

Advances in gravure printed Li/Na batteries

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Introduction:

Printed batteries are increasingly involved in our daily life to feed small, portable and wearable electronic devices. Among printing technologies, gravure is the most appealing printing technique for the manufacturing of functional layers thanks to its unique characteristic to couple high speed and high resolution and we demonstrated the possibility to use gravure printing for lithium-ion printed batteries, successfully manufacturing electrodes and answering to many challenges related to the selected printing technique. Gravure printing is industrially widespread, for this reason each result obtained at lab-scale could be easy to scale up.

LiBs:

Different electrodes formulations:

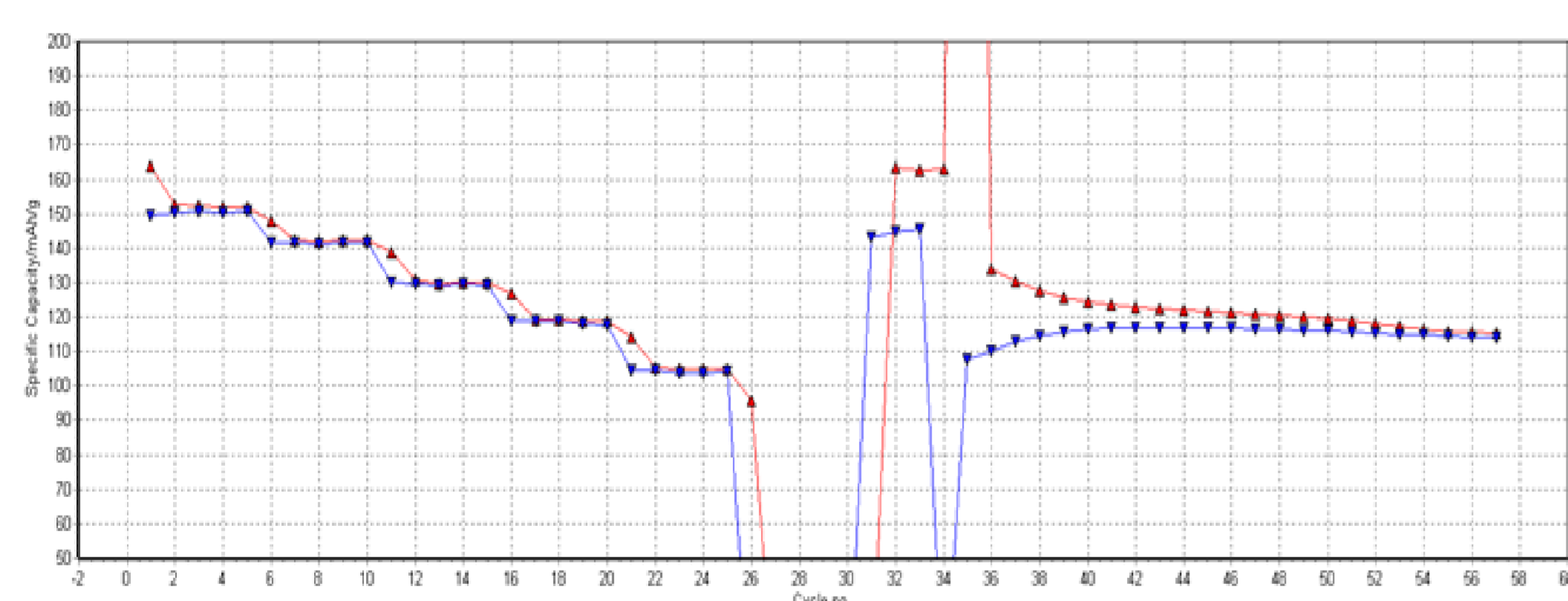
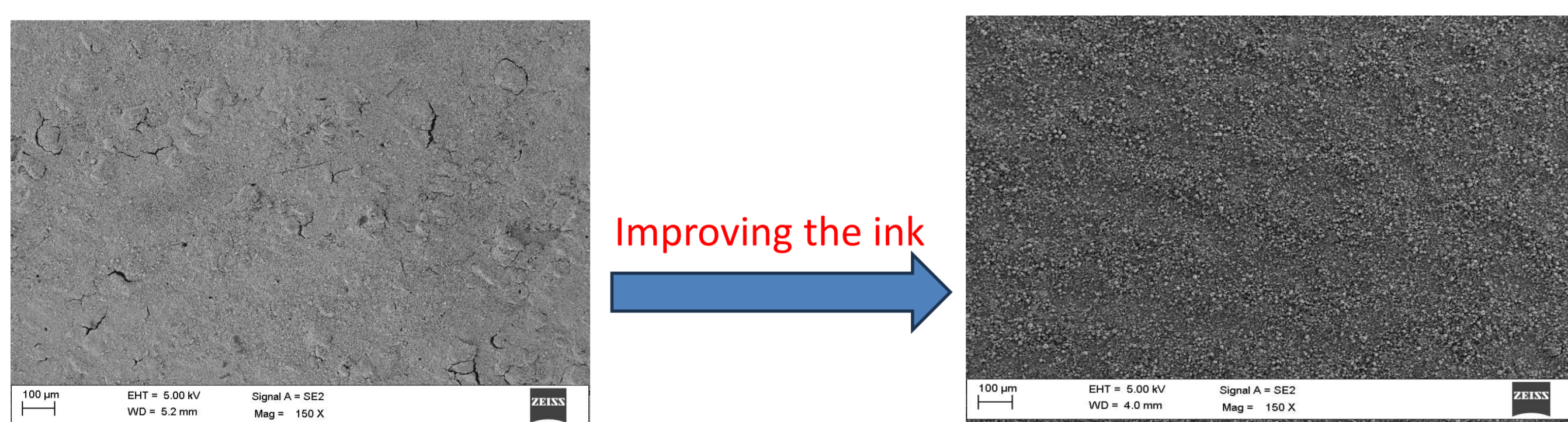
Trying new active materials, new binders and solvents, also aiming to produce an experimental database.

Ink	dry solid content [wt%]	ball mulling	viscosity [mPa s]	surface tension [mN m ⁻¹]	printing		Ca	number of layer	Electrode	
					printing speed [m s ⁻¹]	printing force [N]			mass loading [mg cm ⁻²]	thickness [μm]
LFP										
15	No	74	30	0.6	700	1.5	10	1.8	20 ± 1	0.9
15	Yes	43	30	0.6	700	0.9	10	1.4	15 ± 1	0.9
LMO										
18	No	78	42	0.6	700	1.1	7	0.7	19 ± 4	0.4
18	Yes	86	42	0.6	700	1.2	7	2.0	24 ± 2	0.8
CAM										
14	Yes	100	30	0.6	700	2.0	10	1.3	22 ± 2	0.6
14	Yes	100	30	0.6	700	2.0	15	1.7	30 ± 3	0.6

High performances active materials:

NMC 111

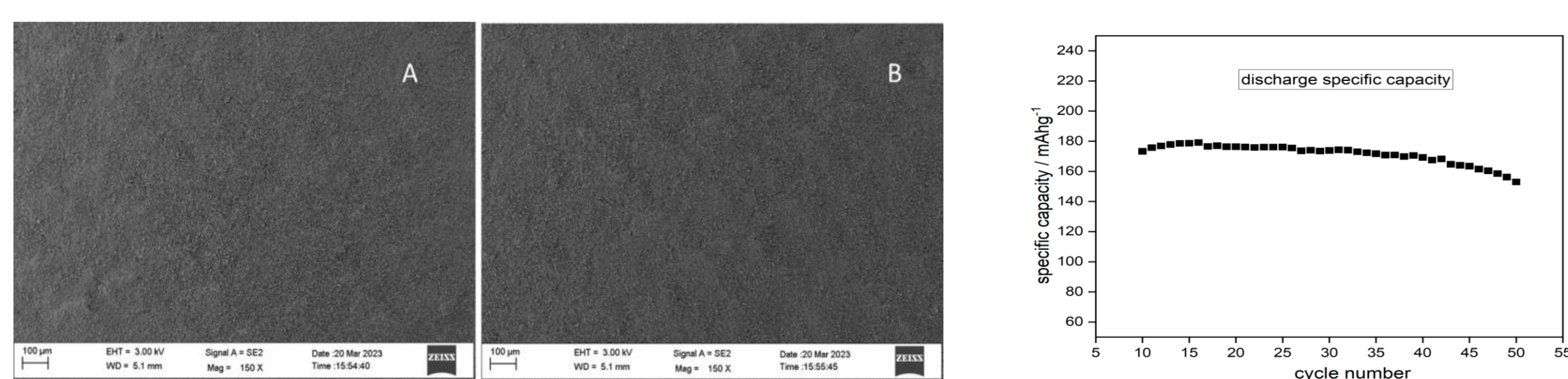
High performance Niche Manganese Cobalt Lithium oxide (Binder CMC, prevalent solvent water)



Large Area tests:

Up to 20 cm²

Statistic investigation by SEM images to test the layer homogeneity

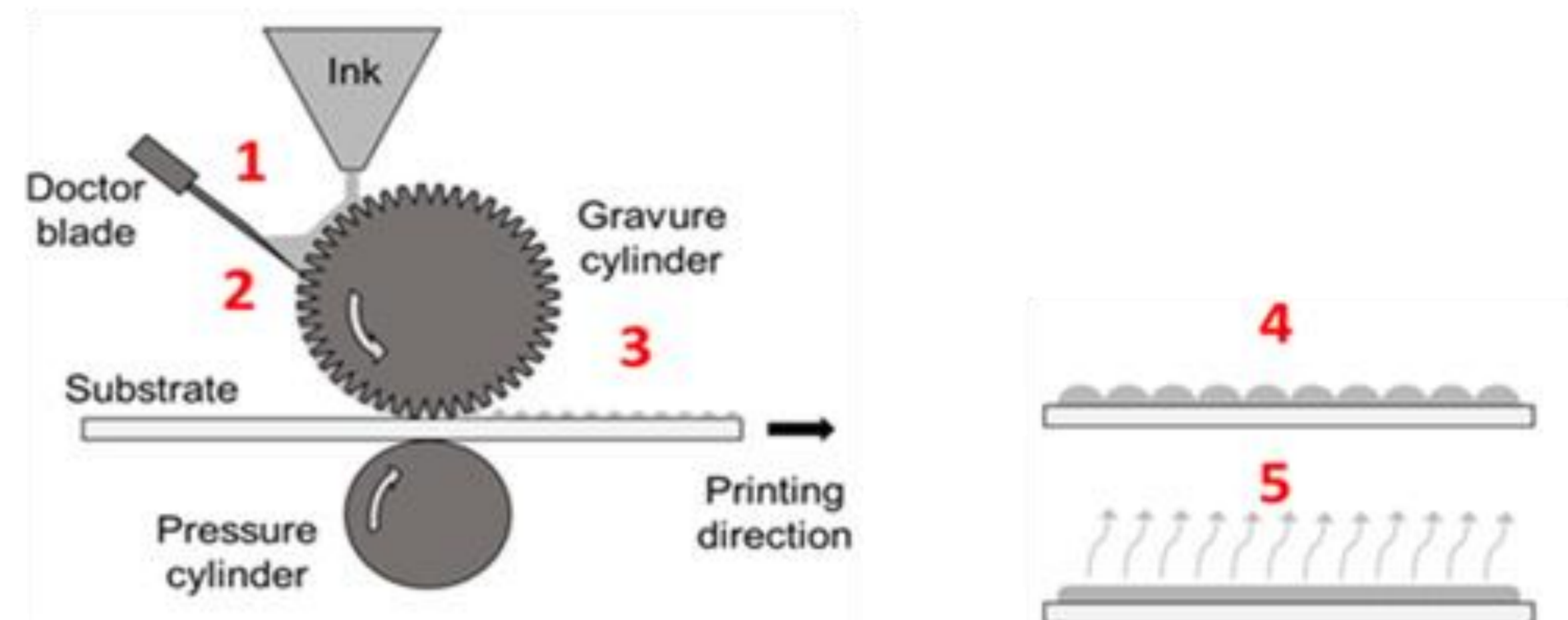


Reference:

Montanino, M.; Sico, G. Gravure Printing for Lithium-Ion Batteries Manufacturing: A Review. *Batteries* 2023, 9, 535.

Montanino, M.; Paoletti, C.; De Girolamo Del Mauro, A.; Sico, G. The Influence of the Gravure Printing Quality on the Layer Functionality: The Study Case of LFP Cathode for Li-Ion Batteries. *Coatings* 2023, 13, 1214.

1. Inking
2. Doctoring
3. Transfer
4. Spreading
5. Drying



NaBs:

Experimental:

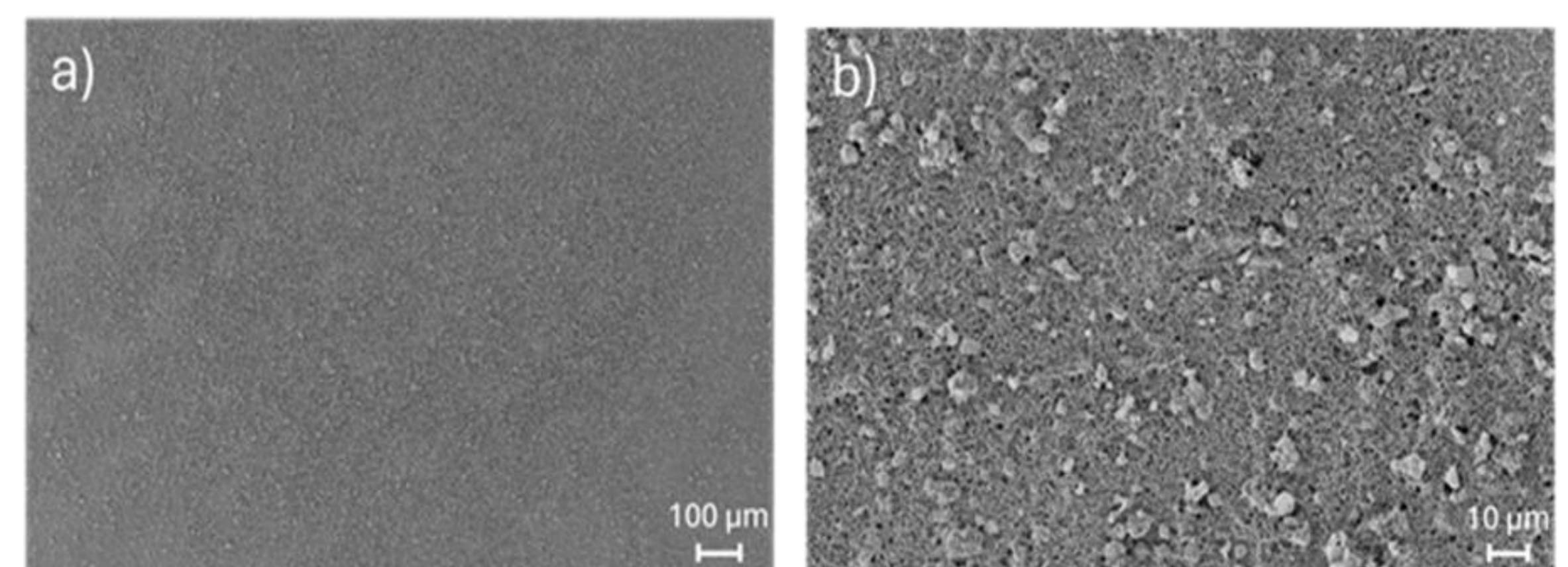
➤ **Active material:** $\text{NaLi}_{0.2}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_2$

➤ Sustainability: water soluble binder carboxymethyl cellulose allowing to use water as prevalent solvent

➤ Ink: active material (80%), Sodium salt of the carboxymethyl cellulose (CMC) (10%) as binder and carbon Super P as electric conductor (10%)

➤ Best printable ink: 15 % of solid content had best viscosity was (75 mPa s). The Ca was calculated 1.1 at a printing speed of 36 m min⁻¹ thus, such speed was used for printing layers.

➤ Print: 10 overlapped layers on Al foil



Results:

- Good coverage and high homogeneity of the printed layer without critical defects such as voids, scratches, undulations
- Achievement of cathodic functionality thanks to the high printing quality
- Poor electrochemical performances due to specific issues related to the active material such as sensitivity to water, oxygen moisture and CO₂ even when exposed to not controlled environment
- The effect of these environmental agents on the structure and the electrochemical performance of such materials makes necessary stabilization strategies, for not decreasing their potential capacity when used in an industrial ambient manufacturing process