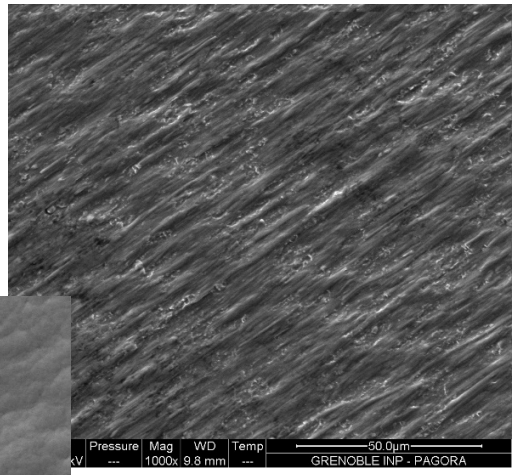


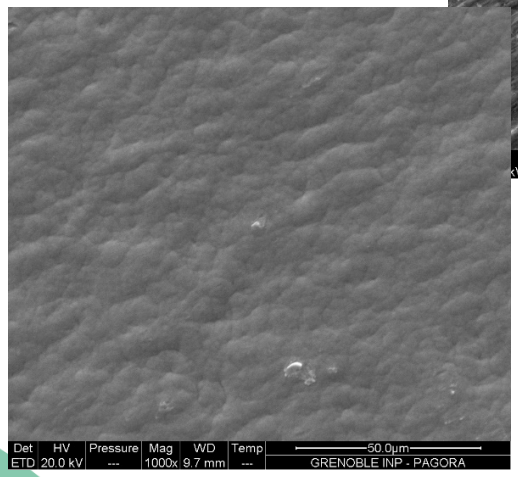
Schema of a speed mixer

Copper strip

- Weight : $G = 71{,}93\ g.m^{-2} \pm 1{,}20\ g.m^{-2}$
- Thickness : $e = 8\ \mu m\ \pm 1\ \mu m$

Mat side of the copper





Shiny side of the copper

✓ Surface free energy measured by contact angle

	Shiny side of copper	Mate side of copper
Polar *mN.m^{-1}*	51,17	24,87
Dispersive *mN.m^{-1}*	0,14	4,09
Surface energy *mN.m^{-1}*	51,31	28,96

✓ Bekk roughness

	Shiny side of copper	Mate side of copper
Time *s*	8013	6315

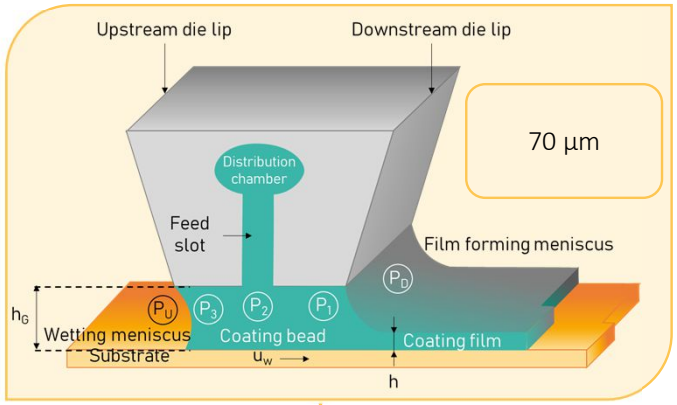
➡ Mate side is rougher than the glossy side

➡ Differences in roughness and surface energy of the copper can lead to :

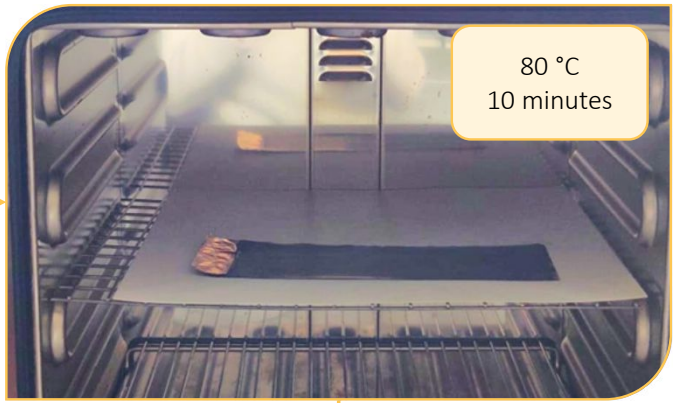
- differences in slurry adhesion
- differences in electrochemical performances between the two sides

Lab manufacturing

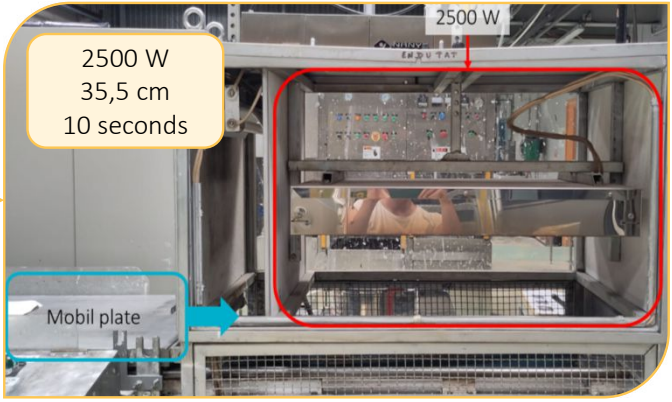
Slot die coating[10]



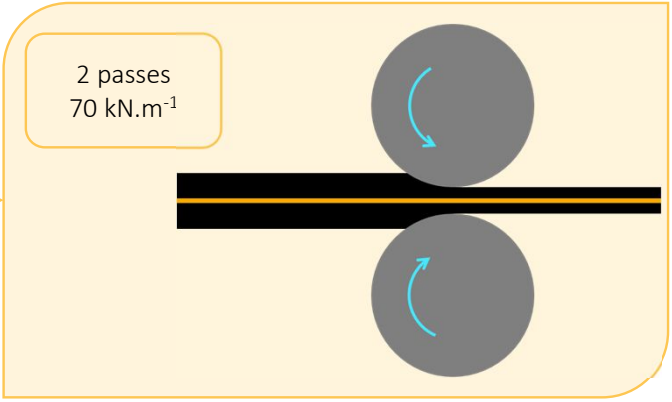
Oven drying



IR drying



Calendering

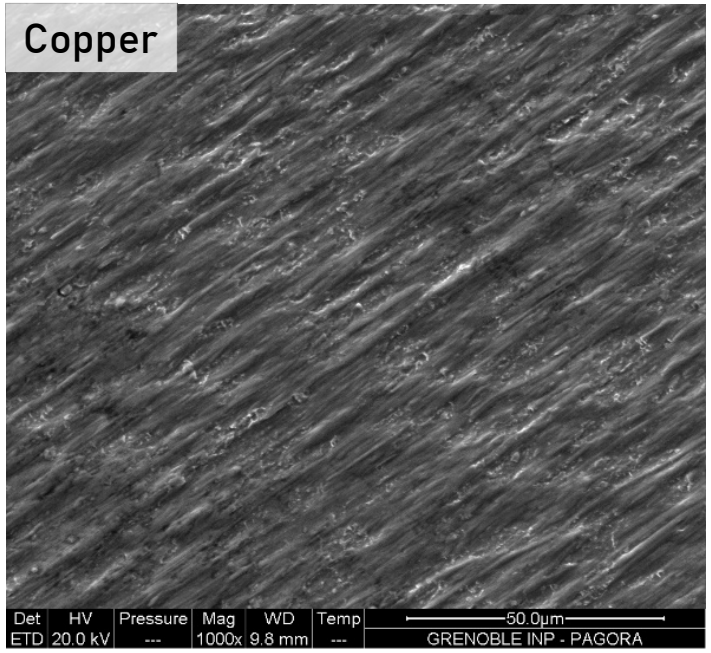


Porosity :
50% ⇒ 30 %

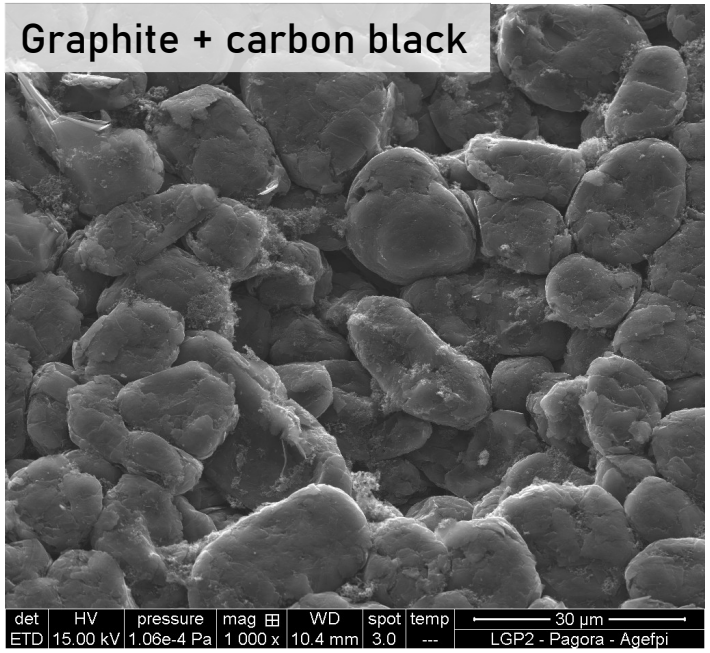
Conductive components

Observation on the matte side of the copper

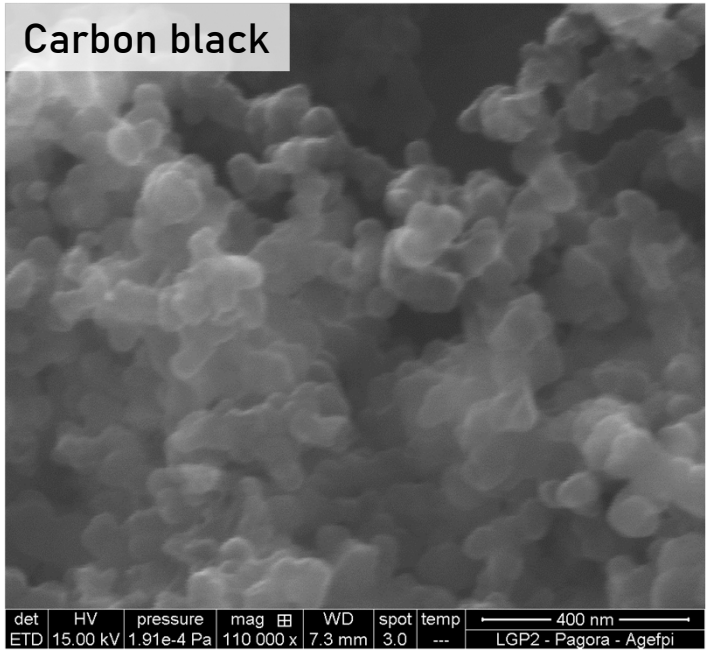
Copper



Graphite + carbon black



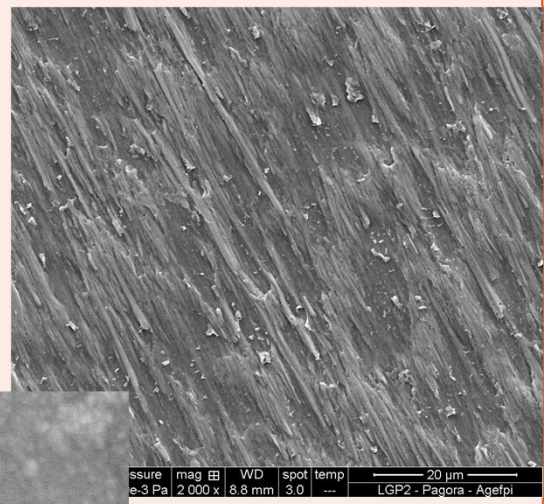
Carbon black



What about polymers ?

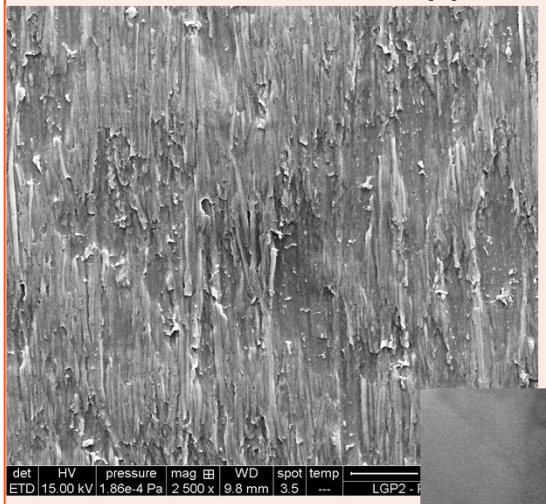
CMC observation

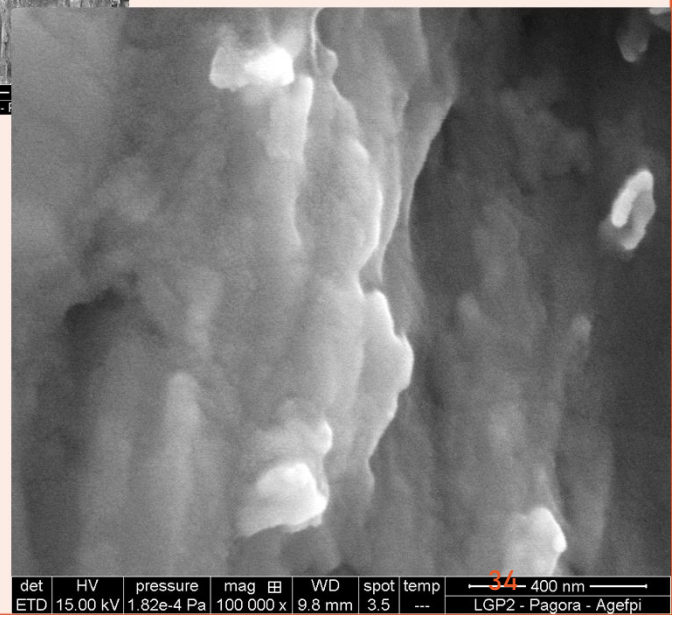
CMC



Speckled on the surface of the copper

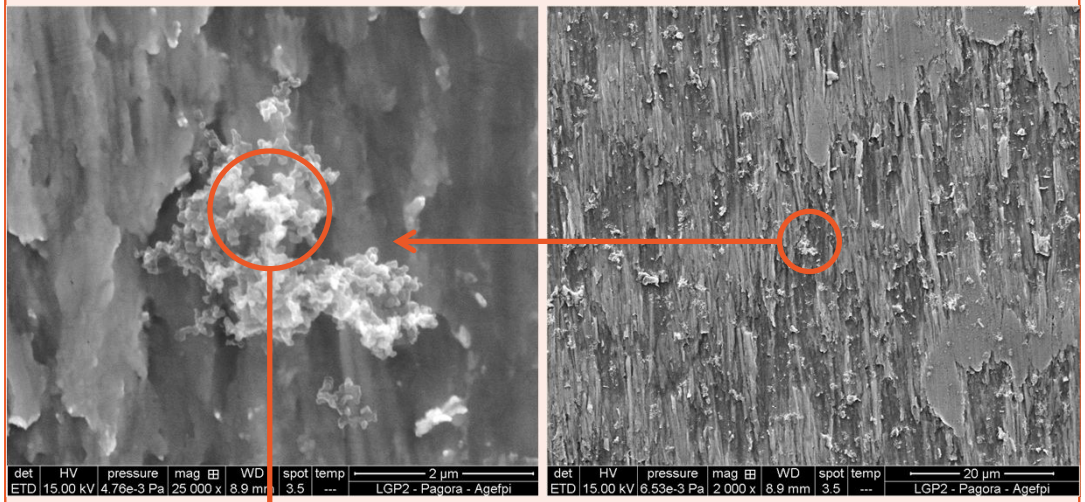
Copper mate side





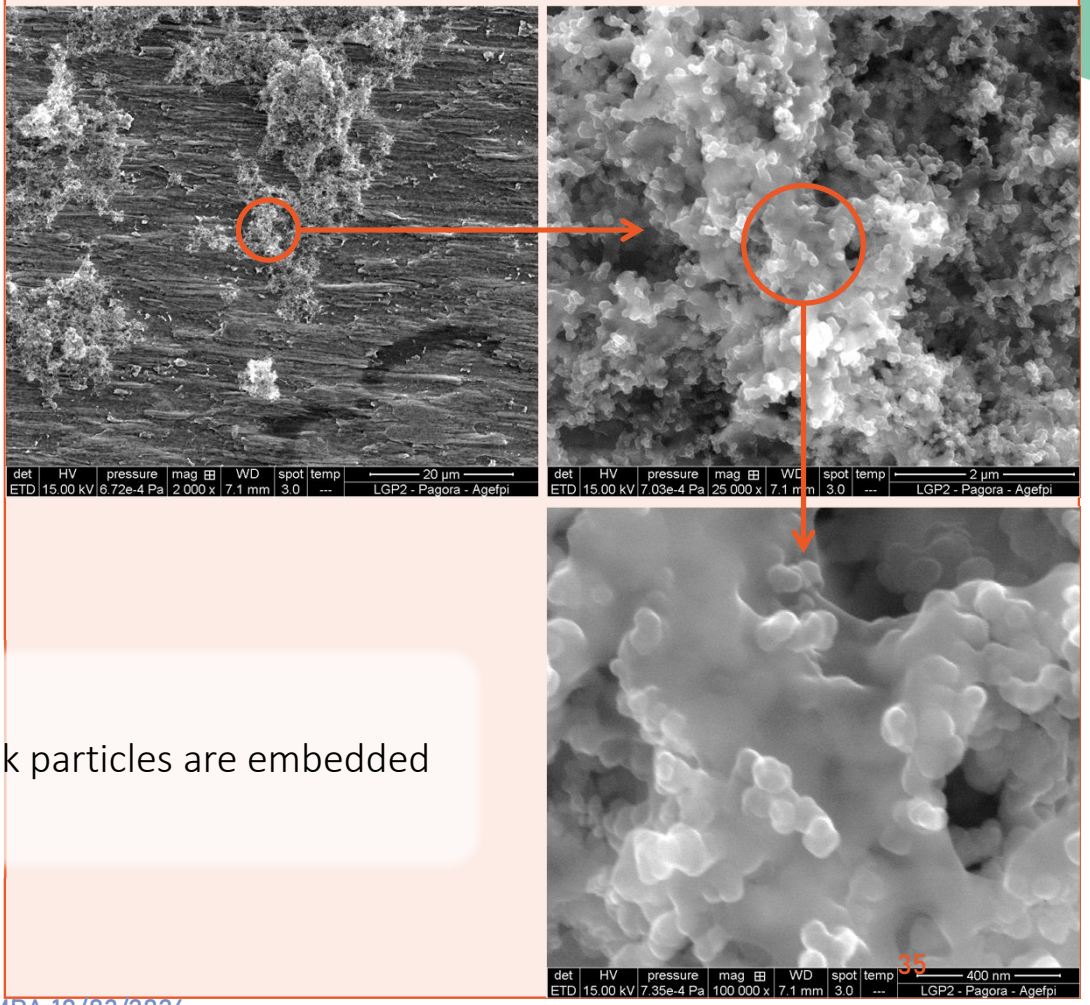
SBR observation

CMC + CB



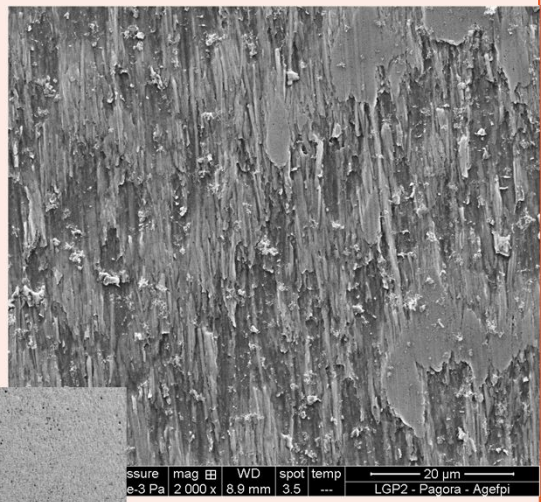
With SBR carbon black particles are embedded

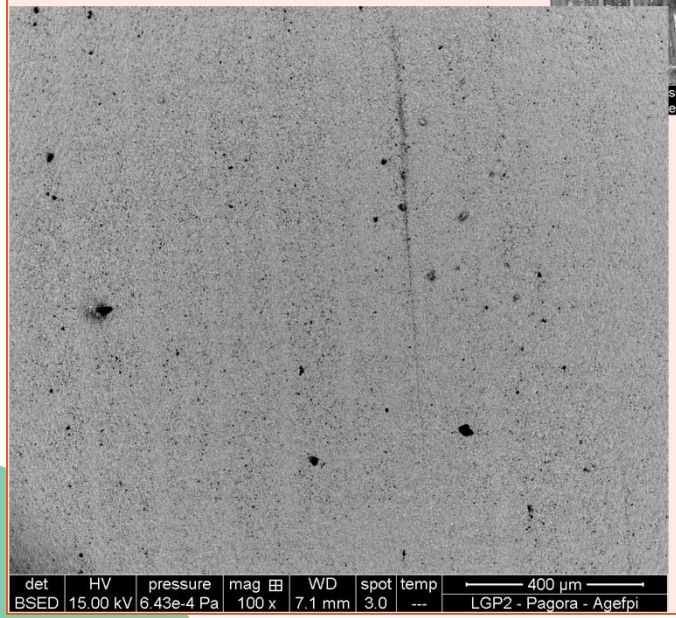
SBR + CB



Carbon black dispersion

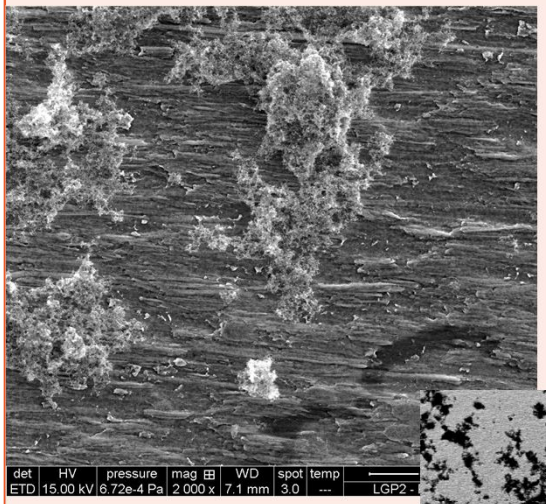
CMC + CB

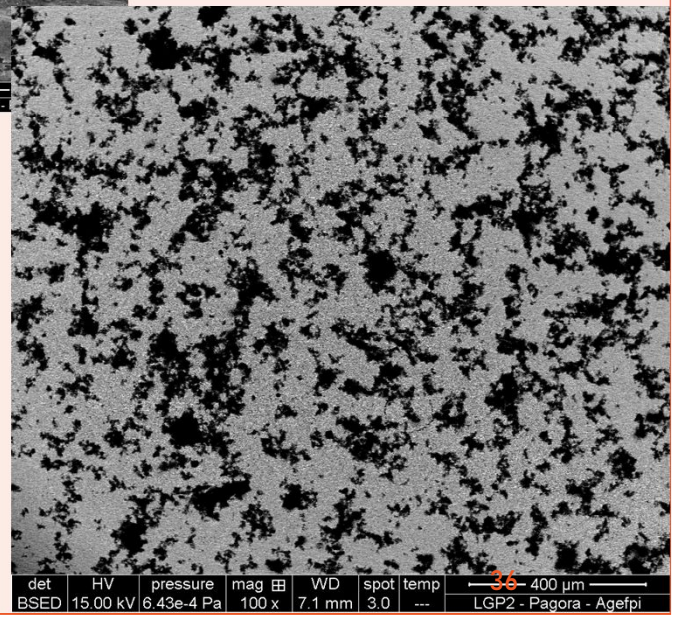




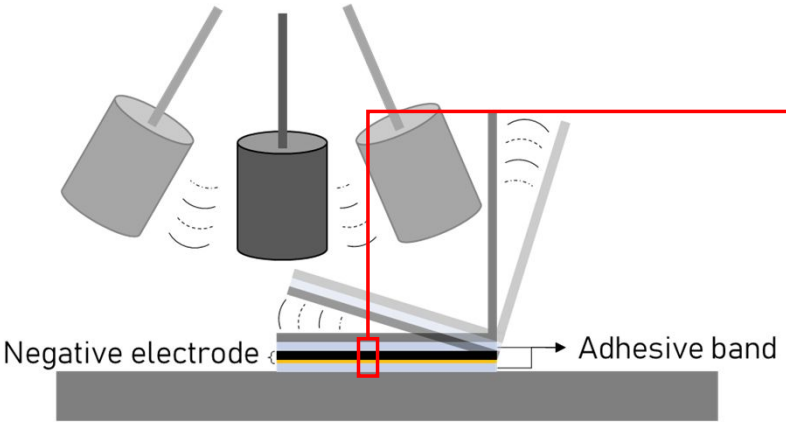
Better dispersion in CMC than SBR

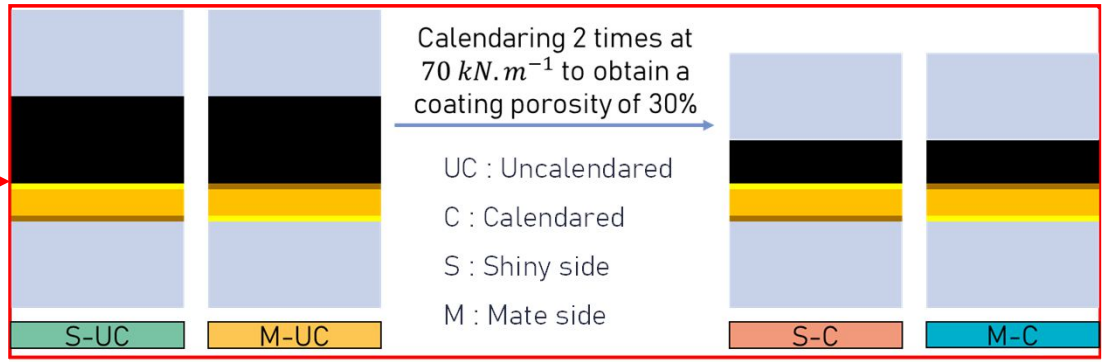
SBR + CB

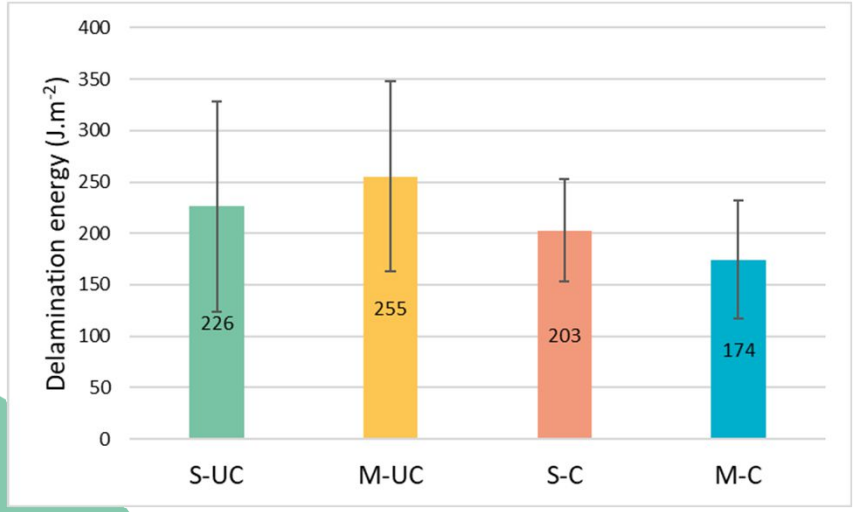


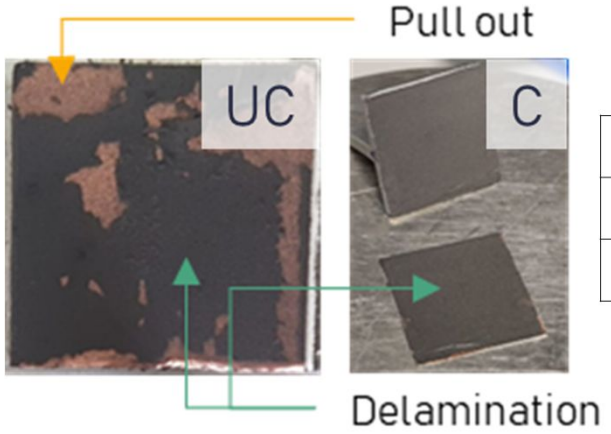


Adhesion test









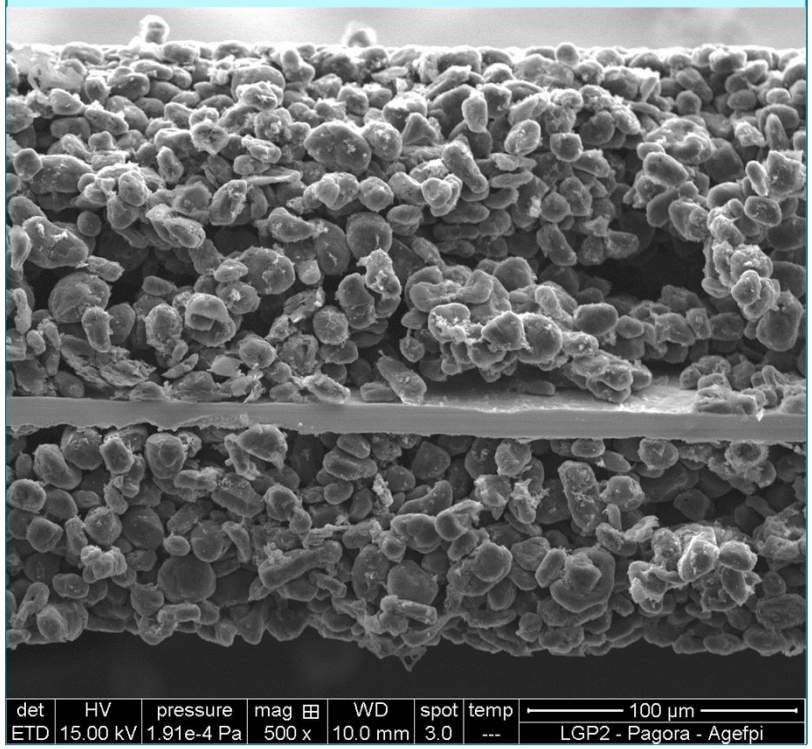
	Pull-out	Delamination
Uncalendared (UC)	→	→
Calendared (C)	X	→

- No improvement in the internal cohesion of the coating.
- But a decrease in measurement heterogeneity.

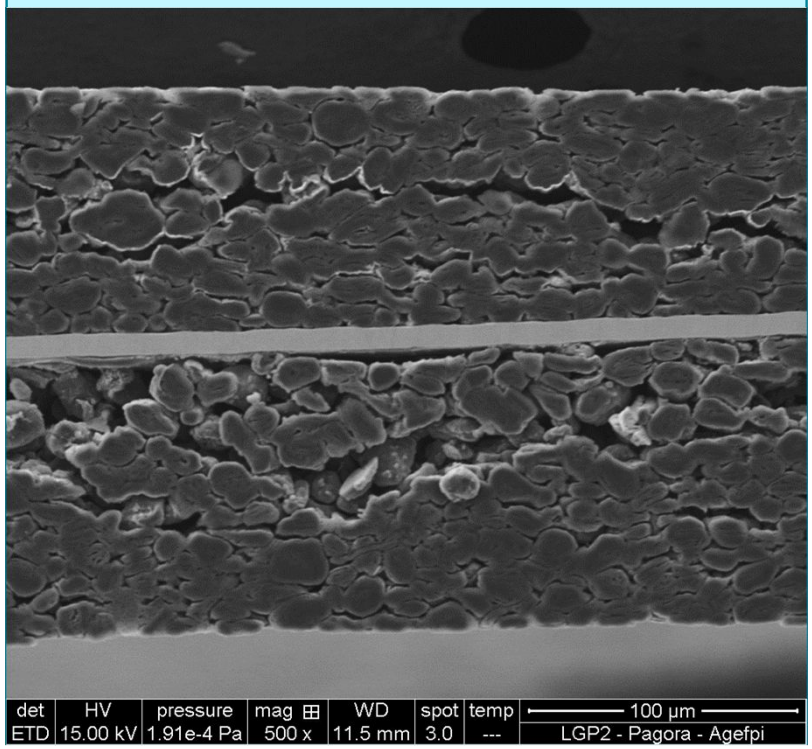
Adhesion/pull-out: observation

Cross sectioning performed by cold ion abrasion by IMN Nantes

Uncalendered

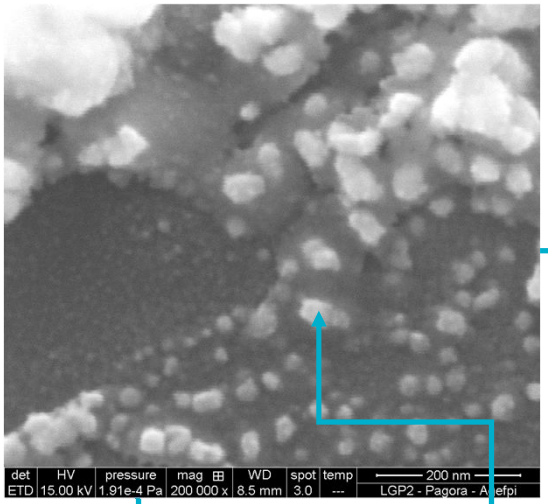


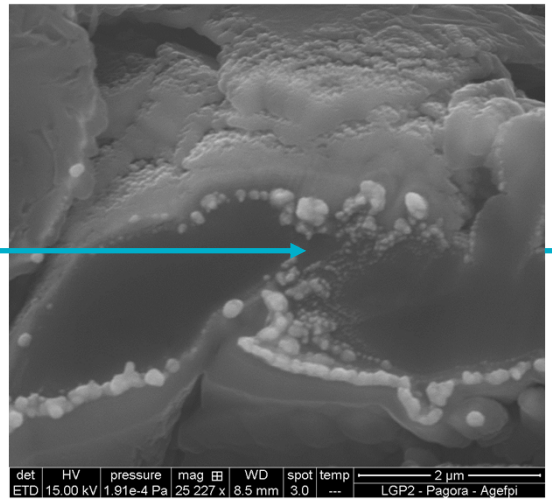
Calendered

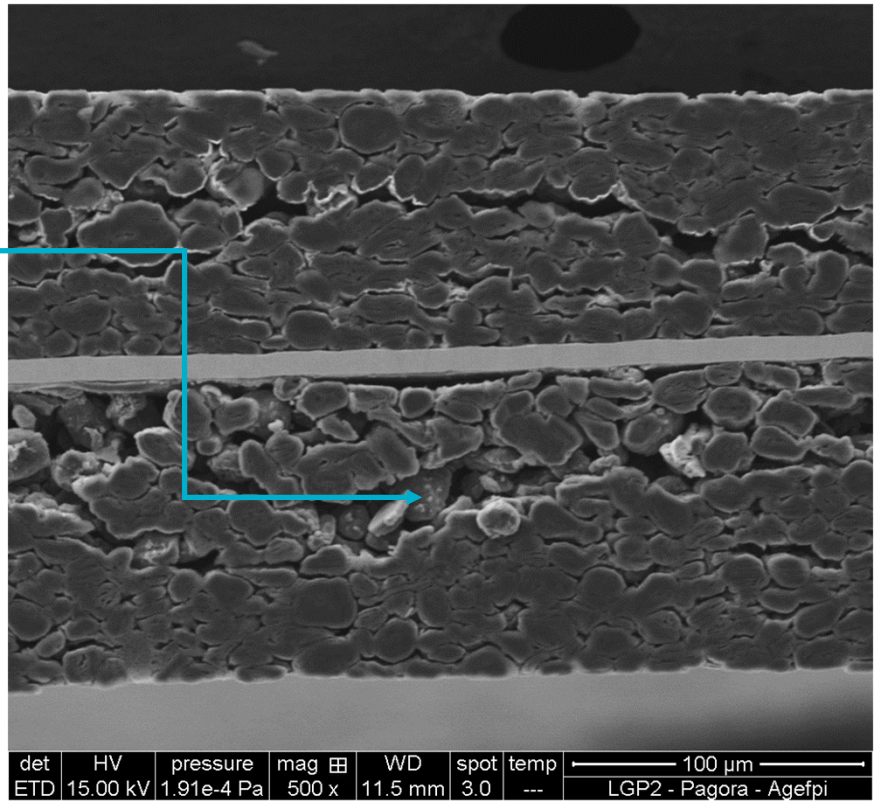


- Improved cohesion during cutting for the calendered electrode
- Delamination during calendaring

Delamination zone

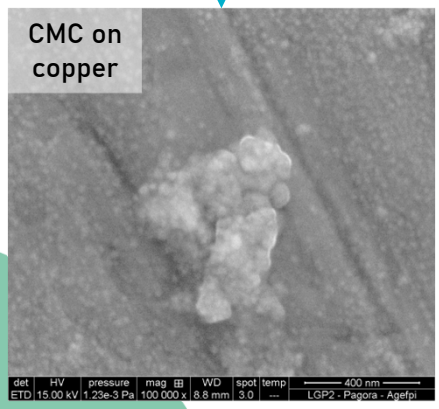






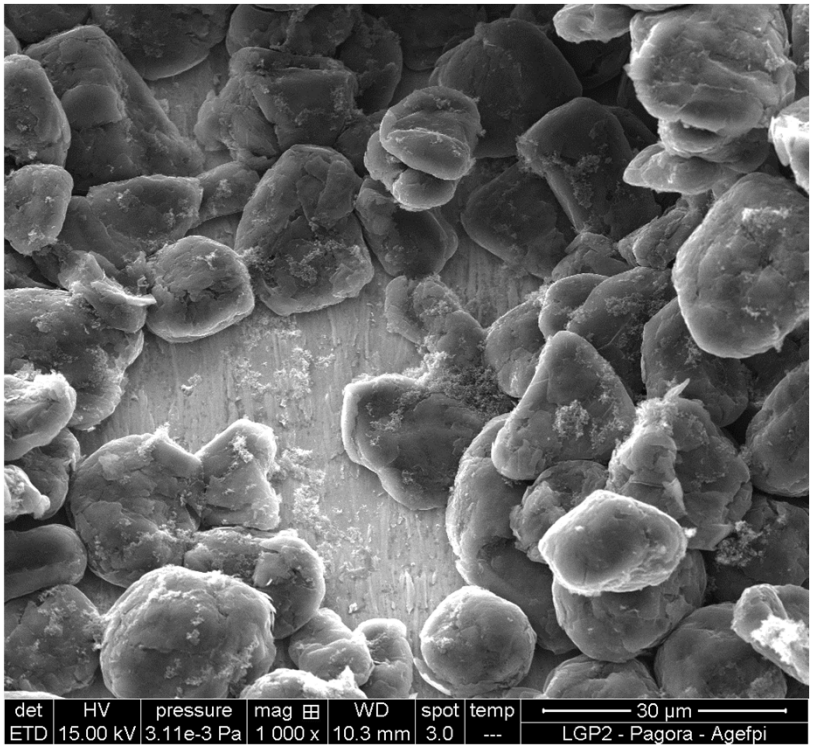
?

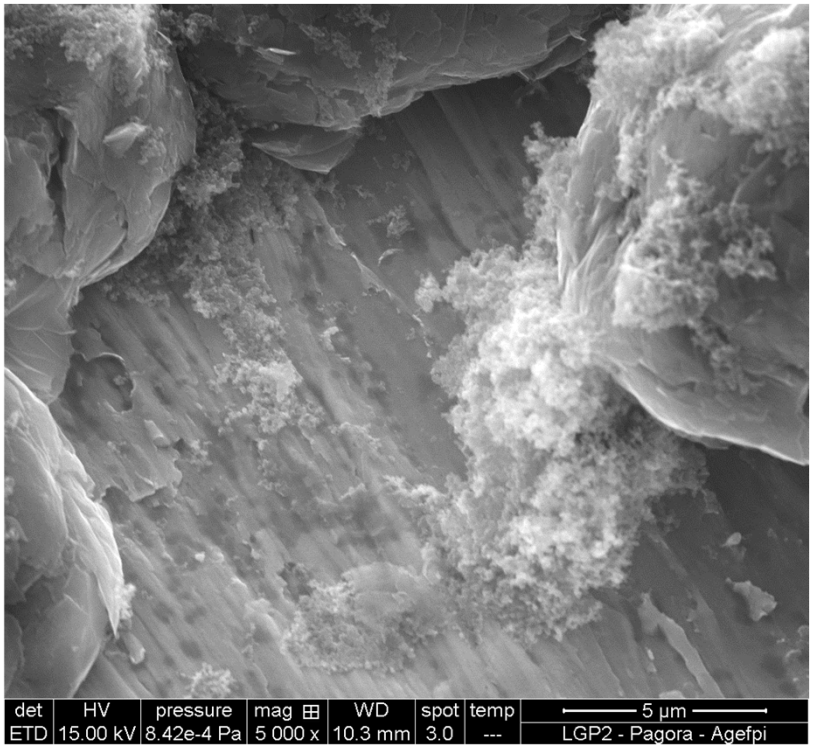
CMC on copper



- Looks like what observed on the copper coated with CMC
- White particles ?

2. Adhesion





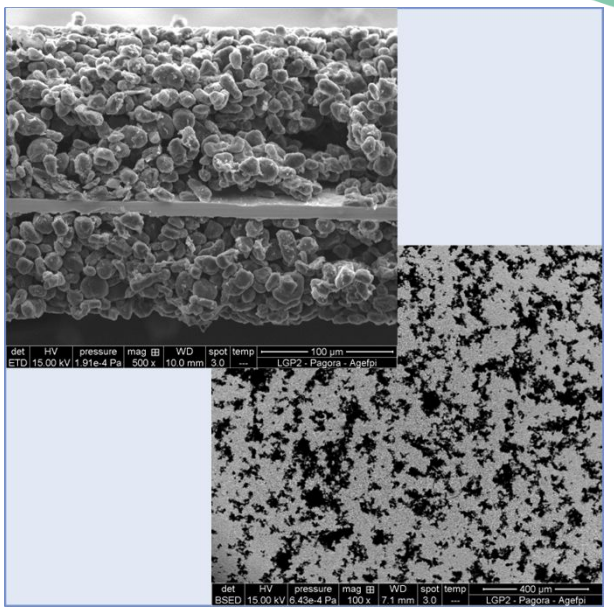
Particles seem to exhibit weak adhesion to copper

1. Conclusions and perspectives

1. Identification of the different components in the anode, both at the surface and in cross section

2. Cohesion tests allow the characterization of resistance to peeling and delamination
   - ⇒ Further investigation of the distribution of components is required, particularly for CMC and SBR

3. The previous observation lead to:
   - ⇒ Modification of the slurry composition: increas binders content
   - ⇒ Adjustment of the formulation by first dispersing carbon black in CMC to improve carbon black dispersion around graphite particles.
   - ⇒ To be verified by electrical resistivity measurement and SEM imaging

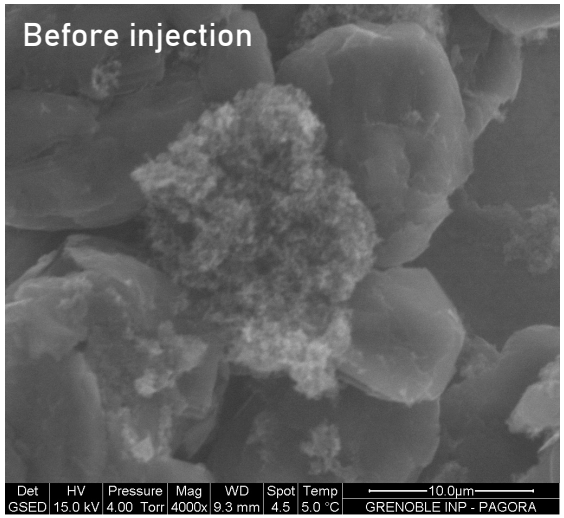


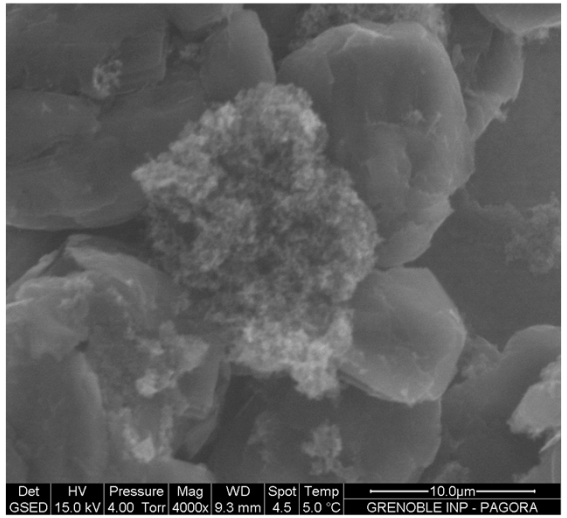
2. Perspectives

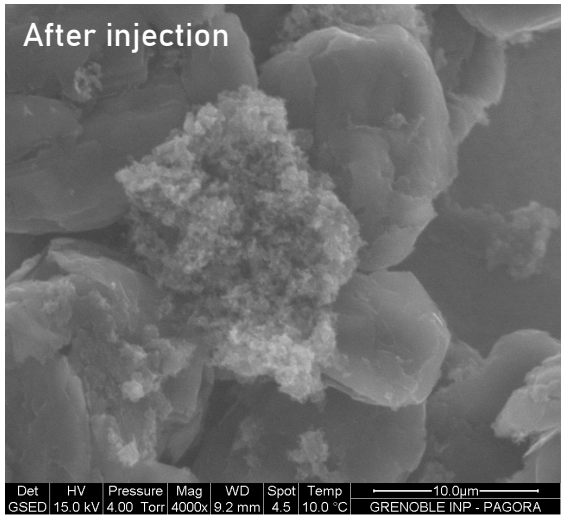
4 Investigation of the electrode surface behaviour in the presence of lithium salt

⇒ Injection of DMSO as a model fluid with rheological properties close to those of the electrolyte

- Environmental mode
- 4 Torr
- Between 5 and 15 °C







5 Electrochemical testing in progress at LEPMI